New Nickel(II) Complexes with N-donor Ligands and Anions as Coligands

Structures and Optical Properties

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‘’It is common sense to take a method and try it. If it fails, admit it frankly and try another one. But above all, try something.‘’

Franklin D. Roosevelt

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Meinen Eltern

Abstract

The aim of this thesis was the preparation of new Ni(II) coordination compounds with N-donor ligands and anions as co-ligands. In total, five different ligands were used in the course of this work and these are 2,4,6-Tri(2-pyridyl)-1,3,5-triazine (tptz), Pyridine-2,6-dicarboxylic acid (2,6-pda), 4,4'-Bipyridine (4,4-bipy), 2,2'-Bipyridine (2,2-bipy) and 1,10-Phenanthroline (phen). All coordination compounds were analyzed by single-crystal XRD and UV-VIS measurements. Almost all coordination compounds described in this work exhibit H-bonding or π–π stacking, in some cases both. The ligands tptz and 2,6-pda represent multimodal ligands, which can be of great interest for the production of supramolecules, and were thus extensively used in this work. This resulted in the four new coordination compounds $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$. By using SCN^- as a co-ligand, the new mixed-ligand complex $[Ni(SCN)_2(tptz)(H_2O)]$ was obtained. Similarly, a mixed ligand coordination compound $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$ resulted from the reaction of both multimodal ligands tptz and 2,6-pda with nickel acetate. 4,4'-bipy was successfully used as a linker ligand in the preparation of the first tptz containing dimeric coordination compound $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$. The use of the 2,2'-bipy isomer yielded the new coordination compounds $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ and $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$. The presence of 2,2'-bipy in $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ and $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ as a chelating ligand, while 4,4'-bipy is a linker ligand in $[Ni_2(4,4'\text{bipy})(tptz)_2(H_2O)_4](NO_3)_4\ (H_2O)_2$, is a typical example of the effect of isomers on the type of coordination mode. Phen, which is an N-heterocyclic ligand related to 2,2'-bipy, was also extensively used in this work. This resulted in the preparation of $[Ni(Phen)_3](BF_4)_2(H_2O)$, $[Ni(phen)_3](pda)(H_2O)_{11}$, $[Ni(phen)_3](I_3)_2(H_2O)$, $[Ni(Cl)(phen)_2H_2O)](Cl)(H_2O)_2$ and $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$. The novel coordination compound $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ is the first example of a mixed 2,6-pda/phen ligand system with three crystallographically independent Ni(II) metal centers. The multimodal 2,6-pda ligand acts mainly as a tridentate chelating ligand coordinating in a k^3 *N,O,O'* mode to the Ni(II) metal center. In contrast, the 2,6-pda ligand in $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$ is non coordinating and exists as a counter ion. An attempted synthesis of a bimetallic Ni(II)/Nd(III) complex was not feasible, where only the $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6](H_2O)_7$ complex was obtained. Interestingly,

the 2,6-pda ligand shows both chelating and bridging coordination modes, linking the three Nd(III) metal centers through the oxygen atoms.

Kurzzusammenfassung

Ziel dieser Arbeit war die Herstellung neuer Koordinationsverbindungen mit Ni(II), N-Donor-Liganden und Anionen, die als Co-Liganden fungieren, sowie eine Bestimmung der jeweiligen Kristallstruktur und ihrer optischen Eigenschaften. Ebenfalls wurde der Einfluss der Co-Liganden (Anionen) auf die Struktur der Koordinationsverbindungen geprüft; deshalb folgten systematische Untersuchungen mit gleichen Liganden aber verschiedenen Co-Liganden. Wasserstoffbrückenbindungen und/oder π–π-Stacking-Wechselwirkungen konnten in den meisten Koordinationsverbindungen beobachtet werden. Insgesamt fünf N-Donor-Liganden wurden für die Reaktionen in dieser Arbeit verwendet. Es sind: 2,4,6-Tri(2-pyridyl)-1,3,5-triazin (tptz), Pyridin-2,6-dicarbosäure (2,6-pda), 4,4'-Bipyridin (4,4-bipy), 2,2'-Bipyridin (2,2-bipy) und 1,10-Phenanthrolin (phen). Diese Auswahl erfolgte aufgrund der besonderen Eigenschaften, die die Liganden auszeichnen. Die Liganden tptz und 2,6-pda sind mehrzähnige Liganden, die von großem Interesse in der supramolekularen Chemie sind. Vier neue Koordinationsverbindungen $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ und $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ mit dem $[Ni(tptz)_2]^{2+}$ Ion konnten erhalten werden. Bei der Verwendung von Thiocyanat als Co-Ligand wurde hingegen der Mixed-Ligand-Komplex $[Ni(SCN)_2(tptz)(H_2O)]$ erhalten. In ähnlicher Art und Weise wurde bei der Reaktion der tptz-und 2,6-pda-Liganden mit Ni(II)-Acetat die neue Mixed-Ligand-Koordinationsverbindung $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$ erhalten. Hervorzuheben ist die neue tptz-haltige dimere Koordinationsverbindung $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$, die unter Einsatz des 4,4'-bipy-Liganden als Linker-Ligand erhalten werden konnte. Unter Verwendung von 2,2'-bipy wurden die neuen Koordinationsverbindungen $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ und $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ erhalten. Da von den beiden bipy-Isomeren Verbindungen dargestellt werden konnten, ist es möglich, die Resultate für $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ und $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ mit $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2)$ zu vergleichen und von der Isomerie auf das Koordinationsverhalten zu schließen. Desweiteren wurde phen-Ligand in zahlreichen Reaktionen verwendet, und es konnten die neuen Koordinationsverbindungen $[Ni(phen)_3](BF_4)_2(H_2O)$, $[Ni(phen)_3](pda)(H_2O)_{11}$, $[Ni(phen)_3](I_3)_2(H_2O)$, $[Ni(Cl)(phen)_2H_2O)](Cl)(H_2O)_2$ und $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ erhalten werden. Die Mixed-Ligand-

Koordinationsverbindung $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2]_2(H_2O)_9$ stellt ein erstes 2,6-pda/phen-Liganden-System dar, bei dem drei kristallographisch unabhängige Ni(II)-Lagen vorliegen. 2,6-pda fungierte in den meisten Koordinationsverbindungen als dreizähniger Chelatligand. $[Ni(phen)_3](pda)(H_2O)_{11}$ stellt die einzige Ausnahme dar, dort agiert 2,6-pda als Anion. Weitere Koordinationsstellen des 2,6-pda-Liganden sollten durch die Herstellung einer heterometallischen Ni(II)/Nd(III)-Verbindung aktiviert werden. Dies resultierte in einer neuen Nd(III)-Koordinationsverbindung, $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$. In $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$ verhält sich 2,6-pda als dreizähniger Chelatligand, welches zusätzlich über die Sauerstoffatome der Carboxylgruppen die einzelnen Monomere zum Koordinationspolymeren verbrückt.

Abbreviations

EtOH	Ethanol
MeOH	Methanol
RT	Room temperature
UV-Vis	Ultraviolet-Visible
HSAB	Hard and Soft Acids and Bases
LFT	Ligand Field Theory
tptz	2,4,6-Tri(2-pyridyl)-1,3,5-triazine
2,2’-bipy	2,2'-Bipyridine
4,4’-bipy	4,4'-Bipyridine
2,6-pda	Pyridine-2,6-dicarboxylic acid
phen	1,10-Phenanthroline

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1. Introduction

1.1 Overview

The key objective of this thesis was the synthesis and characterization of new Ni(II) complexes with N-donor ligands and anions as co-ligands. In addition this work aimed to study:

1. The influence of anions on the structure of the Ni(II) coordination compounds.
2. The influence on the structure by using different isomers of ligands (2,2'-bipy vs. 4,4'-bipy).
3. The structures of new Ni(II) mixed-ligand systems.

The results will be discussed in the results and discussion section. At the beginning it is worth taking some theoretical and preparative aspects into consideration. In order to understand and be able to predict the coordination numbers, the role of ligands, the influence of anions (co-ligands), the chemistry of nickel will be shortly discussed. This is followed by a short summary of the theories and concepts relevant to the interpretation and prediction of the results. The results are also affected by methods of preparation. For this reason, these will also be discussed.

1.2 The Element Nickel

Nickel is a transition metal, which belongs to group 8. In this group the horizontal similarity between Fe, Co, and Ni is greater than that between these and the corresponding elements in the second and third transition series. This leads to a separation of these nine elements into the iron triad, Fe-Co-Ni, and the light and heavy platinum triads, Ru-Rh-Pd and Os-Ir-Pt. Nickel occurs in nature mainly in combination with arsenic, antimony, and sulphur, for example as *millerite* (NiS), as a red nickel ore that is mainly NiAs, and in deposits consisting chiefly of NiSb, $NiAs_2$, NiAsS, or NiSbS. The commercially most important deposits are garnierite, a magnesium-nickel silicate of variable composition, and certain varieties of the iron mineral pyrrhotite (Fe_nS_{n+1}), which contain 3-5 % Ni.

Elemental nickel is also found alloyed with iron in many meteors and the central regions of the earth are believed to contain considerable quantities [1].

Nickel was first isolated in 1751 from Swedish ores by Swedish chemist *A. F. Cronstedt.* In 1775, it was closely characterized by the Swedish chemist and mineralogist T. Bergman [2].

Its color is silver-white, with high electrical and thermal conductivities (both approximately 15% of those of silver) and a melting point of 1452℃, and it can be drawn, rolled, forged, and polished. It is quite resistant to attack by air or water at normal temperatures when compact and is therefore often electroplated as a protective coating. Because nickel reacts slowly with fluorine, the metal and certain alloys (Monel) are used to handle F_2 and other corrosive fluorides. It is also ferromagnetic, but not as much as iron [3].

Nickel has the electronic configuration $(n-1)d^8ns^2$ and shows chiefly the +2 oxidation state. However, nickel compounds in the other oxidation states -1, 0, +1, +3, +4 are also known. It generally forms octahedral and square planar complexes in the Ni^{2+} oxidation state [4]. Hydrated Ni(II) salts are green, because of the bright green $[Ni(H_2O)_6]^{2+}$ ion. The square planar complexes are usually red or yellow [5]. The aqueous chemistry of nickel deals mainly with nickel(II), where the +2 oxidation state is the most stable one and its complexes are redox stable. Nickel(II) forms a large number of complexes with coordination numbers ranging from 3 to 6. The maximum coordination number of Nickel(II) is 6. The coordination geometry around the metal center and physical properties of the complexes are defined through the interactions between the central atom and the ligands. Neutral ligands, especially amines, displace some or all of the water molecules in the octahedral $[Ni(H_2O)_6]^{2+}$ ion and form new octahedral complexes, with other physical and chemical properties in contrast to the bright green $[Ni(H_2O)_6]^{2+}$ complex. The ligands provide also the thermodynamic stability of complexes. Octahedral nickel(II) complexes show relatively simple magnetic behavior [6].

For the better understanding of nickel complex compounds and their physical properties, ligand field theory can be applied; it is a part of his work and follows below. Since complexes consist of Lewis acids and Lewis bases, the Pearson HSAB concept can also be used for their qualitative description [7]. These theories make it possible to plan and synthesize new coordination compounds and predict their chemical and physical properties.

The inexhaustible variety of organic ligands makes it possible to synthesize an infinite number of new complex compounds. The anions of metal salts can also be varied and their influence on structures and their chemical and physical properties examined.

For instance, complex compounds with pyridyl and tptz ligands are of great interest because they can serve as building blocks for supramolecules. Metal complexes of tptz and pyridyl ligands with such metal centers as for example Ag^{I} have extensively been examined [8]. Currently the chemistry of d^8 metal complexes, for instance of nickel(II), is of growing interest.

1.3 Theoretical Background

1.3.1 Lewis acids and bases [9]

In 1923, Lewis proposed a new definition for acids and bases. A Lewis acid is a chemical species that can accept an electron-pair from a Lewis base, which acts as an electron-pair donor. This Lewis definition is based on chemical bonding theory. The smallest Lewis acid is the proton H^+, other typical Lewis acids are: Fe^{3+}, BH_3, AlF_3, SiF_4, PCl_5, etc. Typical examples for Lewis bases are: water, ethers, ketones, carbon monoxide etc. The product formed in the reaction of a Lewis acid with a Lewis base is a coordination compound, wherein metal (ion) is a Lewis acid and the ligands are Lewis bases. In 1963, forty years after Lewis postulated his new theory, Pearson introduced the HSAB concept.

1.3.2 HSAB Concept [10]

The HSAB concept is used for the qualitative description of aspects that are responsible for chemical reactions and formation of the resulting compounds. It is extensively used in transition metal chemistry, where it makes possible to understand reaction mechanisms and pathways, also the stability of compounds can be explained applying it. According to the HSAB concept, stable acid-base compounds are formed from the combination of hard acids with hard bases and soft acids with soft bases, other possible combinations are less preferable. 'Hard' species are small, their charge states are high (actual for acids, to a lesser extent for bases). 'Soft'

species are big, strong polarizable and their charge states are low. The precise assignment of N-donor ligands in terms of hard/soft is not always possible. Because of its small size the nitrogen atom is hard, but the presence of polarizable substituents can change its properties. According to the HSAB-concept, Ni(II) is a moderate-soft acid. Soft metal ions possess a bigger number of d-electrons than the hard ones and prefer substituents containing the following atoms in descending order S > N > O. The substituents can also change the properties of the coordinating acid center in terms of hard or soft. Thus by introducing soft polarizable substituents, a hard center can be made softer, and vice versa by introducing electron-withdrawing groups, the soft center can be made harder.

1.3.3 The Ligand Field Theory (LFT)

The ligand field theory (LFT) describes bonding in complexes in terms of molecular orbitals built from the metal center d-orbitals and ligand orbitals. It is assumed that ligands are attached to the central metal atom or ion by a covalent bond. A number of useful information such as magnetic and optical properties, preferable oxidation states, coordination numbers and absorption spectra of some transition metals can be predicted with help of LFT.

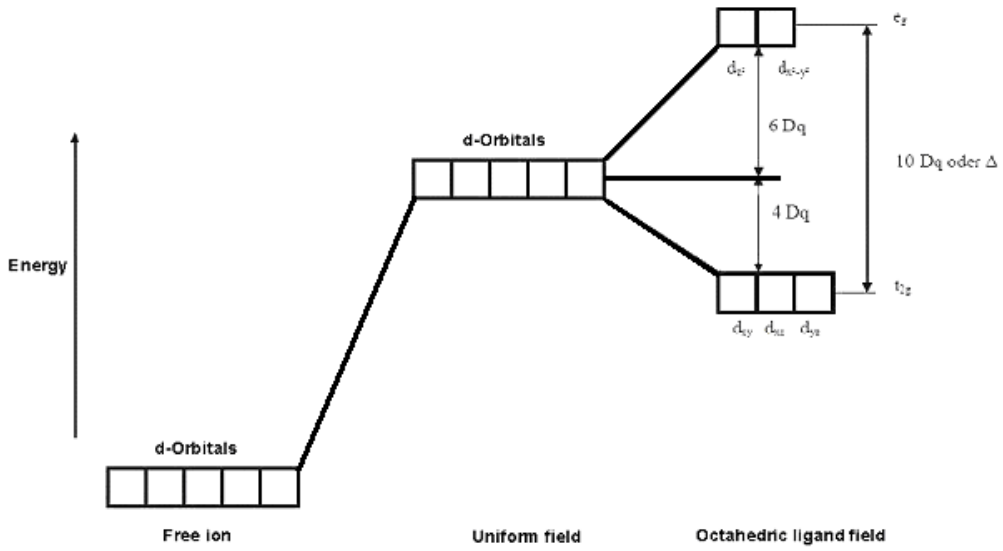
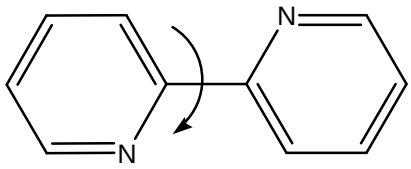


Fig. 1.0 The energy levels of the d-orbitals in an octahedral complex with the ligand field splitting Δ_0.

All new compounds presented in this work have octahedral coordination around the Ni(II) metal center. This can be explained in terms of LFT. The five d-orbitals of the free Ni^{2+} ions are degenerate. The energy difference between them is denoted by Δ_0, or, alternatively, 10 Dq. If the ligand field splitting is large, the t_{2g}-orbitals are occupied first, and a low-spin complex is expected. If the ligand field splitting is small, the e_g-orbitals are occupied before spin-pairing begins in the t_{2g}-orbitals, and a high-spin complex is expected. The ligand strength is therefore a very important characteristic that has to be taken into account in the syntheses of coordination compounds.

1.3.4 Properties and structures of N-donor ligands and coligands used for the syntheses [11]

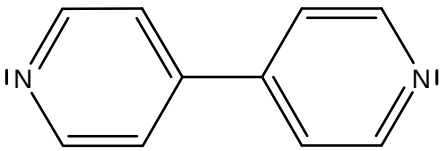
1. 2,2'-Bipyridine (2,2'-bipy)



2,2'-Bipyridine (bipy)

2,2’-bipy is a classical N-heterocyclic ligand and was used in this work as a bidentate chelating ligand both in mixed-ligand and simple complexes. 2,2’-bipy is a colorless solid. It is prepared from pyridine; the mechanism of its formation is shown below in Fig. 1.2. The lowest energy conformation of 2,2’-bipy both in solid state and in solution is coplanar, with the nitrogen atoms in *trans* position.

2. 4,4'-Bipyridine (4,4'-bipy)



4,4'-Bipyridine (4,4'-bipy)

4,4’-bipy is an isomer of 2,2’-bipy. Its formation is described by the same mechanism describing the formation of 2,2’-bipy. 4,4’-bipy can function as a linker between metal centers giving coordination polymers [12].

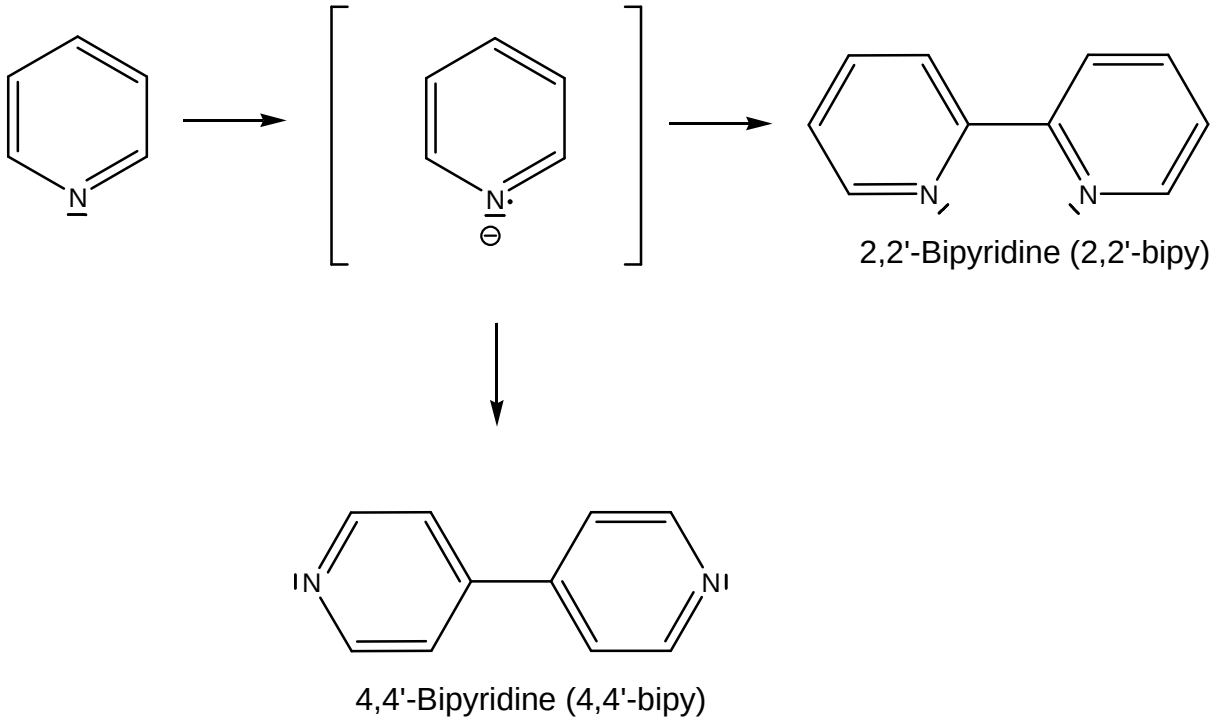
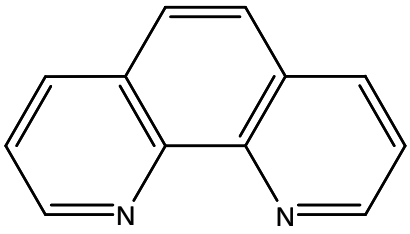


Fig. 1.2: Mechanism of formation through dimerisation of 2,2’-bipy and 4,4’-bipy [13].

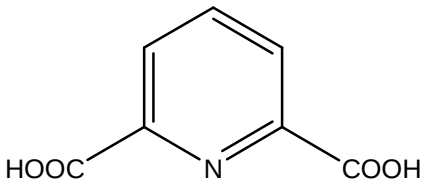
3. 1,10-Phenanthroline (phen)



1,10-Phenanthroline (phen)

Phen is an N-heterocyclic ligand related to 2,2’-bipy. Its aromatic system contains two carbon atoms more than 2,2-bipy, these lead to the loss of the conformational flexibility, characteristic for 2,2’-bipy. Phen tends, therefore, to bind metal ions more strongly.

4. Pyridine-2,6-dicarboxylic acid (pda)



Pyridine-2,6-dicarboxylic acid (pda)

Pyridine-2,6-dicarboxylic acid (2,6-pda) is a pyridine derivative, with carboxylic acid substituents in the 2 and 6 positions. This ligand possesses five potential coordination sites and can function both as a chelating and a bridging ligand (Fig. 1.3).

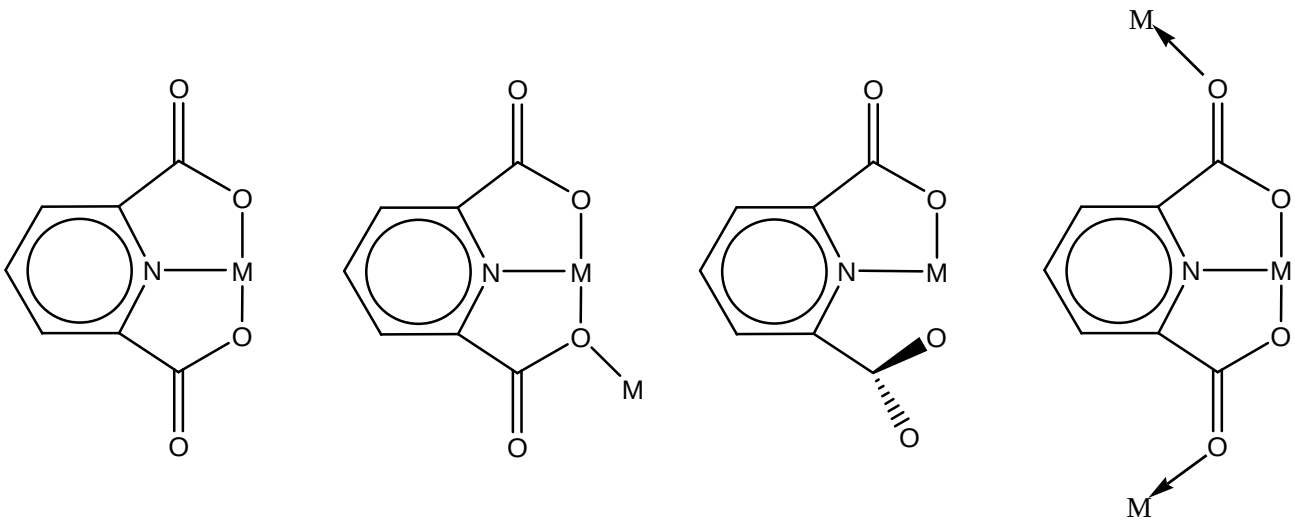
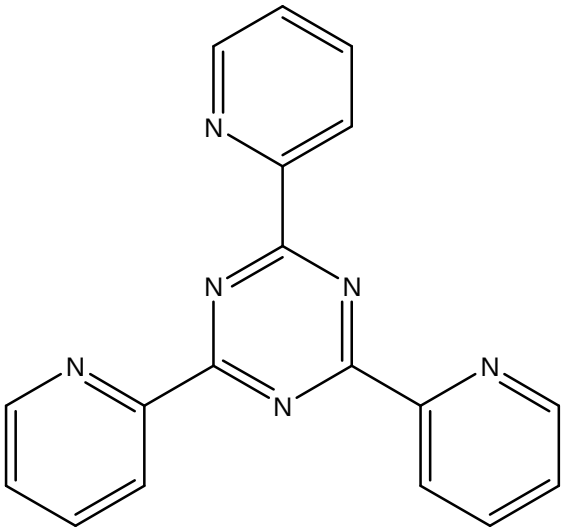


Fig. 1.3: Possible coordination modes of the anion of Pyridine-2,6-dicarboxylic acid (2,6-pda), M = Metal [14].

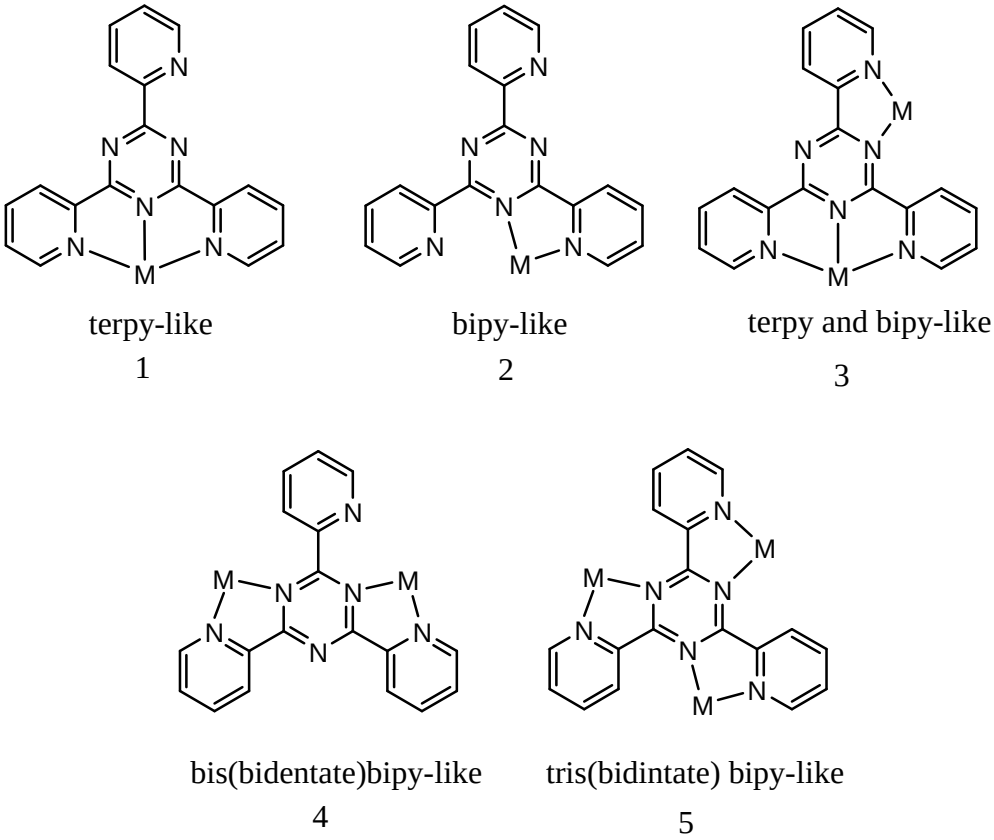
4. 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz)

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) is a versatile neutral N-donor ligand that can simultaneously function as a bidentate and a tridentate agent and therefore can be used as a potential spacer in the design of supramolecular complexes. A schematic drawing of the binding sites of the tptz ligand is depicted in Fig. 1.4.



2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz)

Most often, tptz acts as a tridentate ligand, adopting the terpy-like binding mode. In contrast, the bidentate bipy-like binding mode is much more rare, where only few examples have been reported so far [15].



terpy-like 1 | bipy-like 2 | terpy and bipy-like 3

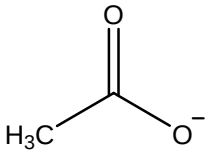
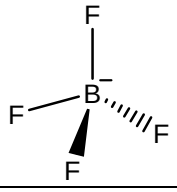
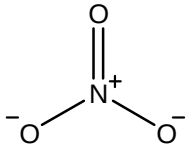
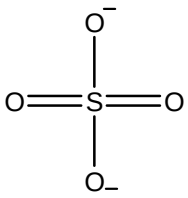
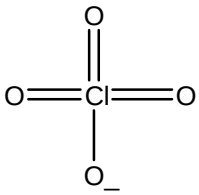
bis(bidentate)bipy-like 4 | tris(bidintate) bipy-like 5

Fig. 1.4: Binding modes of the tptz ligand.

1.3.5 Properties of anions (co-ligands)

In order to study the effects of anions (co-ligands) on the structures of the complexes, different Ni(II) salts were used systematically in the syntheses of the new Ni(II) complexes. These negatively charged co ligands (Table 1.0) can be classified in terms of strong or weak coordinating species. This aspect will be discussed in the results and discussion section.

Tabele 1.0: Co-ligands used for the syntheses.

Nickel(II) salt	Co-ligand
Ni(II) acetate-tetrahydrate **$Ni(AcO)_2 \cdot 4H_2O$**	
Ni(II) tetrafluoroborate **$Ni(BF_4)_2$**	
Ni(II) nitrate-tetrahydrate **$Ni(NO_3)_2 \cdot 4H_2O$**	
Ni(II) sulfate-hexahydrate **$NiSO_4 \cdot 6H_2O$**	
Ni(II) perchlorate-hexahydrate **$Ni(ClO_4)_2 \cdot 6H_2O$**	
Ni(II) iodide **NiI_2**	I^-
Ni(II) chloride-hexahydrate **$NiCl_2 \cdot 6H_2O$**	Cl^-
Ni(II) thiocyanate **$Ni(SCN)_2$**	SCN^-

2. Results and Discussion

In the course of this work, new Ni(II) complexes were synthesized (Table 2.0). In total, five N-donor heterocyclic ligands and eight co-ligands were used for the syntheses. The influence of co-ligands on the structures of coordination compounds was systematically investigated. Furthermore, N-heterocyclic ligands containing both N and O donor atoms were used. Also mixed ligand complexes were synthesized and characterized.

Table 2.0: Synthesized complex compounds.

Nickel(II) complexes with N donor ligands
$[Ni(tptz)_2](BF_4)_2(H_2O)$
$[Ni(tptz)_2](I)_2(H_2O)$
$[Ni(tptz)_2](I)_2(H_2O)_2$
$[Ni(tptz)_2](NO_3)_2(H_2O)_7$
$[Ni(SCN)_2(tptz)(H_2O)]$
$[Ni(2,6\text{-}pda)(tptz)](H_2O)_5$
$[Ni_2(4,4'\text{-}bipy)(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$
$[Ni(phen)_3](BF_4)_2(H_2O)$
$[Ni(phen)_3](2,6\text{-}pda)(H_2O)_{11}$
$[Ni(phen)_3](I_3)_2(H_2O)$
$[Ni(Cl)(phen)_2H_2O)](Cl)(H_2O)_2$
$[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$
$[Ni(2,6\text{-}pda)(2,2'\text{-}bipy)(H_2O)](H_2O)_2$
$[Ni(2,6\text{-}pda)(2,6\text{-}pdaH)]_2[Ni(2,2'\text{-}bipy)_2(H_2O)_2](H_2O)_6$
$[Nd(2,6\text{-}pda)_3][Nd(2,6\text{-}pda)(H_2O)_6]_2(H_2O)_7$*

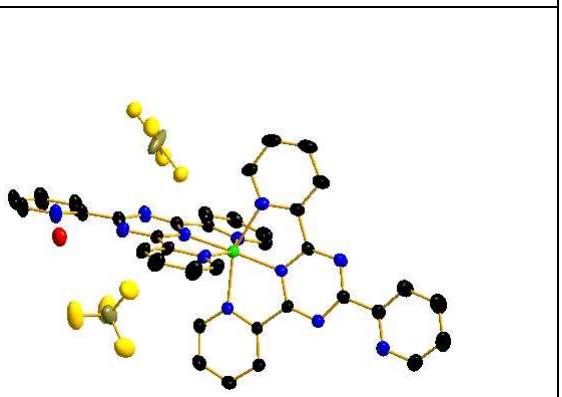
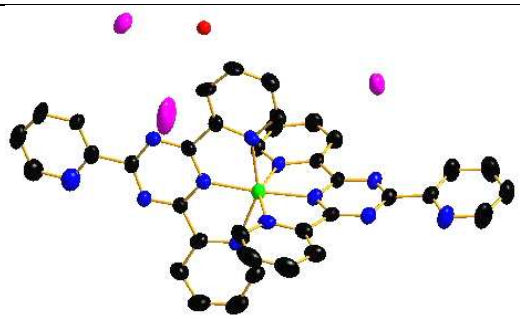
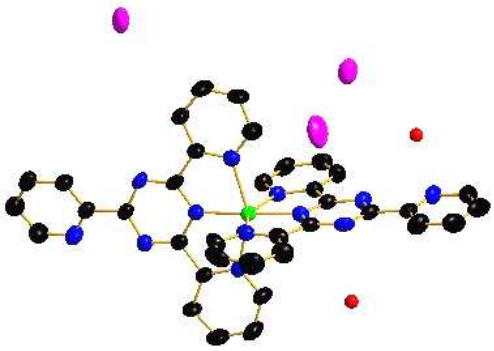
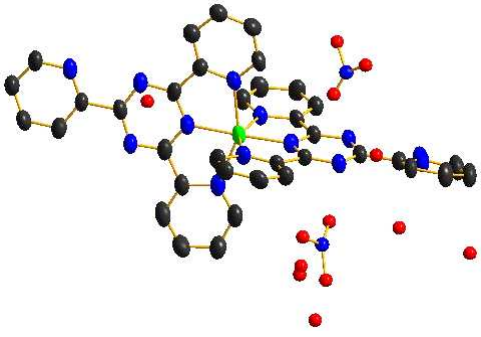
* See Appendix.

One of the five ligands used for the syntheses of Ni(II) coordination compounds is tptz. Tptz belongs to the class of *multi-modal* ligands (defined by Champness and co-workers), as it can simultaneously function as a bidentate and a tridentate agent. Depending on the isomer of tptz, not only chelating, but also monodentate donor sites are possible [16]. It is important to point out that tptz and other 1,3,5-triazine based derivates are of great interest, because they can serve as building blocks for supramolecules. This is due to both their π-interaction abilities and for their aptitude to be involved in intricate H-bonding networks [17]. The newly synthesized Ni(II) coordination compounds with tptz can be categorized as follows:

1. Coordination compounds containing the $[Ni(tptz)_2]^{2+}$ ion and different co-ligands.
2. Mixed-ligand coordination compounds containing tptz as a ligand.
3. A dimeric coordination compound containing tptz as a ligand.

In total, four new structures, of $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$, containing the $[Ni(tptz)_2]^{2+}$ ion were obtained. Two of the four compounds, $[Ni(tptz)_2](I)_2(H_2O)$ and $[Ni(tptz)_2](I)_2(H_2O)_2$, also contain the same co-ligand, but differ in the number of lattice water molecules. Moreover, they crystallize in different crystal systems; $[Ni(tptz)_2](I)_2(H_2O)_2$ crystallizes in the higher symmetry monoclinic (space group C2/c), while $[Ni(tptz)_2](I)_2(H_2O)$ (Table 2.1) is triclinic. In both structures, H-bonding and π–π-stacking effects can be observed (see Special Section). $[Ni(tptz)_2](BF_4)_2(H_2O)$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ have different co-ligands, which can be classified in terms of strong or weak coordinating species, where tetrafluoroborate is a weak coordinating anion and nitrate the stronger coordinating one. These negatively charged co-ligands compete with the organic N-donor ligands for the coordination sphere on the positively charged Ni(II) metal center. Despite differences in their strength, both anions are in remote positions and are not coordinating to the Ni(II) metal center. This was more anticipated for tetrafluoroborate than for nitrate. The probable explanation for such a result could be the composition and concentration of the used species as well as the method of preparation. The aspect of stoichiometry of metal-salt:ligand:co-ligand and the coordinating strength of the co-ligand play a key role for the prediction of the respective structure [18].

Table 2.1: New Ni(II) coordination compounds containing the $[Ni(tptz)_2]^{2+}$ ion.

New Ni(II) coord. compounds		Figures of the coord. compounds
$[Ni(tptz)_2](BF_4)_2(H_2O)$		
Empirical formula	$C_{36}H_{24}N_{12}O_1B_2F_8$	
Crystal system	orthorhombic	
Space group	Pcca (54)	
Crystal color	orange	
Unit cell dimensions	a = 20.69 (2) Å	
	b = 10.84 (1) Å	
	c = 16.71 (1) Å	
Cell volume	3749.31 $Å^3$	
Z	4	
$[Ni(tptz)_2](I)_2(H_2O)$		
Empirical formula	$C_{36}H_{26}N_{12}O_1Ni_1I_2$	
Crystal system	triclinic	
Space group	P-1 (2)	
Crystal color	orange	
Unit cell dimensions	a = 9.092 (2) Å	
	b = 13.076 (3) Å	
	c = 16.002 (3) Å	
	α = 84.91(2)°	
	β = 77.87(2)°	
	γ = 89.09(2)°	
Cell volume	1852.7(7) $Å^3$	
Z	2	
$[Ni(tptz)_2](I)_2(H_2O)_2$		
Empirical formula	$C_{36}H_{28}N_{12}O_2Ni_1I_2$	
Crystal system	monoclinic	
Space group	$C2/_C$	
Crystal color	orange	
Unit cell dimensions	a = 41.915(5) Å	
	b = 9.348(1) Å	
	c = 20.668(3) Å	
	β = 108.17(1)°	
Cell volume	7694.2(3) $Å^3$	
Z	8	
$[Ni(tptz)_2](NO_3)_2(H_2O)_7$		
Empirical formula	$C_{36}H_{28}N_{14}O_{13}Ni_1$	
Crystal system	monoclinic	
Space group	$P2_1/c$ (14)	
Crystal color	orange	
Unit cell dimensions	a = 12.721(2) Å	
	b = 16.081(2) Å	
	c = 19.759(3) Å	
	β = 90.64 (1)°	
Cell volume	4041.7 (1) $Å^3$	
Z	4	

The coordinating tptz ligand adopts a terpy-like binding mode and chelates the Ni(II) metal center as a tridentate ligand. Hence the chelate effect must be taken into account while comparing tptz with a competing nitrate anion. In terms of HSAB nitrate is a hard Lewis base (Table 2.4), whereas Ni(II) is a moderate-soft acid and would prefer soft Lewis bases such as cyanide or thiocyanate. Another important aspect is the concentration factor. By regulating the concentrations of the used educts, it is often possible to achieve certain goals. For example, by adjusting the preparation method, *Diaz de Vivar et al.* could synthesize $[Ni(SO_4)(tptz)(H_2O)_2$ [19], where a strongly coordinating sulfate co-ligand coordinates to the Ni(II) metal center. So it is probable that the same might occur in case of the strong coordinating nitrate co-ligand.

All four compounds have the same dark orange color. The color is thought to result from shifts in the absorption bands when the H_2O ligands in the octahedral $[Ni(H_2O)_6]^{2+}$ ion are replaced by tptz ligands lying toward the stronger end of the spectrochemical series. According to the Tanabe-Sugano energy level diagram for d^8 ions (Fig. 2.0), three spin-allowed transitions are possible. Consequently, it is possible to assign the three observed bands in the spectrum as shown in Table (2.2).

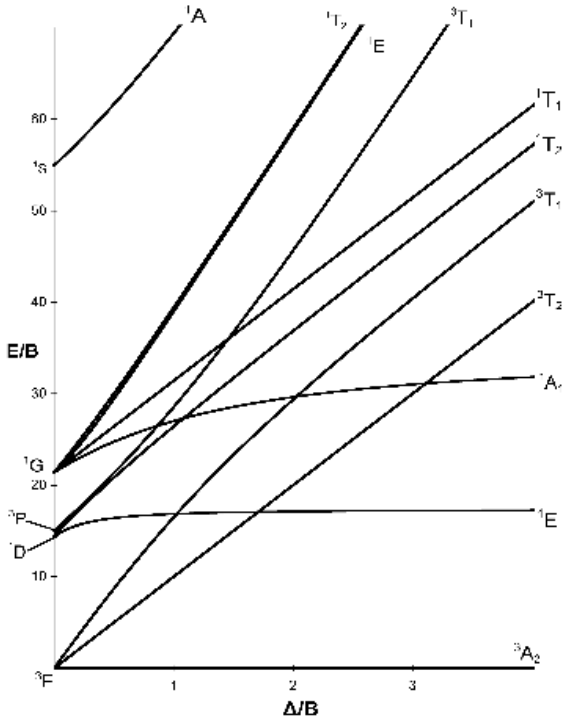


Fig. 2.0: Tanabe-Sugano energy level diagram for d^8 ions [20].

Table 2.2 Spectra of octahedral Nickel(II) complexes.

	Approximate band positions (nm)	
Transitions	$[Ni(H_2O)_6]^{2+}$	$[Ni(tptz)_6]^{2+}$
$^3A_{2g} \rightarrow {}^3T_{2g}$	1110	850
$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	715	460
$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	400	320

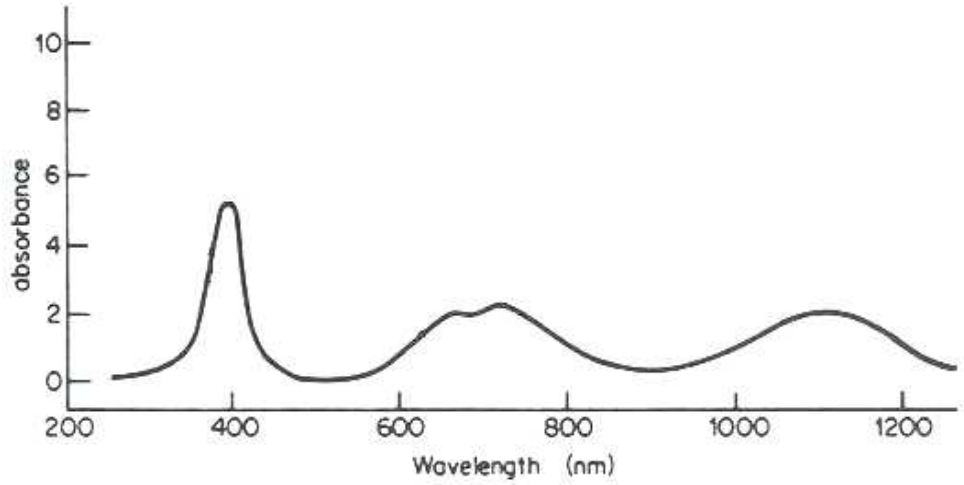


Fig. 2.1 UV-Vis absorption spectrum of $[Ni(H_2O)_6]^{2+}$ [21].

Due to the spin-orbit coupling which mixes the $^3T_{1g}$ (F) and ^1E_g states, the splitting of the middle band in the $[Ni(H_2O)_6]^{2+}$ spectrum occurs at approximately 715 nm (Fig. 2.1). In the stronger field of the tptz and other similar ligands, the $^3T_{1g}$ (F) and ^1E_g states are far apart at the Δ_0 value, so that nearly no mixing occurs.

The absorption in the visible area of the spectrum at approximately 460 nm is responsible for the dark yellow/ orange color of the above listed compounds. The analysis of the UV-VIS-spectra of $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ is based on the analysis of the absorption spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ [21].

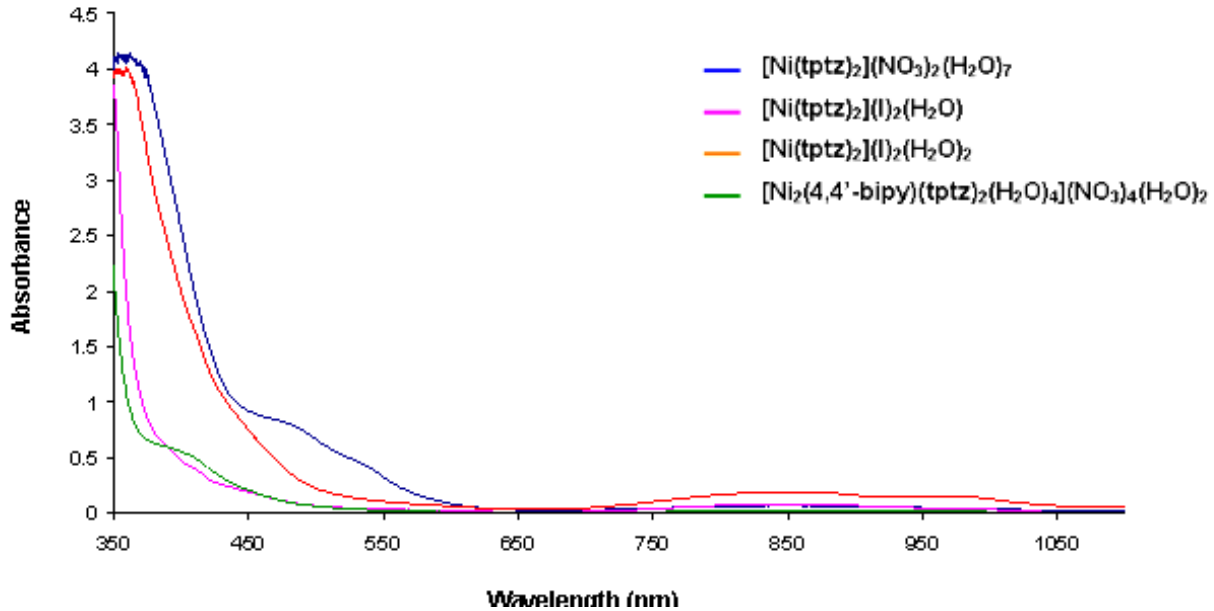


Fig. 2.2 UV-VIS Spectra of $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

Table 2.3: Ligands from the spectrochemical series sorted according to a HSAB principle.

Hard	Borderline	Soft
F^-, OH^-, O^{2-}, ClO_4^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, CO_3^{2-}, H_2O,	Br^-, NO_2^-, SO_3^{2-}, N_3^-, N_2	CO, CN^-, H^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, C_6H_6

Table 2.4: Lewis acids sorted according to a HSAB principle.

Hard	Borderline	Soft
H^+, Li^+, Na^+, Al^{3+}, Fe^{3+}, Cr^{3+}	Ni^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}	Pd^{2+}, Pt^{2+}, Cu^+, Ag^+, Hg^{2+}, BH_3

Table 2.5: Spectrochemical series.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < NCO^- < OH^- < ONO^-$ < Oxalate < H_2O < NCS^- < NC^- < Pyridine < NH_3 < Ethylendiamine < Bipyridine < Phenanthroline< NO_2^- < CNO^- < CN^- < CO

Another interesting result was obtained by the reaction of $Ni(SCN)_2$ with tptz. Although the synthetic method was similar to that of the previous coordination compounds, the result was different.

Instead of the expected $[Ni(tptz)_2]^{2+}$ cationic complex with isolated thiocyanates as counter ions, the novel compound $[Ni(SCN)_2(tptz)(H_2O)]$ was obtained. It is obvious that the change in the coordination sphere results from using another type of co-ligand. Despite the chelate effect of the tptz ligand and appropriate concentrations of 1:2 for metal and ligand, respectively, used in the synthesis, only one tptz ligand coordinates to the metal center. The reason for this can be the nature of the co-ligand. According to the HSAB-concept, Ni(II) is a moderate-soft acid and thiocyanate is a soft base. Therefore, a stable acid-base compound can be formed. The ambidentate thiocyanate anions coordinate via the N atoms, not via S, to the Ni(II) metal center. The size of the coordinating atom must also be taken into account. Sulfur is bigger than the nitrogen atom and would need more space in the coordination sphere, what would probably not fit in the octahedral coordination.

$[Ni(SCN)_2(tptz)(H_2O)]$ represents a mixed ligand complex. This type of compound is very interesting, because the different nature of coordinating ligands combined in one system may lead to absolutely new chemical and physical properties. For instance, the tptz containing $[Ni(SCN)_2(tptz)(H_2O)]$ has a different color compared to that of $[Ni(tptz)_2]^{2+}$ complexes. The presence of thiocyanate and aqua ligands, which are lying towards the weaker end of the spectrochemical series than tptz, leads to the shift in the absorption band toward the red end of the spectrum. The color is therefore green and not dark orange. The same applies to the yellow colored $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ and $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$ coordination compounds. These are yellow in contrast to the orange $[Ni(tptz)]^{2+}$ complexes. The novel coordination compound $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ also represents a mixed-ligand system and contains two Ni(II) metal centers. It is the first tptz containing coordination compound of such type. Due to the properties of the 4,4'-bipy, it was possible to not only use it as a coordinating ligand, but also as a linker ligand. In $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ (Table 2.6), both Ni(II) metal centers are linked through a conjugated 4,4'-bipy ligand, whose electrons can be delocalized between the two metal centers.

This might give rise to magnetic properties not previously observed in monomeric coordination compounds. Unfortunately, it was not possible to get a clean sample for magnetic susceptibility measurements.

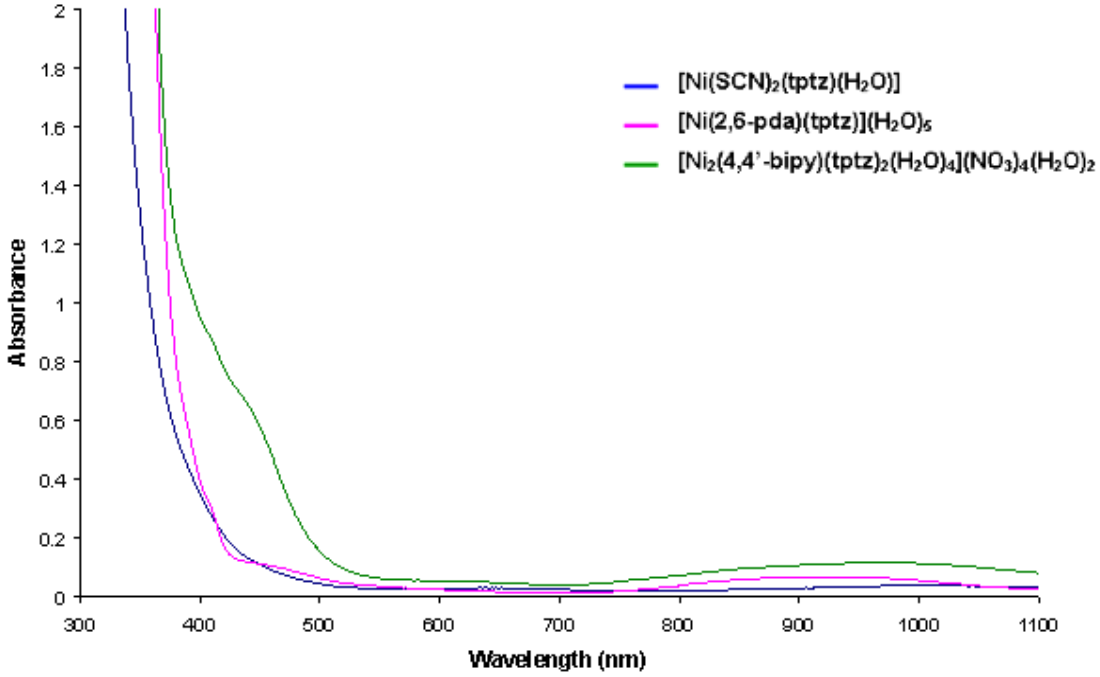


Fig. 2.3 UV-VIS spectra of $[Ni(SCN)_2(tptz)(H_2O)]$, $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ and $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$.

As an isomer of 4,4'-bipy, 2,2'-bipy was also extensively used in this work. However, it exhibits other coordinating properties compared to that of 4,4'-bipy. By comparing $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ with the coordination compounds of 2,2'-bipy, the difference in the coordination mode of both isomers can be compared.

The phen ligand was also extensively used in this work. It is worth pointing out, that bipy and phen metal complexes have been of interest for many years [22], especially as part of an effective method for metal analysis, particularly for complexes with Ni(II). Numerous reports of spectral and magnetic properties as well as formation constants were published [23]. In phen, the aromatic system contains two carbon atoms more than 2,2-bipy, which leads to the loss of conformational flexibility. As a result, the phen ligand tends to bind metal ions more strongly. Reaction of phen with different Ni(II) salts yielded mainly the coordination compounds $[Ni(phen)_3](BF_4)_2(H_2O)$, $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$ and $[Ni(phen)_3](I_3)_2(H_2O)$ with the

$[Ni(phen)_3]^{2+}$ ion and different co-ligands (Table 2.7). In $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11,}$ where acetate was used as a co-ligand, the 2,6-pda was deprotonated and acts as an anion. The probable explanation for this reaction pattern is the basisity of the acetate anion. Its pK_B value is 9.24, it is hence a strong enough base to deprotonate the weak 2,6-pda ligand. As a result, acetate is protonated and can not act as a co-ligand.

The use of chloride as a co-ligand yielded the novel coordination compound $[Ni(Cl)(phen)_2H_2O)](Cl)(H_2O)_{2.}$ In this compound one chloride coordinates to the Ni(II) metal center and another one is counter balancing the charge of the $[Ni(Cl)(phen)_2(H_2O)]^+$ cationic complex. This compound is an exception, since the formation of the $[Ni(phen)_3]^{2+}$ is more common. The reason for this can, on one hand, be the chelate effect (phen vs. monodentate ligands) or, on the other hand, the influence of solvents or the stoichiometry of the reactants used.

As the concentration of ligands and solvents were changed, the novel coordination compound $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ was obtained. It is not simple to explain the mechanism of formation of this compound, but it is obvious that concentration and solvent factors can lead to the formation of different compound compositions despite using the same educts.

Similarly, when 2,2'-bipy is used, two novel mixed-ligand coordination compounds $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ and $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ were obtained. $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ (Table 2.8) is very similar to $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_{9.}$ $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ is similar to the reported $[Ni(2,6\text{-pda})(phen)(H_2O](H_2O)$ coordination compound [24].

In all coordination compounds presented in the present work, except $[Ni(Phen)_3](2,6\text{-pda})(H_2O)_{11}$, 2,6-pda acts as a tridentate chelating ligand coordinating in a k^3-*N,O,O* mode. On the other hand, in $[Ni(Phen)_3](pda)(H_2O)_{11}$, 2,6-pda is non-coordinating and is a counterion. The attempt to synthesize a coordination compound where the 2,6-pda as a multimodal ligand exhibits another coordination mode was partially successful. By trying to synthesize a heterometallic Ni(II)/Nd(III) coordination compound, the novel structure of $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$ containing three crystallographically independent Nd(III) metal centers was obtained (see Appendix).

Table 2.6: New Ni(II) tptz containing coordination compounds.

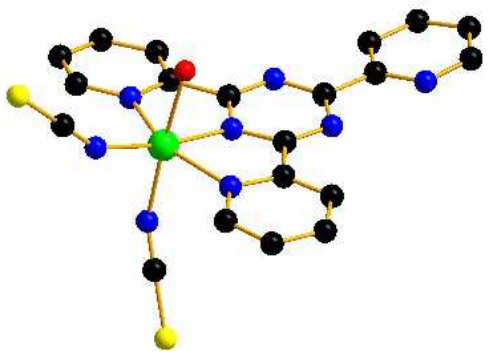
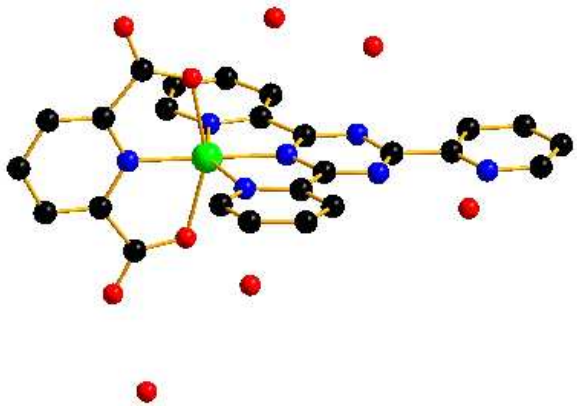
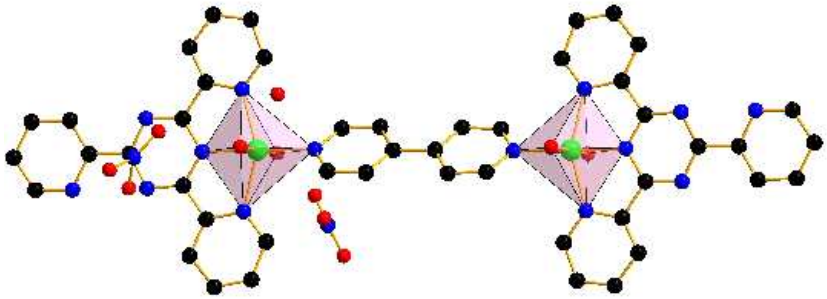
New Ni(II) coord. compounds		Figures of the coord. compounds
$[Ni(SCN)_2(tptz)(H_2O)]$		
Empirical formula	$C_{20}H_{12}N_8Ni_1O_1S_2$	
Crystal system	orthorhombic	
Space group	$Pna2_1$ (33)	
Crystal color	green	
Unit cell dimensions	a = 15.692(2) Å b = 9.314(8) Å c = 14.717(2) Å α = β = γ = 90°	
Cell volume	2150.9(4) $Å^3$	
Z	4	
$[Ni(2,6\text{-}pda)(tptz)](H_2O)_5$		
Empirical formula	$C_{25}H_{28}N_7Ni_1O_9$	
Formula weight	529.10 $g \cdot mol^{-1}$	
Crystal system	triclinic	
Space group	P-1 (2)	
Crystal color	yellow	
Unit cell dimensions	a = 9.442(2) Å b = 10.230(2) Å c = 16.658(4) Å α = 74.53(2) β = 83.95(2) γ = 66.17(2)	
Cell volume	1418.4(6) $Å^3$	
Z	2	
$[Ni_2(4,4'\text{-}bipy)(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$		
Empirical formula	$C_{46}H_{50}N_{18}Ni_2O18$	
Crystal system	monoclinic	
Space group	C2/c (2)	
Crystal color	yellow	
Unit cell dimensions	a = 18.479(4) Å, b = 14.490(4) Å, c = 23.256(6) Å, β = 107.18(2)	
Cell volume	5949.0(3) $Å^3$	
Z	4	
		

Table 2.7: New Ni(II) coordination compounds with phen ligand and various co-ligands.

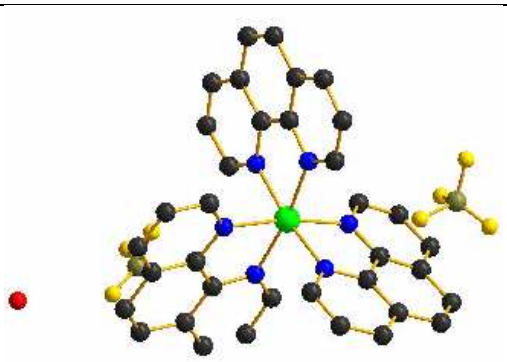
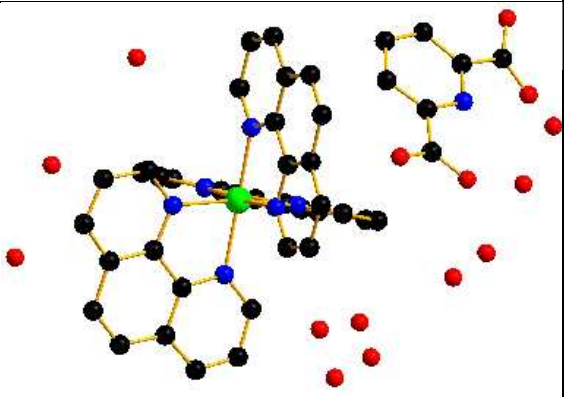
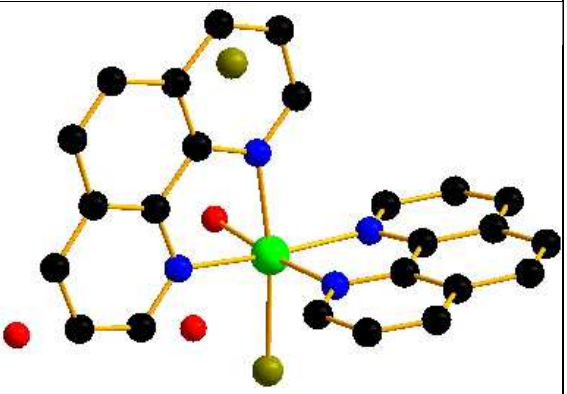
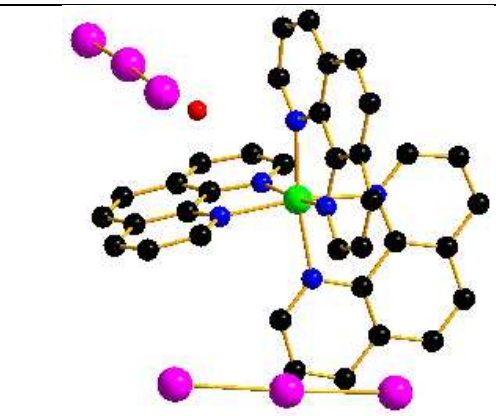
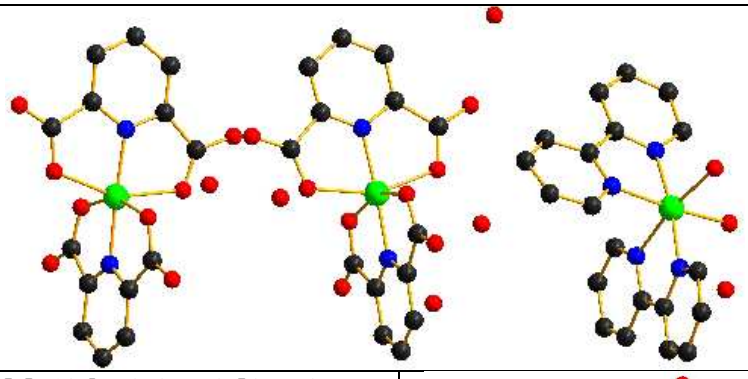
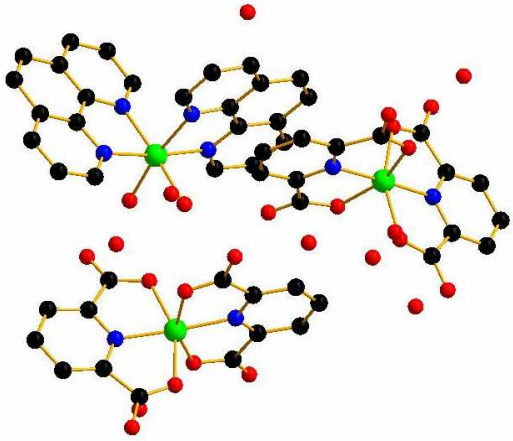
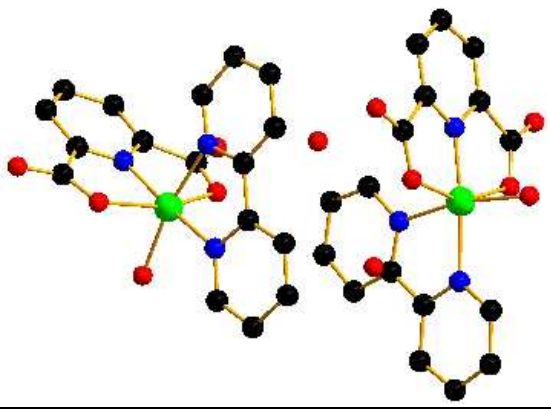
New Ni(II) coord. compounds	Figures of the coord. compounds
$[Ni(Phen)_3](BF_4)_2(H_2O)$	
Empirical formula $C_{36}H_{24}N_6Ni_1O_1F_8$ Crystal system triclinic Space group P-1 (2) Crystal color red Unit cell dimensions a = 9.085(2) Å b = 12.764(2) Å c = 15.099(3) Å α = 95.84(1)°, β = 90.48(1)°, γ = 95.23 (1)° Cell volume 1734.1(1) $Å^3$ Z 2	
$[Ni(Phen)_3](pda)(H_2O)_{11}$	
Empirical formula $C_{43}H_{27}N_7Ni_1O_{15}$ Crystal system monoclinic Space group C2/c (15) Crystal color red Unit cell dimensions a = 28.683(3) Å b = 19.070(1) Å c = 21.049(2) Å β = 129.49(7)° Cell volume 8885.29 (14) $Å^3$ Z 8	
$[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$	
Empirical formula $C_{24}H_{22}Cl_2N_4Ni_1O_3$ Crystal system triclinic Space group P-1 (2) Crystal colour green Unit cell dimensions a = 9.632(1) Å b = 11.475(2) Å c = 12.863(2) Å α = 63.87(1)°, β = 108.17(1)°, γ = 79.40(1)° Cell volume 1254.5(3) $Å^3$ Z 2	
$[Ni(Phen)_3](I_3)_2(H_2O)$	
Empirical formula $C_{36}H_{24}N6Ni_1I_6O_1$ Crystal system triclinic Space group P-1 (2) Crystal colour red Unit cell dimensions a = 10.035(1) Å b = 12,698(2) Å c = 18.091(2) Å α = 79.77(2)°, β = 87.04(2)°, γ = 67.253(2)° Cell volume 2091.8(7) $Å^3$ Z 2	

Table 2.8: New Ni(II) mixed-ligand coordination compounds with 2,6-pda ligand.

New Ni(II) coord. compounds	Figures of the coord. compounds
$[Ni(2,6\text{-}pda)(2,6\text{-}pdaH)]_2[Ni(2,2'\text{-}bipy)_2(H_2O)_2](H_2O)_6$	
Empirical formula $C_{48}H_{46}N_8Ni_3O_{24}$ Crystal system triclinic Space group P-1 (2) Crystal color blue Unit cell dimensions a = 10.201(2) Å, b = 15.034(3) Å, c = 19.227(3) Å α = 112.11(1)°, β = 93.14(1)°, γ = 103.25(1)° Cell volume 2626.7(8) $Å^3$ Z 2	
	
$[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$	
Empirical formula $C_{52}H_{52}N_8Ni_3O_{27}$ Crystal system triclinic Space group P-1 (2) Crystal color blue Unit cell dimensions a = 13.545(2) Å b = 14.717(2) Å c = 15.590(2) Å α = 77.60(1)° β = 72.86(1)° γ = 76.32.(1)° Cell volume 2849.7(6) $Å^3$ Z 2	
$[Ni(H_2O)(2,2'\text{-}bipy)(2,6\text{-}pda)](H_2O)_2$	
Empirical formula $C_{17}H_{15}N_3Ni_1O_6$ Crystal system monoclinic Space group $P2_1/c$ (14) Crystal colour blue Unit cell dimensions a = 10.652(2) Å b = 20.624(3) Å c = 17.699(3) Å β = 98.21(1)° Cell volume 3848.4(1) $Å^3$ Z 8	

Almost all coordination compounds described in this work exhibit H-bonding and/or π–π stacking. π–π interactions are important noncovalent intermolecular forces [25]. They are well known for stabilizing structures especially in supramolecules. For example they play an important role in DNA, where they add to the stability of the molecular structure [26].

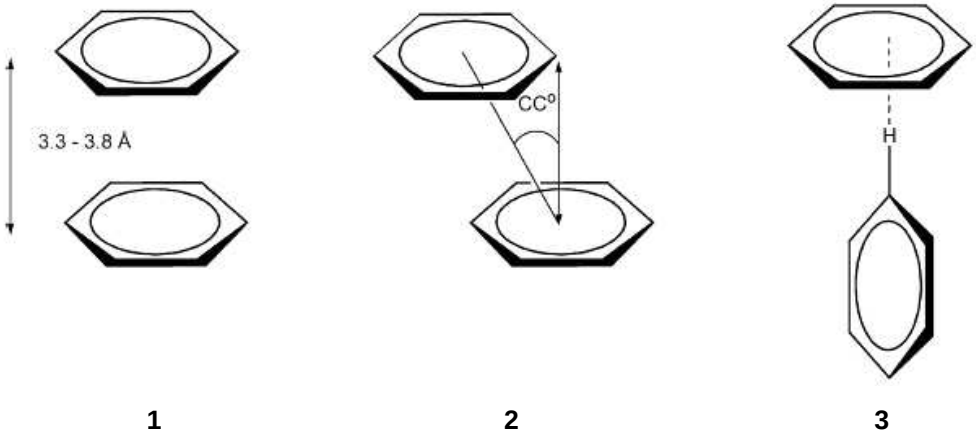


Fig. 2.4: π–π interactions of monoaromatic systems [27].

There are three different patterns of π–π stacking interactions in monoaromatic systems (Fig. 2.4). (1) represents a perfect face-to-face alignment of atoms, (2) represents an offset or slipped packing and (3) depicts the T-shaped conformation. In the face-to-face π–π interaction most of the ring-plane area overlaps. It is considered a rare phenomenon [28]. In $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ (9) this phenomenon could be observed. In the rest of the compounds the offset conformation predominated.

In all Ni(II) coordination compounds described in this work nickel has the coordination number 6. It is important to stress that Ni(II) can also form complexes with other coordination numbers ranging from 3 to 6. Ligands have an influence on the geometry of the formed complexes; this aspect was explained in the introduction in terms of the LFT. Ligands used in this work coordinated to the metal center via N atoms, in case of 2,6-pda and aqua ligands also via O atoms. By using softer ligands coordinating via P or S atoms, Ni(II) complexes with other coordination numbers, generally 4, can be obtained. The preferred geometry for coordination number 4 is

square-planar [29]. There is a tendency to add a further ligand to give 5-coordinate compounds. The ligand exchange processes tend so to be associative. A particular characteristic is the existence of complicated equilibria, commonly temperature and concentration dependent, involving different structural types. These lead to conformational changes. This phenomenon is also known as ‘’anomalous’’ properties of Ni(II) complexes. Mainly three structural and conformational changes that Ni(II) complexes undergo are as follows:

1. Square-octahedral ambivalence: formation of 5- and 6-coordinate complexes by addition of ligands to square-planar complexes:

$$MeL_4 + L' = MeL_4L'$$
$$MeL_4L' + L' = MeL_4L'_2$$

In most cases equilibria strongly favor coordination number 6, with *trans* structures and two unpaired electrons. The complexes are high spin and paramagnetic. The Lifschitz salts represent well-known examples of the square-octahedral ambivalence [30].

$$[Ni(stien)X_2] \rightleftharpoons [Ni(stien)^{2+}] + 2X^-$$

(stien – stilbenediamine, X – various anions)

2. Monomer-polymer equilibria: 4-coordinate complexes associate or polymerize, to give 5- or 6-coordinate Ni(II) complexes.

3. Planar-tetrahedral equilibria and isomerism.

By taking into account the above described aspects and the details that they contain, it becomes obvious that there are many factors influencing the coordination geometry in Ni(II) complexes. These are the choice of the solvent for the reaction, the stoichiometry of the reacting species, the concentration, the method of preparation, the temperature, the properties of the ligands and co-ligands and the properties of the metal center itself. The working conditions and the ligands used in this work undoubtedly made the formation of 6-coordinate complexes preferable.

3. Special Section

3.1 Complexes of nickel(II) with N-heterocyclic ligands

3.1.1 Nickel(II) complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine

3.1.1.1 Crystal structure of bis-(2,4,6-tris(2-pyridyl)-1,3,5-triazine)-nickel(II) ditetrafluoroborate monohydrate, $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1)

$[Ni(tptz)_2](BF_4)_2(H_2O)$ (**1**) crystallizes in the orthorhombic space group Pcca (54) with a = 20.69(2) Å, b = 10.84(1) Å, c = 16.71(1) Å, V = 3749.31 $Å^3$ and Z = 4. Crystallographic and refinement details are listed below in Tables 3.1 and 3.2. The structure of (**1**) consists of one cationic complex $[Ni(tptz)_2]^{2+}$, two tetrafluoroborate counterions and one molecule of lattice water. The $[Ni(tptz)_2]^{2+}$ cation contains a 6-coordinate Ni(II) atom coordinated to two tptz ligands via the N atoms in a slightly distorted octahedral arrangement (Fig. 3.2).

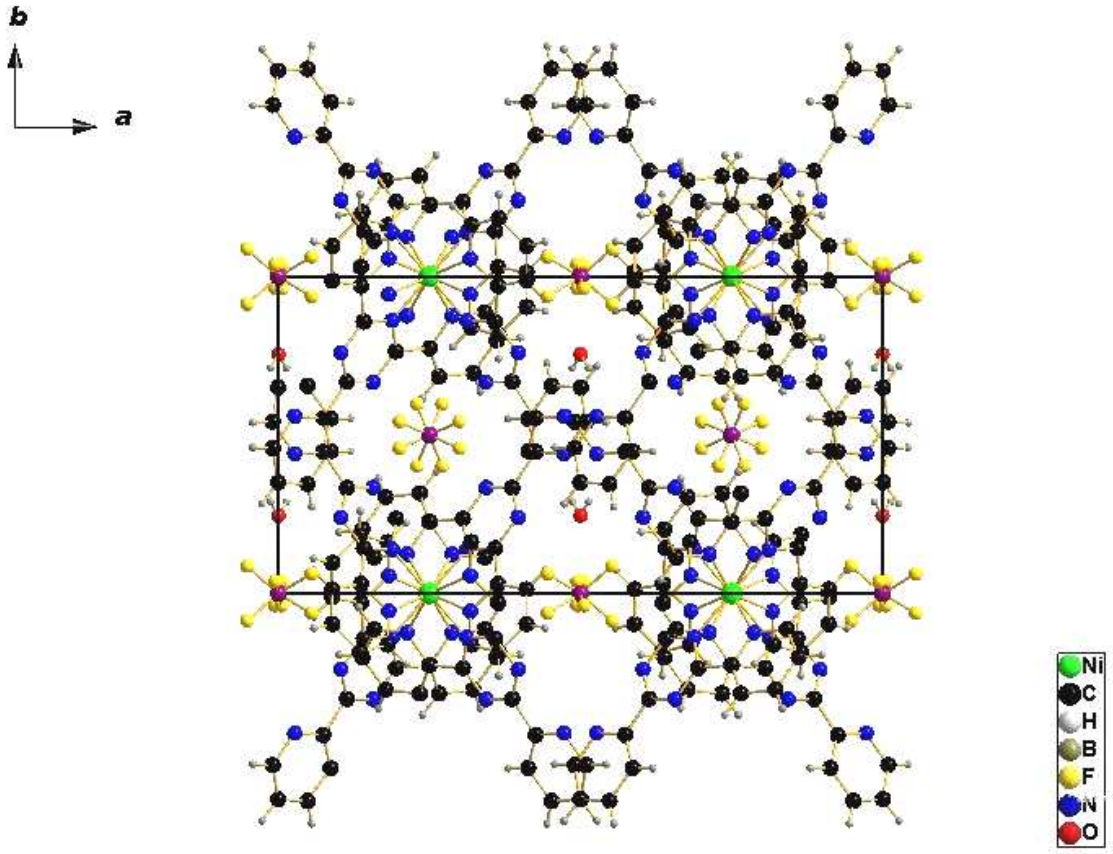


Fig. 3.1: Projection of the unit cell of $[Ni(tptz)_2](BF_4)_2(H_2O)$ along the crystallographic c-axis.

The slightly distorted octahedral arrangement around the Ni(II) metal center is formed by coordination to six N atoms from two tptz ligands (Fig. 3.2). In (**1**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode**,** it coordinates to the Ni(II) metal center through N(1) from the triazine ring and through N(4) and N(6) from the two adjacent pyridyl substituents. The two tptz ligands lie in different planes, with an angle of 87.02(1)°, nearly perpendicular to each othe r.

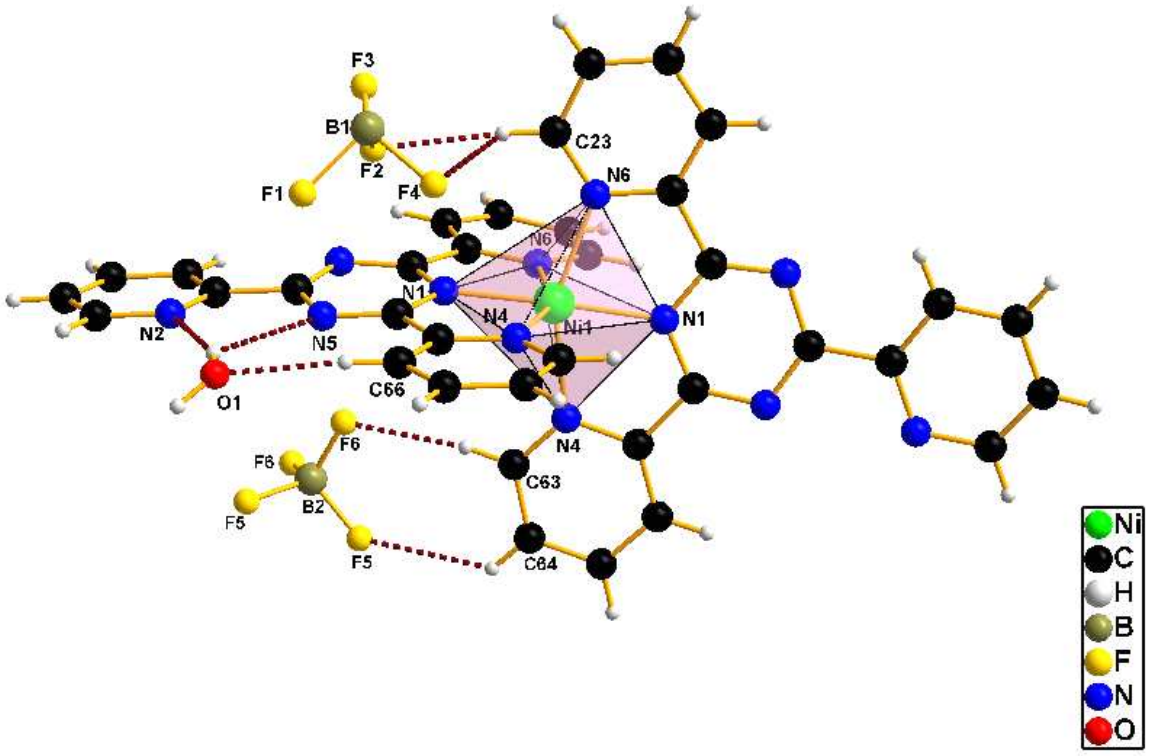


Fig. 3.2: The asymmetric unit of $[Ni(tptz)_2](BF_4)_2(H_2O)$.

The terminal pyridyl groups are rotated from the main least square plane (one triazine ring and two adjacent pyridyl rings, which coordinate to the nickel metal center) by 6.3(1)°. The N-Ni-N angles range from 76.82(7) to 17 7.56(7)°, while the Ni-N bond lengths range from 1.98(2) to 2.15(2) Å. Because of the *trans effect* [31]**,** the Ni(1)-N(6) and Ni(1)-N(4) distances are ca. 0.17 Å longer than Ni(1)-N(1) distances (Table 3.2). The motif in the packing (Fig. 3.1) represents $[Ni(tptz)_2]^{2+}$ monomers along the c-axis with tetrafluoroborate anions between them. One of the two tetrafluoroborate molecules is disordered (Fig. 3.1 and 3.3). Nickel atoms occupy special positions (Fig. 3.3). H-bonds and weak stacking effects control the crystal packing.

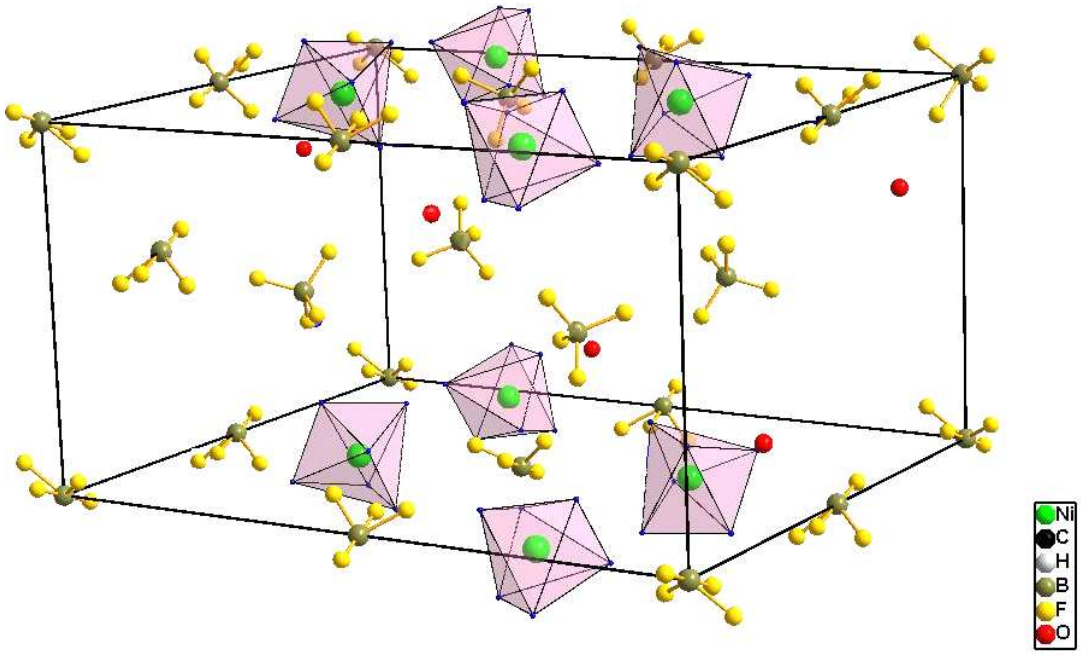


Fig. 3.3: Projection of the unit cell of $[Ni(tptz)_2](BF_4)_2(H_2O)$, atoms other than Ni, B, F and O are omitted for better perspective.

There are hydrogen bonds involving hydrogen atoms of the lattice water and nitrogen atoms of the tptz ligand. The N-H atomic distances range from 2.10 to 2.46 Å. The non coordinating terminal pyridyl ring of the one monomer stacks with the coordinating pyridyl ring of the other monomer. The stacking effect is weak, with a spacing of ca. 4.09 Å (C(63)-C(45) and C(64)-C(44) 4.07 Å. The stacking C-atoms are colored in pink (Fig. 3.5). There are also hydrogen bonds involving aromatic H atoms and fluorine atoms of the BF_4^- anion. The H(C25)-F(5) and the H(C63)-F(6) distances are 2.37 and 2.33 Å, respectively. The H-F interactions appear to link the $[Ni(tptz)_2]^{2+}$ monomers with each other (Fig.3.4), hence influencing the packing of the structure. The slight twisting of the terminal pyridyl groups with respect to the central triazine ring is thought to be caused by weak π-π stacking effects.

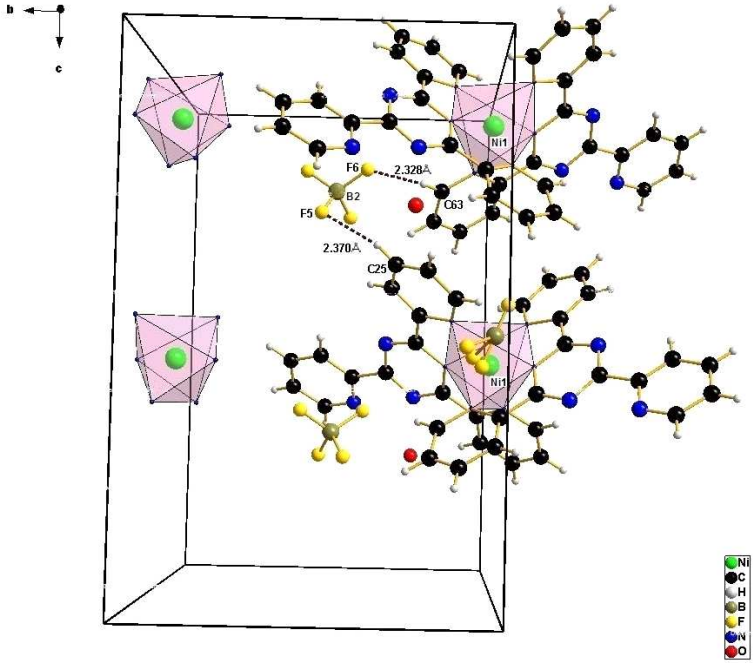


Fig. 3.4: Interconnection of monomers via H-bonds in $[Ni(tptz)_2](BF_4)_2(H_2O)$.

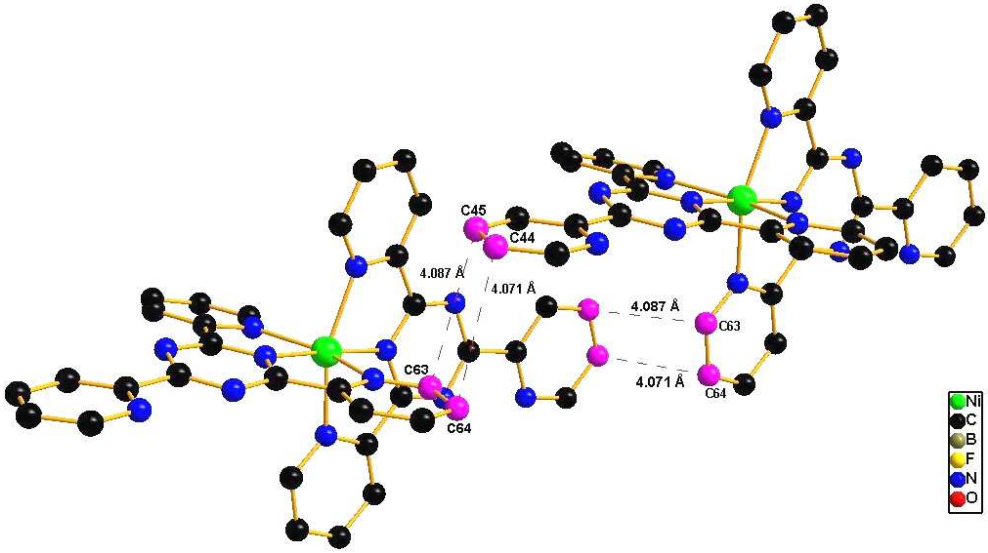


Fig. 3.5: Pyridyl to pyridyl alignment in π-π stacking in $[Ni(tptz)_2](BF_4)_2(H_2O)$.

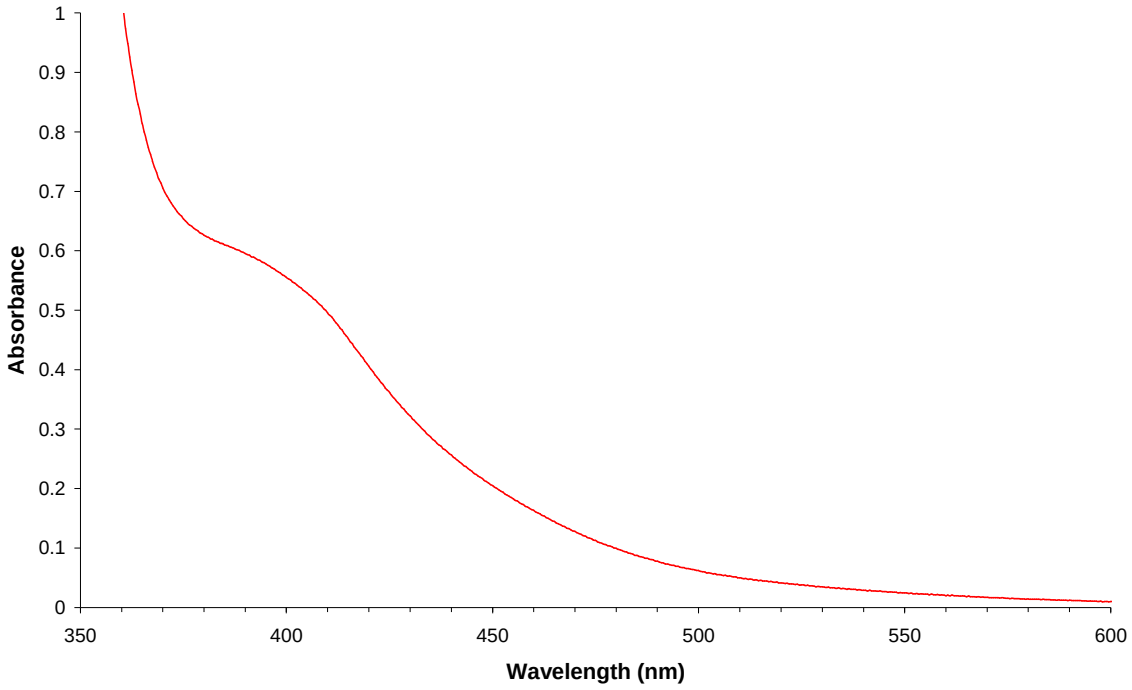
It is common practice to determine the theoretical positions of H atoms in H-X bonds (X= C, N, O, halides…). H atoms attached to carbon were positioned geometrically and refined using a riding model, with C-H = 0.93 Å and U_{iso}(H) values set at 1.2U_{eq}(C). The water H atoms were found in a difference Fourier synthesis and refined with restrained distances of O-H = 0.90 Å. This applies to all structures presented in this work.

3.1.1.1 Experimental

Preparation of $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1)

20 ml of a 0.01-molar aqueous nickel tetrafluoroborate solution were mixed with two equivalents (40 ml) of a 0.01-molar (0.125 g) methanolic tptz solution. The mixture was stirred at approximately 60 ℃ for 45 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After five days orange crystals were collected and subjected to X-ray single crystal analysis. Afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS-Spectrum of $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1)



The absorption in the visible area of the spectrum at approximately 420 nm is responsible for the dark orange color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 3.1: Crystallographic and refinement details for $[Ni(tptz)_2](BF_4)_2(H_2O)$.

Empirical formula	$C_{36}\,H_{24}\,N_{12}\,O_1\,Ni_1\,B_2\,F_8$
Formula weight	875.02 $g \cdot mol^{-1}$
Crystal system	orthorhombic
Space group	Pcca (54)
Crystal color	orange
Unit cell dimensions	a = 20.69 (2) Å
	b = 10.84 (1) Å
	c = 16.71 (1) Å
	α = β = γ = 90°
Cell volume	3749.31 $Å^3$
Z	4
Density (calculated)	1.550 $g \cdot cm^{-3}$
Absorption coefficient	0.61 mm^{-1}
F (000)	1776.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem II
Radiation type, wavelength	Mo-K_α, λ = 71.07 pm
Measurement temperature	170 (2) K
2θ range	3.94° - 54.76°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-26 / 26, -13 / 13, -19 / 21
Reflections collected	44732
Independent reflections	4206
R_{int}	0.0545
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	300
GooF(S)	1.009[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0390, wR_2[b] = 0.0988
R indices (all data)	R_1 = 0.0587, wR_2 = 0.1053

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.
$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 3.2: Selected distances/Å and angles/° in $[Ni(tptz)_2](BF_4)_2(H_2O)$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	1.975(2)
Ni(1)	N(4)	2.145(2)
Ni(1)	N(6)	2.147(2)
B(1)	F(1)	1.572(3)
B(1)	F(2)	1.481(3)
B(1)	F(3)	1.099(5)
B(1)	F(4)	1.487(3)
B(2)	F(5)	1.397(4)
B(2)	F(6)	1.362(3)
F(5)	H(C64)	2.568(2)
F(6)	H(C63)	2.328(2)
F(2)	H(C23)	2.338(3)
F(4)	H(C23)	2.507(3)
O(1)	H(C66)	2.257(2)
N(2)	H(O1)	2.103(3)
N(5)-	H(O1)	2.462(3)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(1)	Ni(1)	N(1)	177.6(7)
N(4)	Ni(1)	N(4)	77.2(7)
N(1)	Ni(1)	N(6)	76.8(7)
N(1)	Ni(1)	N(6)	104.9(7)
N(4)	Ni(1)	N(6)	76.8(7)
N(6)	Ni(1)	N(6)	94.4(6)

3.1.1.2 Crystal structure of bis-(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) Iodide monohydrate, $[Ni(tptz)_2](I)_2(H_2O)$ (2)

$[Ni(tptz)_2](I)_2 \cdot H_2O$ (**2**) crystallizes in the triclinic space group P-1(2) with a = 9.092(2) Å, b = 13.076(3) Å, c = 16.002(3) Å, α = 84.91(2)°, β = 77.87(2)°, γ = 89.09(2)°, V = 1852.7(7) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below in Tables 3.3 and 3.4. The structure of (**2**) consists of one cationic complex $[Ni(tptz)_2]^{2+}$, two iodide counterions and one molecule of lattice water. The $[Ni(tptz)_2]^{2+}$ cation contains a 6-coordinate Ni(II) atom coordinated to two tptz ligands via the N-atoms in a slightly distorted octahedral arrangement (Fig.3.7).

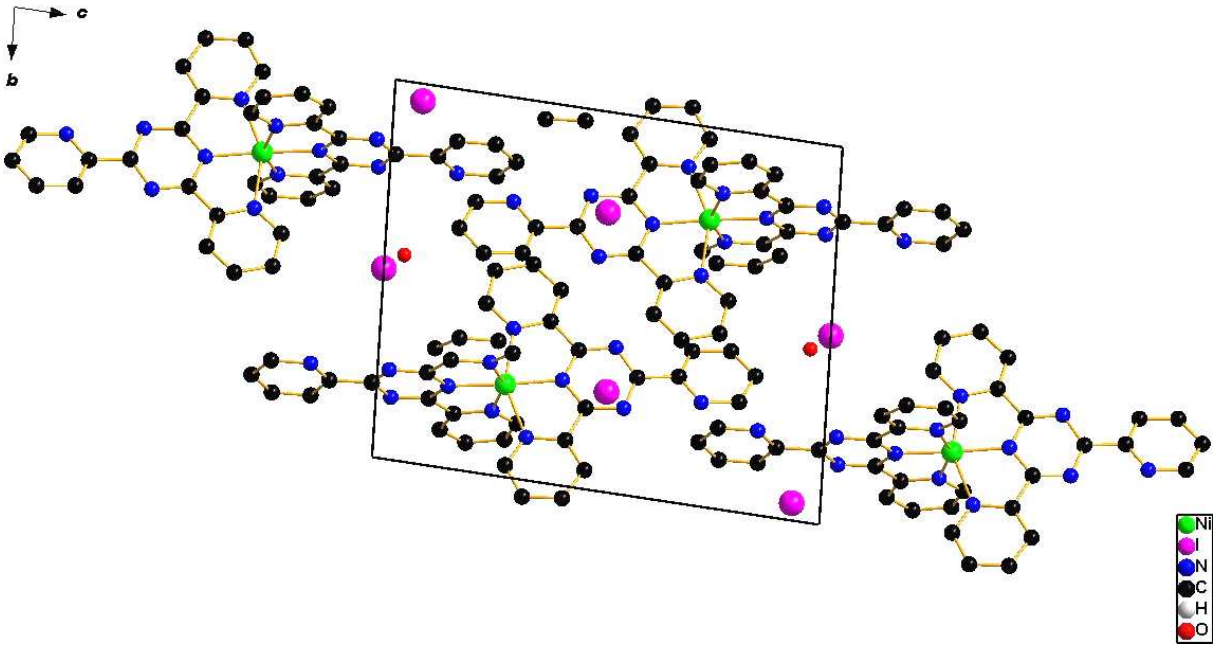


Fig. 3.6: Projection of the unit cell of $[Ni(tptz)_2](I)_2(H_2O)$ along the crystallographic a-axis.

In (**2**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode and coordinates through N(4) and N(10) from the triazine rings and through N(1), N(3) and N(5), N(7) from two adjacent pyridyl substituents to the Ni(II) metal center. The two tptz ligands lie in different planes, whereas the angle between them is about 83.1(1)°.

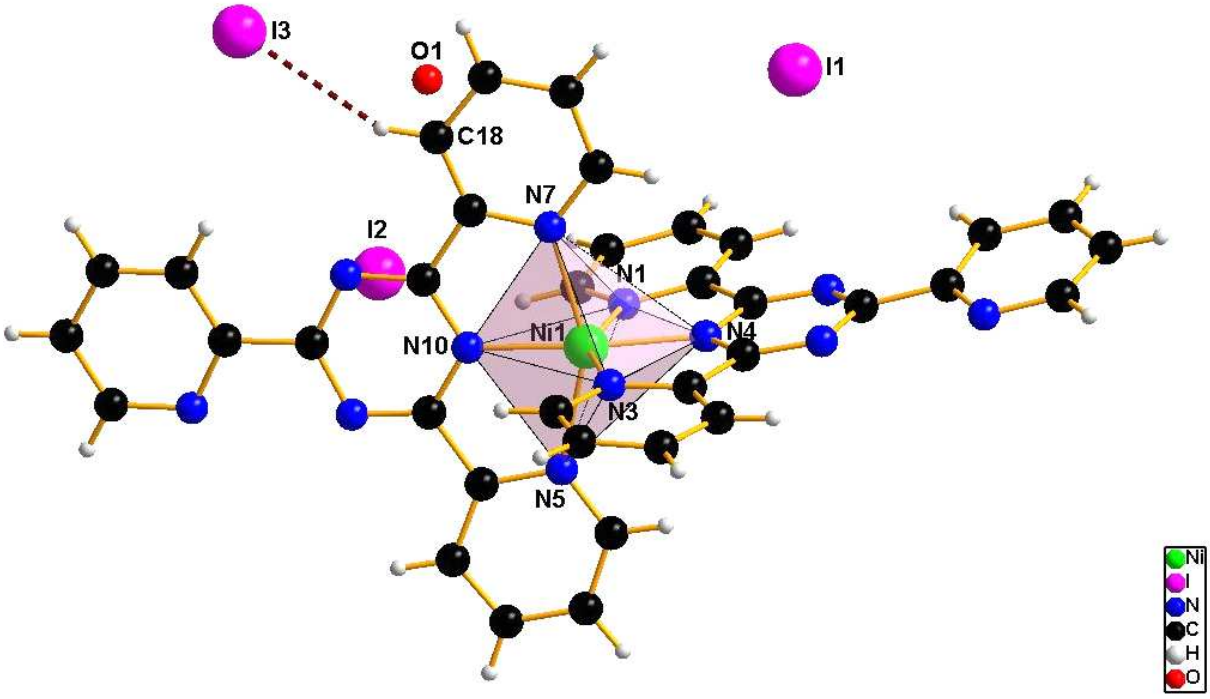


Fig. 3.7: The asymmetric unit of $[Ni(tptz)_2](I)_2(H_2O)$.

The terminal pyridyl groups are rotated from the main least squares plane (one triazine ring and two adjacent pyridyl rings, which coordinate to the nickel metal center through N(7), N(10), N(5) and N(1), N(2), N(5)) by 6.7(2)° and 14.09(2)° respectively. The N-Ni-N angles range from 76.3(3)° to 174.6(3)° and the of Ni-N distances range from 1.981(6) to 2.163(7) Å. Because of the *trans effect***,** the Ni(1)-N(1), Ni(1)-N(3), Ni(1)-N(5) and Ni(1)-N(7) distances are ca. 0.17 Å longer than Ni(1)-N(4) and Ni(1)-N(10) distances (Table 3.4). The motif in the packing (Fig. 3.6) represents monomers along the a-axis. Two of three iodide atoms, I(2) and I(3) occupy special positions (Fig. 3.8). I(3) is bound through a hydrogen bond I(3)···H(C63) to one of the pyridyl rings. There are π–π-stacking interactions between the terminal pyridyl group of the tptz ligand with a coordinating pyridyl ring of the other tptz ligand (Fig. 3.9). The rings are slipped in an offset conformation and the hydrogen atoms are roughly above the ring centers. The centroid-centroid distance is 3.81 Å, ring normal and the vector between the ring centroids form an angle of around 21°. The stacking effects also account for the sligh tly twisted position of the terminal non-coordinating pyridyl groups with respect to the central triazine ring.

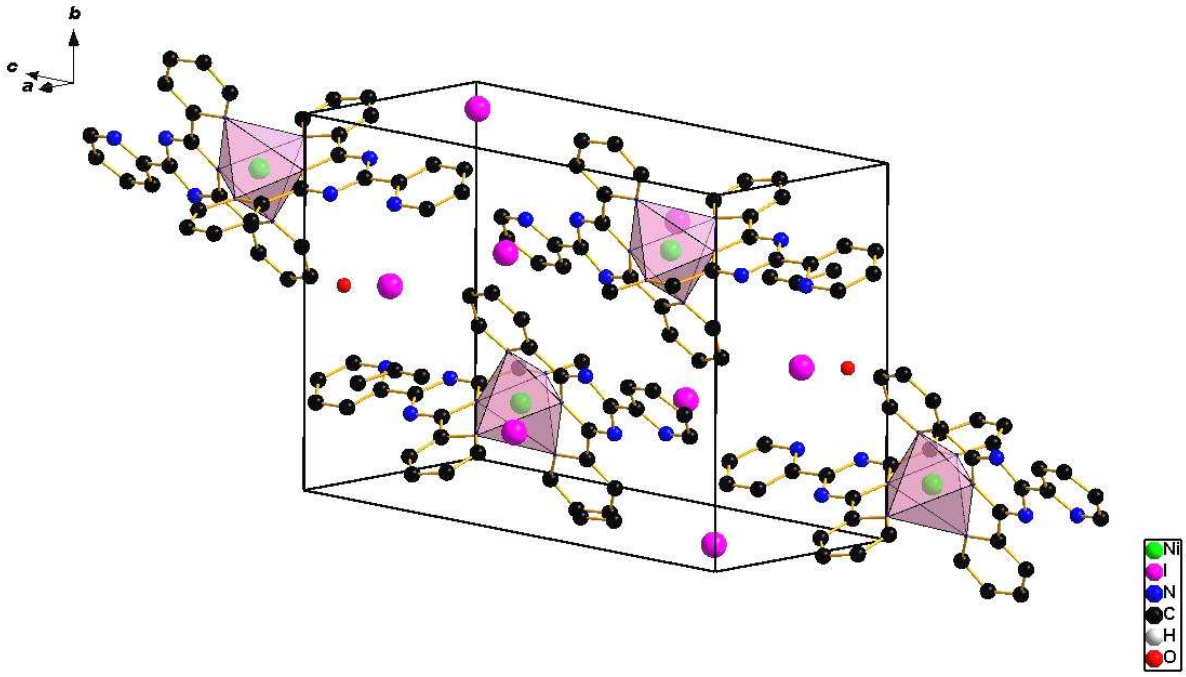


Fig. 3.8: Projection of the unit cell of $[Ni(tptz)_2](I)_2(H_2O)$.

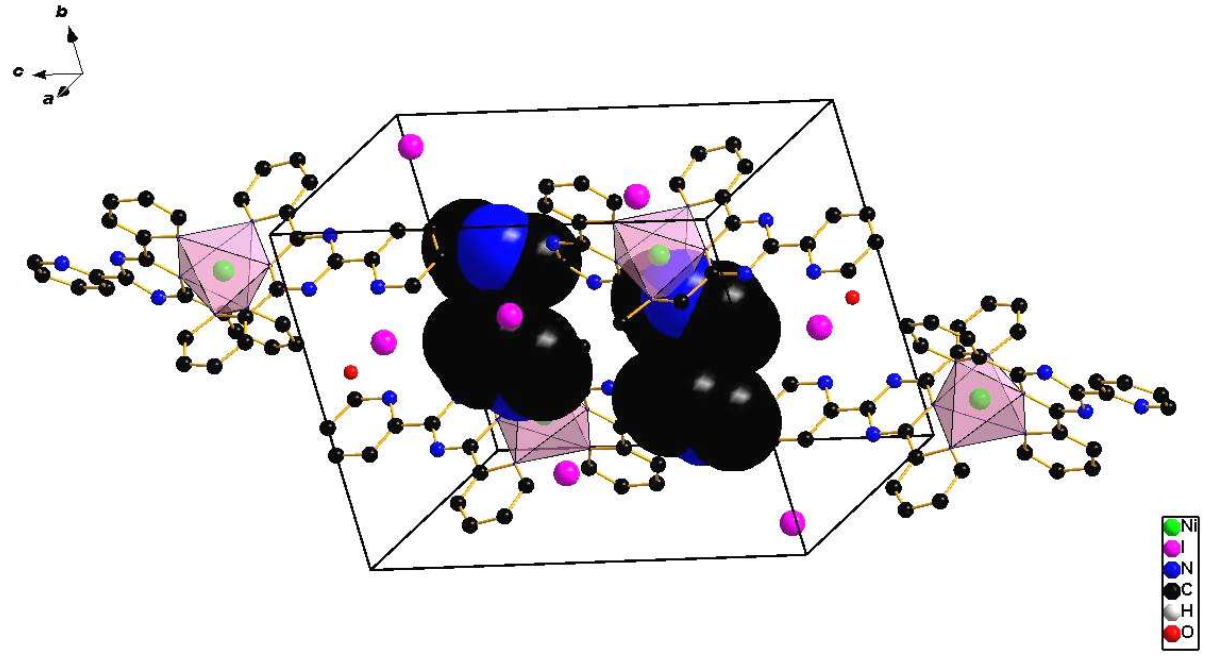


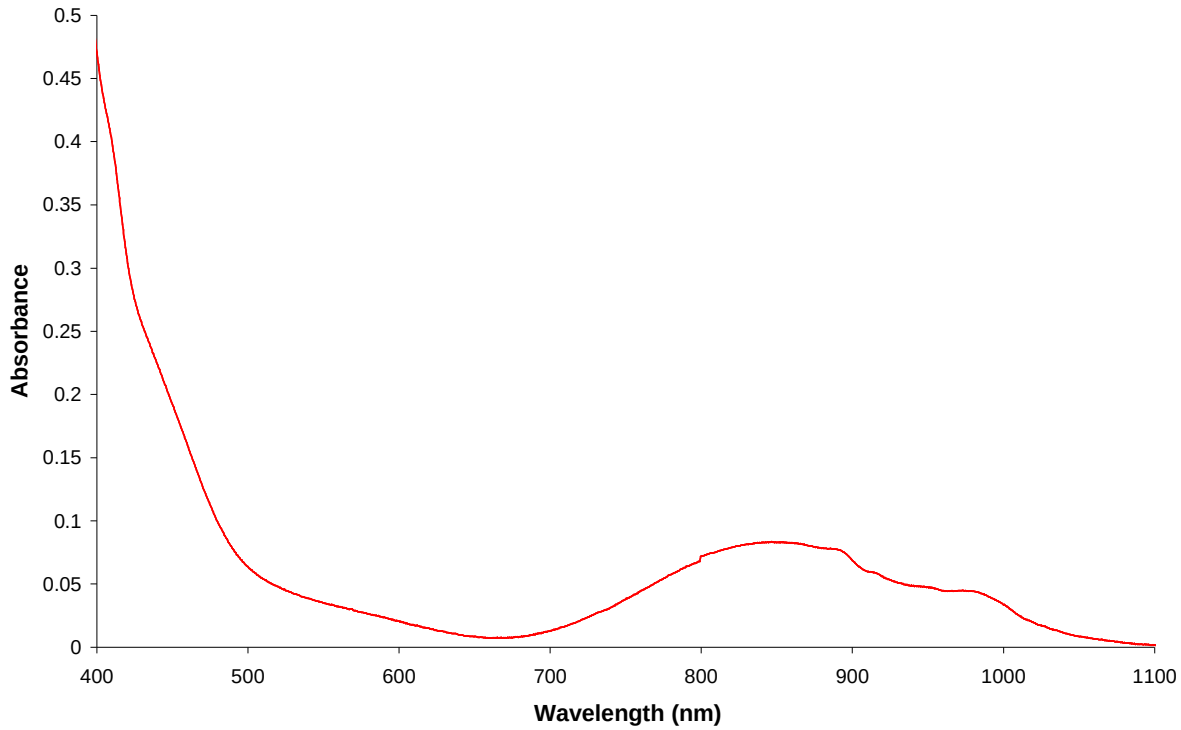
Fig. 3.9: Pyridyl to pyridyl alignment in π-π stacking in $[Ni(tptz)_2](I)_2(H_2O)$.

3.1.1.2 Experimental

Preparation of $[Ni(tptz)_2](I)_2(H_2O)$ (2)

20 ml of a 0.01-molar (0.063 g) aqueous nickel iodide solution were mixed with two equivalents (40 ml) of a 0.01-molar (0.125 g) ethanolic tptz solution. The mixture was stirred at approximately 60 ℃ for 50 min in a beaker . By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After 8 days orange crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS-Spectrum of $[Ni(tptz)_2](I)_2(H_2O)$ (2)



The absorption in the visible area of the spectrum at approximately 440 nm is responsible for the dark orange color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 3.3: Crystallographic and refinement details for $[Ni(tptz)_2](I)_2(H_2O)$.

Empirical formula	$C_{36}\,H_{26}\,N_{12}\,O_1\,Ni_1\,I_2$
Formula weight	955.2 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	orange
Unit cell dimensions	a = 9.092 (2) Å
	b = 13.076 (3) Å
	c = 16.002 (3) Å
	α = 84.91(2)°, β = 77.87(2)°, γ = 89.09(2)°
Cell volume	1852.7(7) $Å^3$
Z	2
Density (calculated)	1.712 $g \cdot cm^{-3}$
Absorption coefficient	2.24 mm^{-1}
F (000)	936.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07 pm
Measurement temperature	293 (2) K
2θ range	3.62°- 56.14°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-11 / 11, -17 / 17, -21 / 21
Reflections collected	22001
Independent reflections	8150
R_{int}	0.1019
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	475
GooF(S)	0.813
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0626, wR_2[b] = 0.1353
R indices (all data)	R_1 = 0.1549, wR_2 = 0.1652

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 3.4: Selected distances/Å and angles/° in $[Ni(tptz)_2](I)_2(H_2O)$.

Distances/Å		
Atom 1	**Atom 2**	**d[1,2]**
Ni(1)	N(1)	2.163(7)
Ni(1)	N(3)	2.150(7)
Ni(1)	N(4)	1.991(6)
Ni(1)	N(5)	2.155(7)
Ni(1)	N(7)	2.140(6)
Ni(1)	N(10)	1.981(6)

Angles/°			
Atom 1	**Atom 2**	**Atom 3**	**Angle [1,2,3]**
N(10)	Ni(1)	N(4)	174.6(3)
N(10)	Ni(1)	N(7)	76.8(3)
N(10)	Ni(1)	N(3)	108.1(3)
N(10)	Ni(1)	N(5)	76.5(3)
N(10)	Ni(1)	N(1)	99.1(3)
N(4)	Ni(1)	N(7)	99.9(3)
N(4)	Ni(1)	N(3)	76.3(3)
N(4)	Ni(1)	N(5)	106.9(3)
N(4)	Ni(1)	N(1)	76.5(3)
N(7)	Ni(1)	N(3)	93.8(3)
N(7)	Ni(1)	N(5)	153.1(3)
N(7)	Ni(1)	N(1)	91.6(3)
N(3)	Ni(1)	N(5)	90.9(3)
N(3)	Ni(1)	N(1)	152.8(3)
N(5)	Ni(1)	N(1)	96.2(3)

3.1.1.3 Crystal structure of bis-(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) Iodide dihydrate, $[Ni(tptz)_2](I)_2(H_2O)_2$ (3)

$[Ni(tptz)_2](I)_2(H_2O)_2$ (**3**) crystallizes in the monoclinic space group $C2/_C$ with a = 41.915(5) Å, b = 9.348(1) Å, c = 20.668(3) Å, β = 108.17 (1)°, V = 7694.2(3) Å ^{3} and Z = 8. Crystallographic and refinement details are listed below in Tables 3.5 and 3.6. The structure of (**3**) consists of one cationic complex $[Ni(tptz)_2]^{2+}$, two iodide counterions and two molecules of lattice water. The $[Ni(tptz)_2]^{2+}$ cation contains a 6-coordinate Ni(II) atom coordinated to two tptz ligands via the N-atoms in a slightly distorted octahedral arrangement (Fig.4.1).

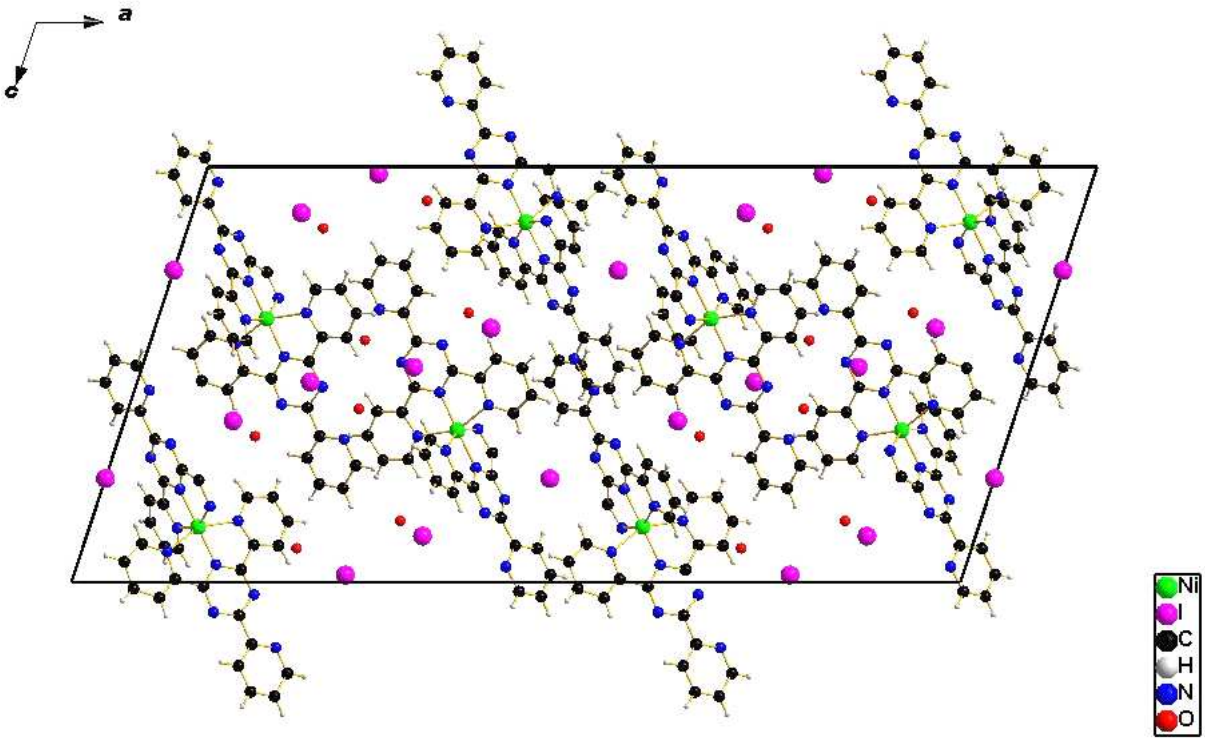


Fig. 4.0: Projection of the unit cell of $[Ni(tptz)_2](I)_2(H_2O)_2$ along the crystallographic a-axis.

In (**3**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode and coordinates through N(2) and N(7) from the triazine rings and through N(1), N(3) and N(5), N(7) from two adjacent pyridyl substituents to the Ni(II) metal center. The two tptz ligands lie in different planes, where the angle between them is about 83.1(1)°, it deviates from the perpendicular position by ca. 7°.

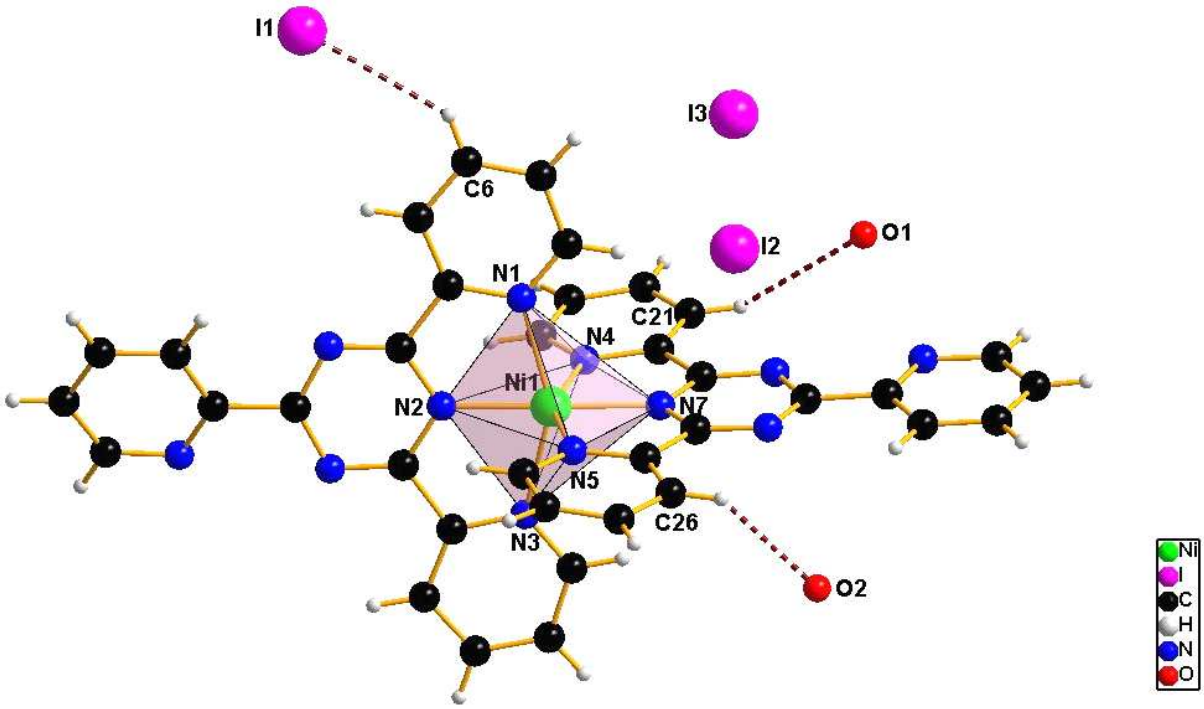


Fig. 4.1: The asymmetric unit of of $[Ni(tptz)_2](I)_2(H_2O)_2$.

The terminal pyridyl groups are rotated from the main least squares plane (one triazine ring and two adjacent pyridyl rings), which coordinate to nickel metal center through N(1), N(2), N(3) and N(4), N(5), N(7) atoms) by 20.54(2)° and 4.79(2)°, respectively. The N-Ni-N angles range from 76.3(3)° to 178.7(3)° and the of Ni-N distances range from 1.977(6) to 2.150(7) Å. Because of the *trans effect***,** the Ni(1)-N(1), Ni(1)-N(3), Ni(1)-N(4) and Ni(1)-N(5) distances are ca. 0.17 Å longer than Ni(1)-N(2) and Ni(1)-N(7) distances (Table 3.6). The motif in the packing represents monomers running along the a-axis, two of three Iodide atoms I(1) and I(3) occupy special positions. I(1) is bound through a I(1)···H(C6) hydrogen bond to one of the coordinating pyridyl rings. Two lattice water molecules wO(1) and wO(2) are also bound through hydrogen bonds to two coordinating pyridyl rings. There are π–π stacking interactions between the terminal pyridyl group of the tptz ligand with a coordinating pyridyl ring of the other tptz ligand (Fig. 4.3). The rings are slipped in an offset conformation, the hydrogen atoms are roughly over the ring centers. The centroid-centroid distances range from 3.64 Å to 3.85 Å, ring normal and the vector between the ring centroids form an angle of around 21°. The stacking effects also account for the twisted position of the terminal non-coordinating pyridyl groups with respect to the central triazine ring.

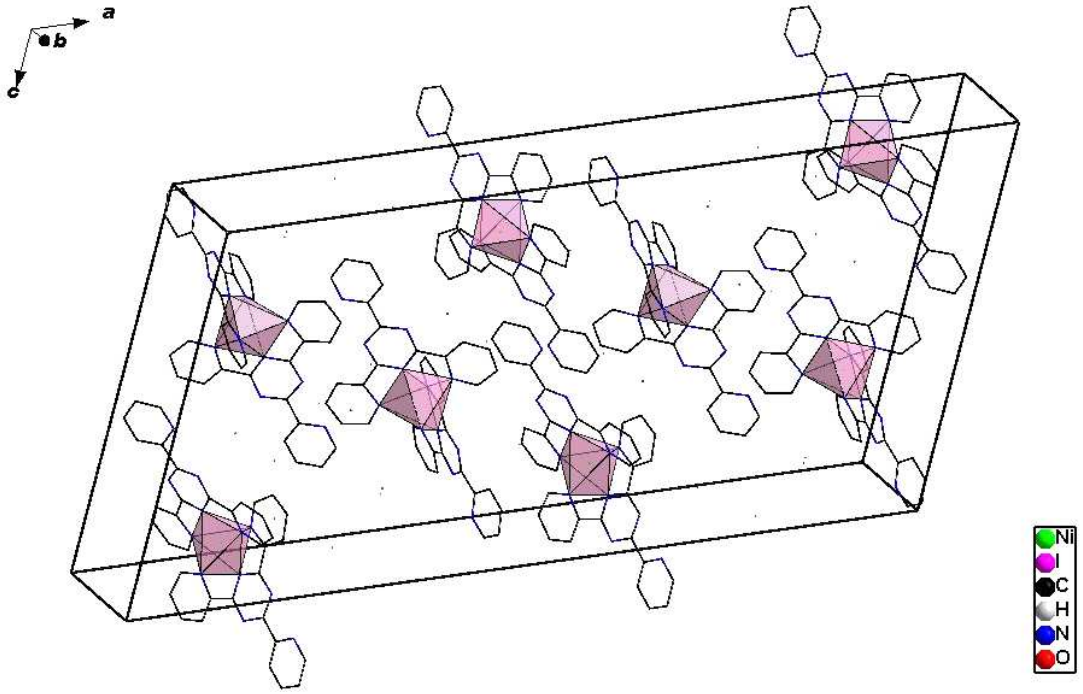


Fig. 4.2: 3D projection of the unit cell of $[Ni(tptz)_2](I)_2(H_2O)_2$.

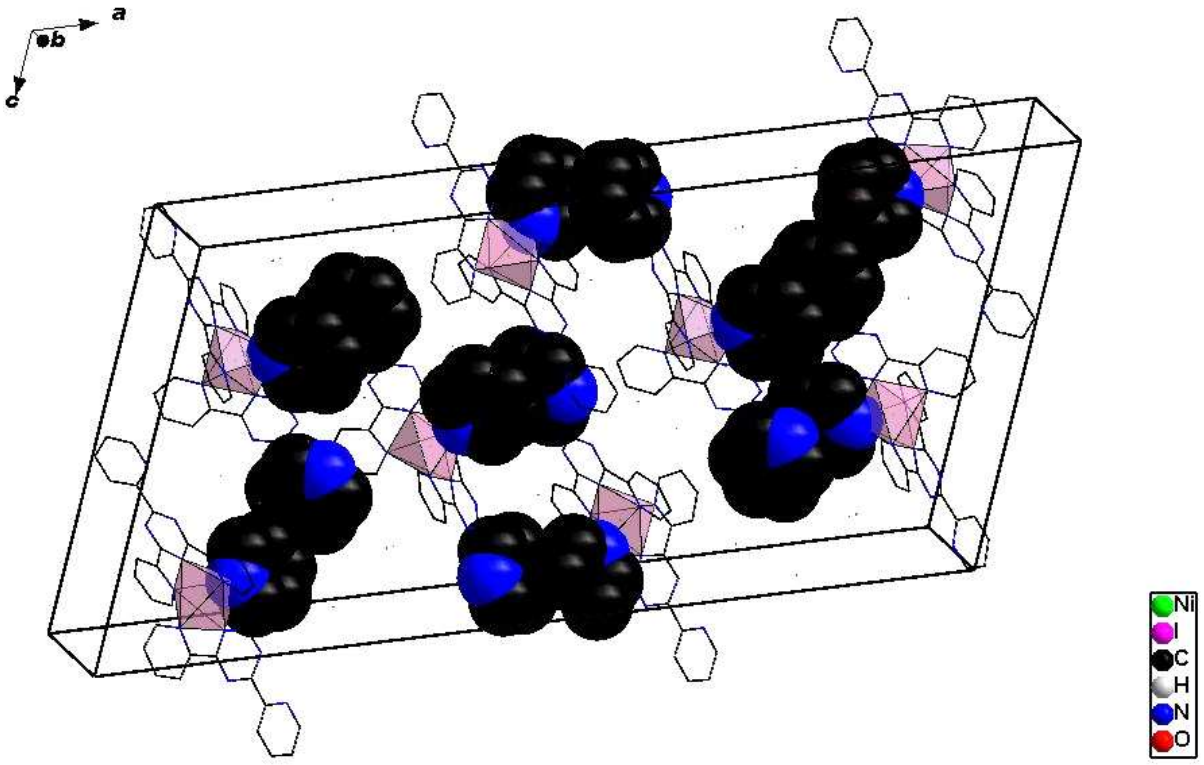


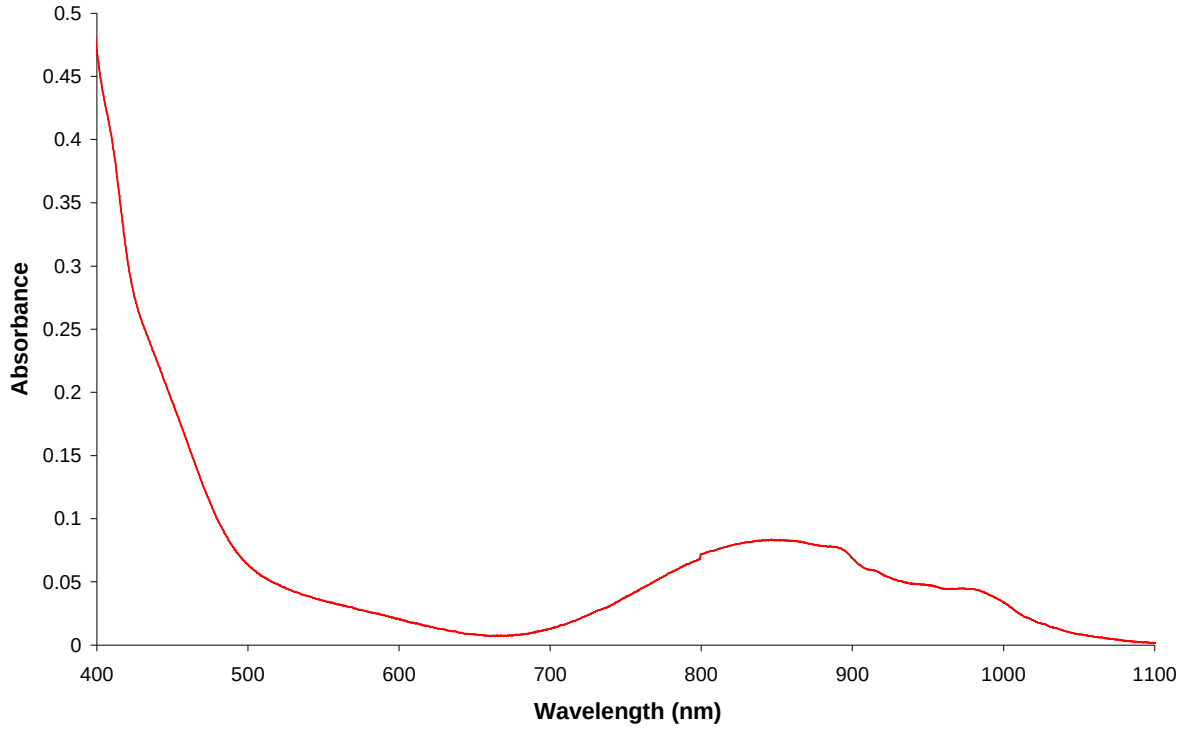
Fig.4.3: Pyridyl to pyridyl alignment in π- π–stacking in of $[Ni(tptz)_2](I)_2(H_2O)_2$.

3.1.1.3 Experimental

Preparation of $[Ni(tptz)_2](I)_2(H_2O)_2$ (3)

20 ml of a 0.01-molar (0.063 g) aqueous nickel iodide solution were mixed with two equivalents (40 ml) of a 0.01-molar (0.125 g) methanolic tptz solution. The mixture was stirred at approximately 60 ℃ for 50 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After ten days orange crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS-Spectrum of $[Ni(tptz)_2](I)_2(H_2O)_2$ (3)



The absorption in the visible area of the spectrum at approximately 440 nm is responsible for the dark orange color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 3.5: Crystallographic and refinement details of $[Ni(tptz)_2](I)_2(H_2O)_2$.

Empirical formula	$C_{36}\,H_{28}\,N_{12}\,O_2\,Ni_1\,I_2$
Formula weight	973.2 $g \cdot mol^{-1}$
Crystal system	monoclinic
Space group	$C2/_C$
Crystal color	orange
Unit cell dimensions	a = 41.915(5) Å
	b = 9.348(1) Å
	c = 20.668(3) Å
	β = 108.17(1)°
Cell volume	7694.2(3) $Å^3$
Z	8
Density (calculated)	1.680 $g \cdot cm^{-3}$
Absorption coefficient	2.16 mm^{-1}
F (000)	3824.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07 pm
Measurement temperature	293 (2) K
2θ range	3.80°- 56.30°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-49 / 49, -11 / 11, -24 / 24
Reflections collected	25713
Independent reflections	6499
R_{int}	0.0863
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	483
GooF(S)	0.821
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0590, wR_2[b] = 0.1409
R indices (all data)	R_1 = 0.1412, wR_2 = 0.1692

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 3.6: Selected distances/Å and angles/° in $[Ni(tptz)_2](I)_2(H_2O)_2$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	2.141(7)
Ni(1)	N(2)	1.978(6)
Ni(1)	N(3)	2.150(7)
Ni(1)	N(4)	2.140(8)
Ni(1)	N(5)	2.131(9)
Ni(1)	N(7)	1.977(6)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(7)	Ni(1)	N(2)	178.7(3)
N(7)	Ni(1)	N(5)	76.3(3)
N(2)	Ni(1)	N(5)	103.2(3)
N(7)	Ni(1)	N(4)	76.8(3)
N(2)	Ni(1)	N(4)	103.8(3)
N(5)	Ni(1)	N(4)	153.0(3)
N(7)	Ni(1)	N(1)	102.6(3)
N(2)	Ni(1)	N(1)	76.3(3)
N(5)	Ni(1)	N(1)	95.2(3)
N(4)	Ni(1)	N(1)	89.7(3)
N(7)	Ni(1)	N(3)	104.6(3)
N(2)	Ni(1)	N(3)	76.6(3)
N(5)	Ni(1)	N(3)	91.8(3)
N(4)	Ni(1)	N(3)	95.9(3)
N(1)	Ni(1)	N(3)	152.8(3)

3.1.1.4 Crystal structure of bis-(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) nitrate heptahydrate, $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ (4)

$[Ni(tptz)_2](NO_3)_2(H_2O)_7$ (**4**) crystallizes in the monoclinic space group $P2_1/c$ with a = 12.721(2) Å, b = 16.081(2) Å, c = 19.759(3) Å, β = 90.64(1)°, V = 4041.7(1) $Å^3$ and Z = 4. Crystallographic and refinement details are listed below, in Tables 3.7 and 3.8. The structure of (**4**) consists of one cationic $[Ni(tptz)_2]^{2+}$ complex, two nitrate counterions and seven molecules of lattice water. The $[Ni(tptz)_2]^{2+}$ cation contains a 6-coordinate Ni(II) atom coordinated to two tptz ligands via the N-atoms in a slightly distorted octahedral arrangement (Fig.4.5).

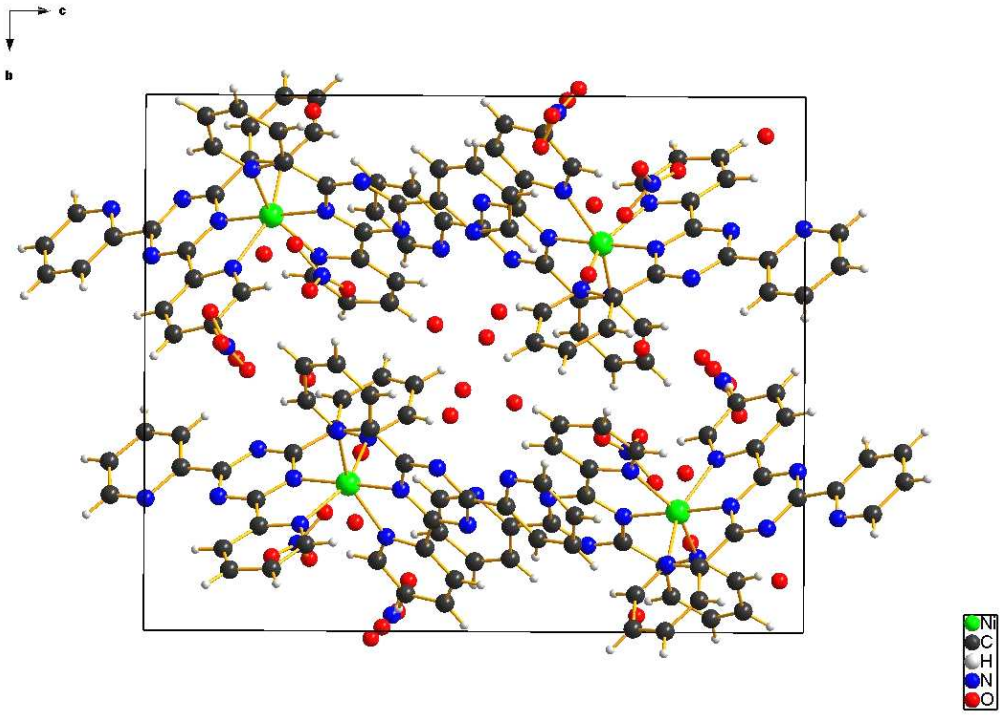


Fig. 4.4: Projection of the unit cell of $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ along the crystallographic a-axis.

In (**4**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode and coordinates through N(3) and N(6) from the triazine rings and through N(9), N(11) and N(12), N(14) from two adjacent pyridyl substituents. The two tptz ligands lie in different planes nearly perpendicular to each other, the angle between them is about 87.94(1)°. The terminal pyridyl groups are rotated from the main least square plane (formed by one triazine ring and two adjacent pyridyl rings, which coordinate on the

nickel metal center through N(3), N(11), N(9) and N(6), N(12), N(14) atoms) by 13.49(2)° and 0.55(2)° respectively.

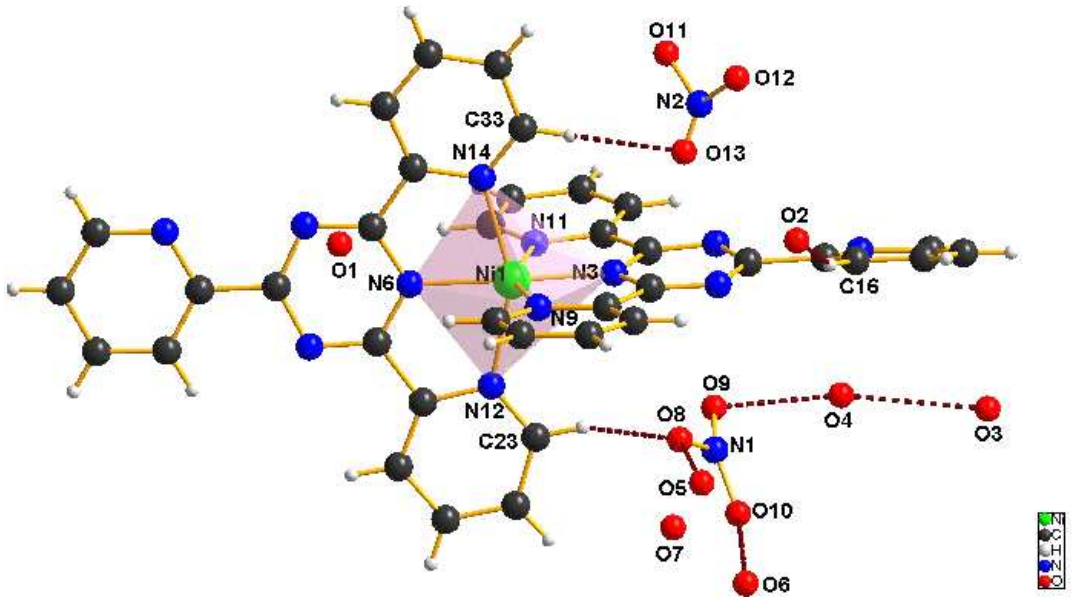


Fig. 4.5: The asymmetric unit of $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

The N-Ni-N angles range from 76.5(3)° to 177.2(3)°, the bond lengths of Ni-N range from 1.995(7) to 2.163(7) Å. Because of the *trans effect*, the Ni(1)-N(9), Ni(1)-N(11), Ni(1)-N(12) and Ni(1)-N(14) distances are ca. 0.17 Å longer than Ni(1)-N(3) and Ni(1)-N(6) distances (Table 3.8). The motif in the packing represents monomers running along the a-axis, the nitrate anions are bound through O(13)···H(C33) and O(8)···H(C23) hydrogen bonds each to one of the coordinating pyridyl rings. One lattice water molecule is bound through a O(2)···H(C16) hydrogen bond to a non coordinating pyridyl ring. Another three lattice water molecules are bound through hydrogen bonds to the nitrate anion. Their hydrogen atoms could not be localized, therefore the O-O atomic distances were chosen and are listed below in Table 3.8. There are π–π stacking interactions between the terminal pyridyl group of the tptz ligand with a coordinating pyridyl ring of the other tptz ligand (Fig. 4.7). The rings are slipped in an offset conformation and the hydrogen atoms are roughly over the ring centers. The centroid-centroid distance is 3.86 Å. The ring normal and the vector between the ring centroids form an angle of around 21°. The stacking effects also account for the slightly twisted position of the terminal non-coordinating pyridyl groups with respect to the central triazine ring.

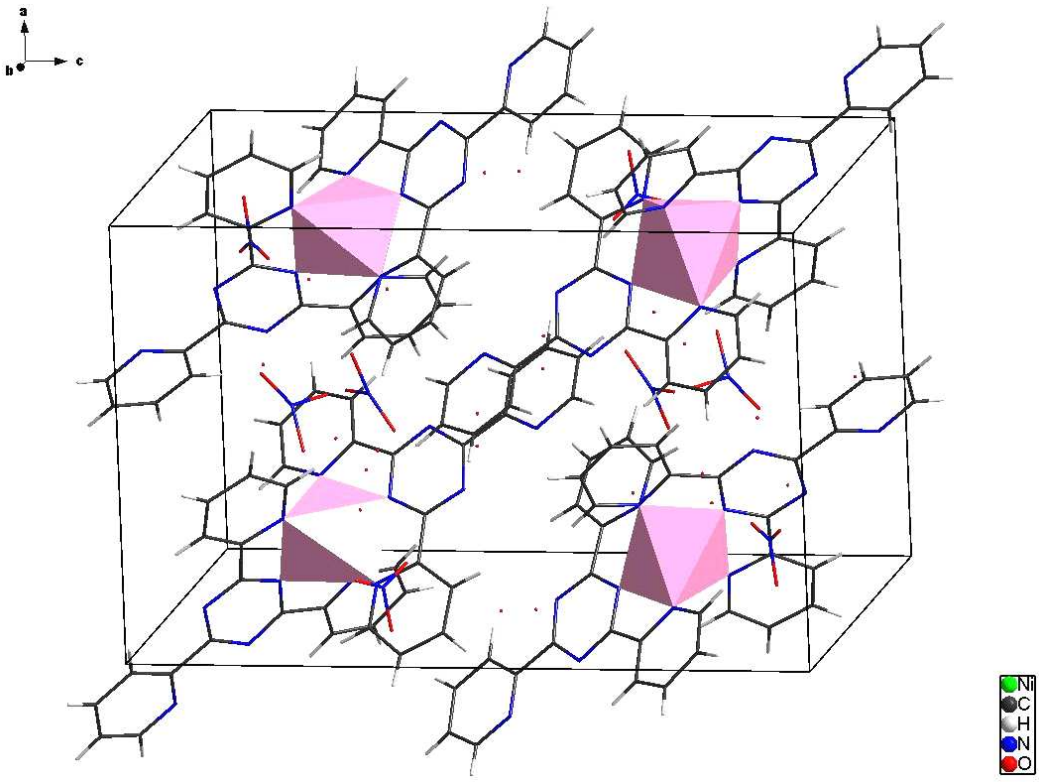


Fig. 4.6: Projection of the unit cell of $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

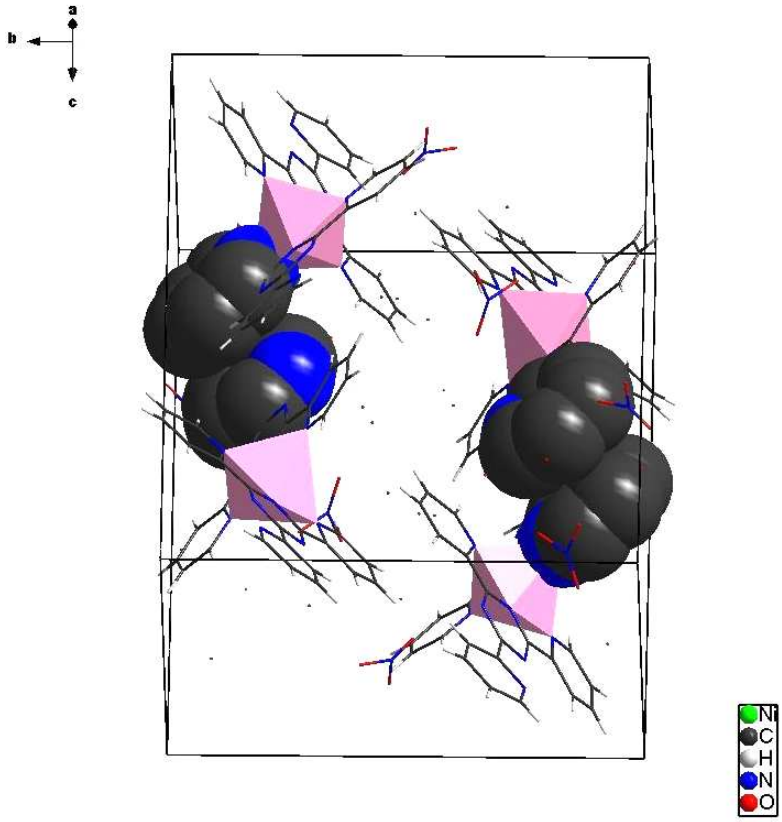


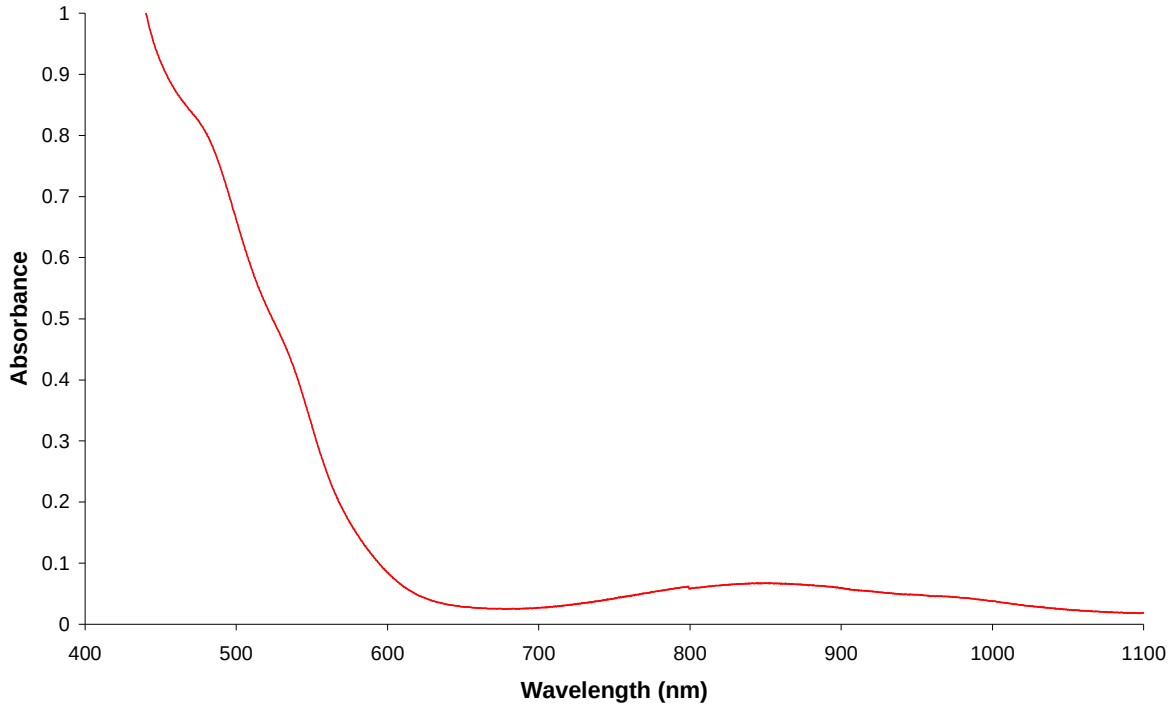
Fig 4.7: Pyridyl to pyridyl alignment in π-π stacking in $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

3.1.1.4 Experimental

Preparation of $[Ni(tptz)_2](NO_3)_2(H_2O)_2$ (4)

20 ml of a 0.01-molar (0.059 g) aqueous nickel nitrate solution were mixed with two equivalents (40 ml) of a 0.01-molar (0.125 g) ethanolic tptz solution. The mixture was stirred at approximately 60 ℃ for 50 min in a beaker . By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After six days orange crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS-Spectrum of $[Ni(tptz)_2](NO_3)_2(H_2O)_2$ (4)



The absorption in the visible area of the spectrum at approximately 480 nm is responsible for the dark orange color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 3.7: Crystallographic and refinement details for $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

Empirical formula	$C_{36}\,H_{28}\,N_{14}\,O_{13}\,Ni_1$
Formula weight	931.5 $g \cdot mol^{-1}$
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
Crystal color	orange
Unit cell dimensions	a = 12.721(2) Å
	b = 16.081(2) Å
	c = 19.759(3) Å
	β = 90.64 (1)°
Cell volume	4041.7 (1) $Å^3$
Z	4
Density (calculated)	1.531 $g \cdot cm^{-3}$
Absorption coefficient	0.564 mm^{-1}
F (000)	1928.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem II
Radiation type, wavelength	Mo-K_α, λ = 71.07 pm
Measurement temperature	170 (2) K
2θ range	3.80°- 56.30°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-16 / 16, -18 / 20, -25 / 25
Reflections collected	39231
Independent reflections	8849
R_{int}	0.1966
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	578
GooF(S)	1.058
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.1440, wR_2[b] = 0.3724
R indices (all data)	R_1 = 0.1976, wR_2 = 0.4071

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 3.8: Selected distances/Å and angles/° in $[Ni(tptz)_2](NO_3)_2(H_2O)_7$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(3)	1.995(7)
Ni(1)	N(6)	1.995(7)
Ni(1)	N(9)	2.149(8)
Ni(1)	N(12)	2.155(9)
Ni(1)	N(11)	2.163(7)
Ni(1)	N(14)	2.143(8)
H(C16)	O(2)	1.963(1)
H(C23)	O(8)	2.510(2)
H(C33)	O(13)	2.587(3)
O(8)	O(5)	2.896(2)
O(6)	O(10)	2.622(3)
O(9)	O(4)	2.916(1)
O(4)	O(3)	2.930(1)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(3)	Ni(1)	N(6)	177.2(3)
N(3)	Ni(1)	N(14)	101.7(3)
N(3)	Ni(1)	N(9)	76.8(3)
N(3)	Ni(1)	N(12)	104.7(3)
N(3)	Ni(1)	N(11)	77.2(3)
N(6)	Ni(1)	N(14)	77.2(3)
N(6)	Ni(1)	N(9)	105.8(3)
N(6)	Ni(1)	N(12)	76.5(3)
N(6)	Ni(1)	N(11)	100.2(3)
N(9)	Ni(1)	N(12)	91.9(3)
N(9)	Ni(1)	N(11)	153.8(3)
N(12)	Ni(1)	N(11)	97.7(3)
N(14)	Ni(1)	N(9)	92.4(3)
N(14)	Ni(1)	N(12)	153.5(3)
N(14)	Ni(1)	N(11)	89.8(3)

3.1.1.5 Crystal structure of aquadithiocyanato(2,4,6-tris(2-pyridyl)-1,3,5-triazine)Ni(II), $[Ni(SCN)_2(tptz)(H_2O]$ (5)

$[Ni(SCN)_2(tptz)(H_2O]$ **(5)** crystallizes in the orthorhombic space group $Pna2_1$ (33) with a = 15.692(2) Å, b = 9.314(8) Å, c = 14.717(2) Å, α = β = γ = 90°, V = 2150.9(4) $Å^3$ and Z = 4. Crystallographic and refinement details are listed below, in Tables 3.9 and 4.0. The structure of **(5)** comprises a mixed-ligand complex with one tptz ligand, two thiocyanates and one aqua ligand in a distorted octahedral arrangement around the Ni(II) metal center (Fig. 4.9).

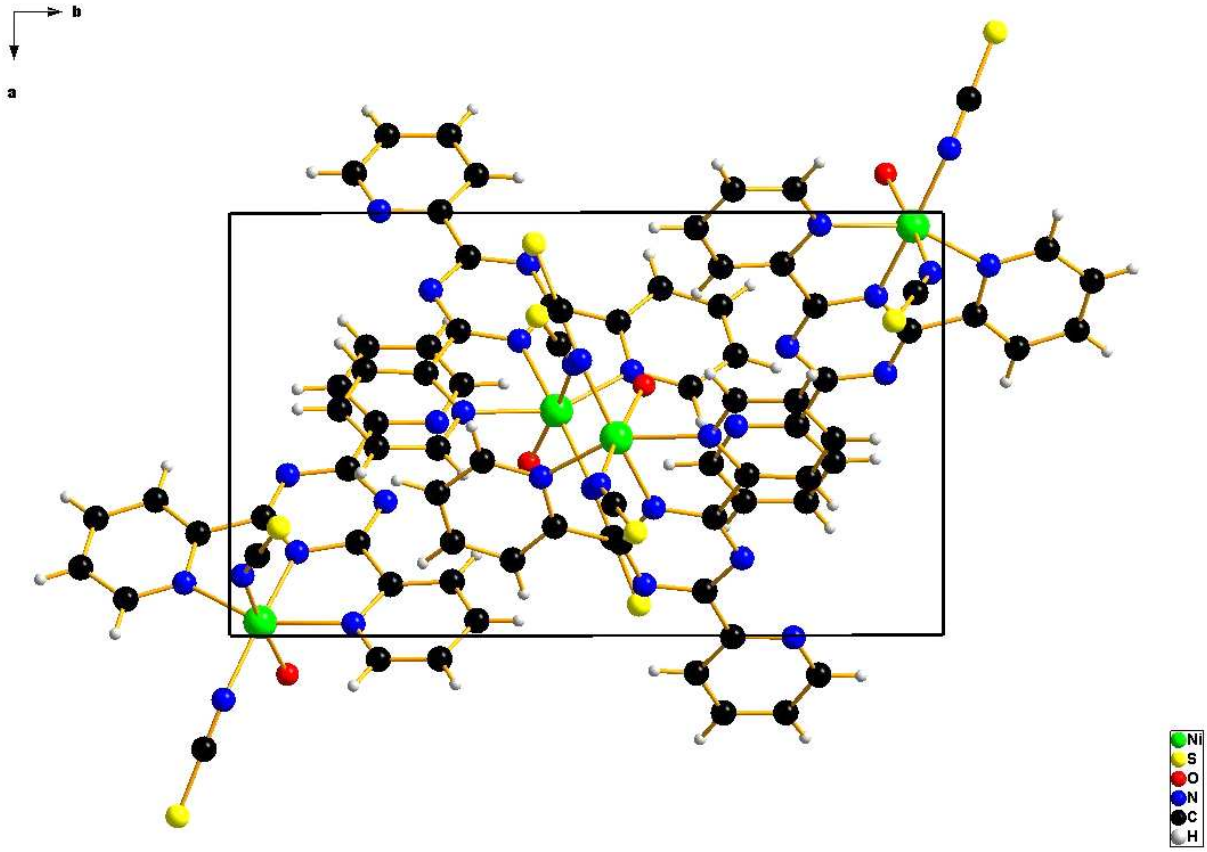


Fig. 4.8: Projection of the unit cell of $[Ni(SCN)_2(tptz)(H_2O)]$ along the crystallographic c-axis.

The distorted octahedral coordination is due to the differences in the donor strengths of the different ligands, which are coordinated to the metal center. Both thiocyanate anions are coordinated through their nitrogen atoms to the metal center. Tptz acts as a tridentate ligand, adopting the terpy-like binding mode and coordinates to Ni(II) through N(6) from the triazine ring and N(1) and N(2) from the two adjacent pyridyl

substituents. The terminal pyridyl group is rotated from the main least squares plane (one triazine ring and two adjacent pyridyl rings) by 11.3(1)°. The N-Ni-N angles range from 76.00(1) to 152.80(1)°, while the Ni-N distances range from 1.98(4) to 2.15(3) Å. Because of the *trans effect***,** the Ni(1)-N(1) and Ni(1)-N(2) distances are ca. 0.17 Å longer than the Ni(1)-N(6) distance (Table 4.0). Three Ni-N distances between the metal center and the nitrogen atoms of the thiocyanate anions are nearly identical, the two anions being *cis* to each other. The Ni-O distance is 2.12(3) Å, a typical value for such atomic distances [32].

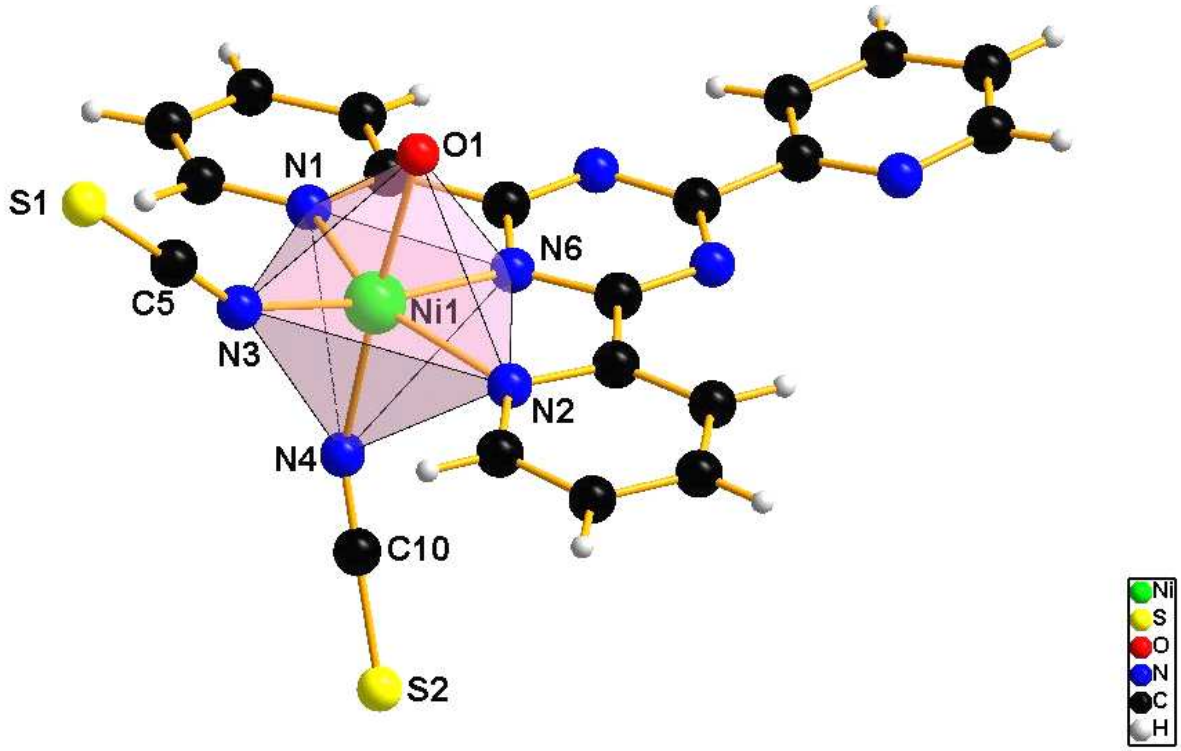


Fig. 4.9: The asymmetric unit of $[Ni(SCN)_2(tptz)(H_2O)]$.

The motif in the packing (Fig. 4.8) represents monomers along the c-axis. Stacking interactions can also be observed in this structure. One terminal non coordinating pyridyl ring of the monomer A stacks with the triazine ring of the monomer B. The centroid-centroid distance is 3.753(3) Å. Similarly, the coordinating pyridyl ring of the monomer B stacks with the triazine ring of the monomer A and the centroid-centroid distance is 3.819(3) Å, (Fig. 5.1).

The rings are slipped in an offset conformation and the hydrogen atoms are roughly above the ring centers.

The ring normal and the vector between the ring centroids form an angle of around 21°, which is in agreement with similar $\pi-\pi$ stacking interactions already reported in this work.

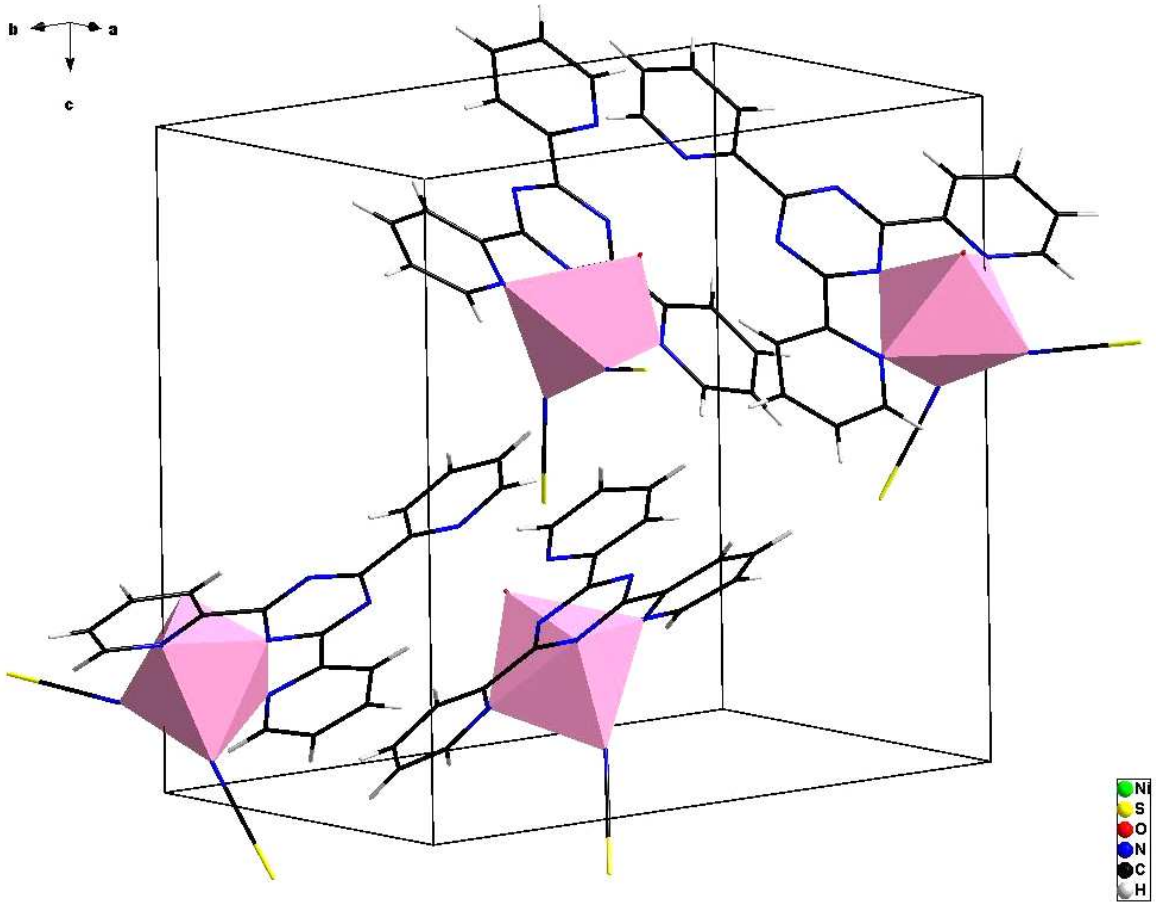


Fig. 5.0: Projection of the unit cell of $[Ni(SCN)_2(tptz)(H_2O)]$.

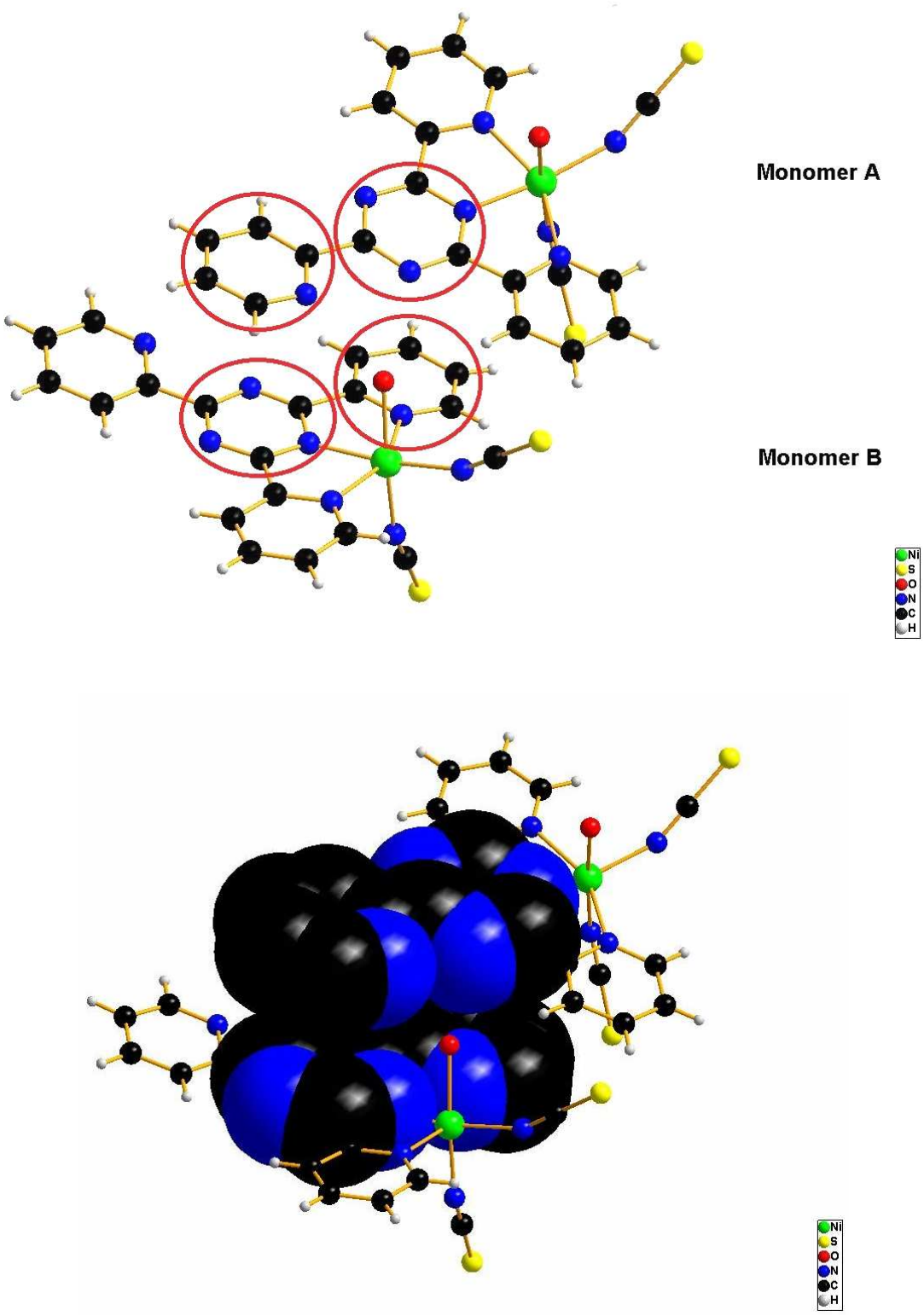


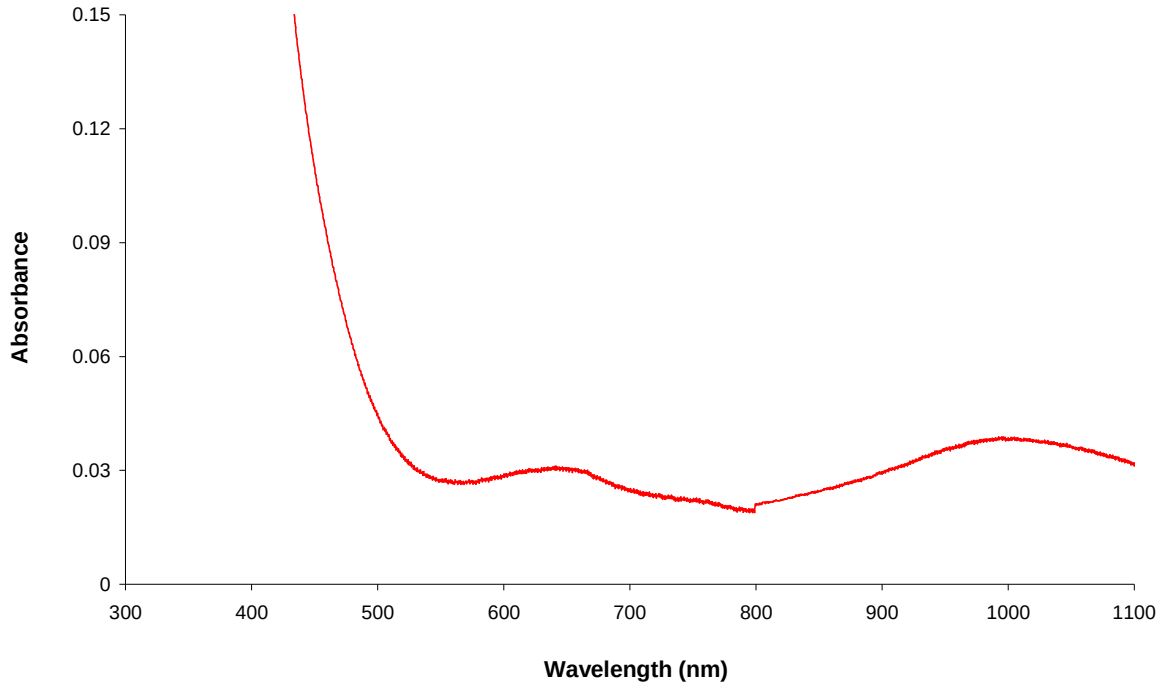
Fig. 5.1: π-π stacking in $[Ni(SCN)_2(tptz)(H_2O)]$.

3.1.1.5 Experimental

Preparation of $[Ni(SCN)_2(tptz)(H_2O)]$ (5)

20 ml of a 0.01-molar (0.035 g) aqueous nickel thiocyanate solution were mixed with two equivalents (40 ml) of a 0.01-molar (0.125 g) ethanolic tptz solution. The mixture was stirred at approximately 60 ℃ for 60 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After nine days dark green colored crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS Spectrum of $[Ni(SCN)_2(tptz)(H_2O)]$ (5)



The absorption in the visible area of the spectrum at approximately 500 nm is responsible for the green color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 3.9: Crystallographic and refinement details for $[Ni(SCN)_2(tptz)(H_2O)]$.

Empirical formula	$C_{20}\,H_{12}\,N_8\,Ni(1)\,O_1\,S_2$
Formula weight	503.21 $g \cdot mol^{-1}$
Crystal system	orthorhombic
Space group	$Pna2_1$ (33)
Crystal color	green
Unit cell dimensions	a = 15.692(2) Å
	b = 9.314(8) Å
	c = 14.717(2) Å
	α = β = γ = 90°
Cell volume	2150.9(4) $Å^3$
Z	4
Density (calculated)	1.554 $g \cdot cm^{-3}$
Absorption coefficient	1.127 mm^{-1}
F (000)	1023.7
Diffractometer	STOE Image Plate Diffraction System I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	5,40°- 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-10 / 10, -20 / 20, -19 / 19
Reflections collected	24915
Independent reflections	4842
R_{int}	0.1013
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	291
GooF(S)	0.853[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0386, wR_2[b] = 0.0612
R indices (all data)	R_1 = 0.0990, wR_2 = 0.0536

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 4.0: Selected distances/Å and angles/° in [Ni $(SCN)_2$(tptz)(H_2O)].

Distances/Å

Atoms1	Atoms 2	d 1,2
Ni(1)	N(6)	1.983(4)
Ni(1)	N(3)	1.997(4)
Ni(1)	N(4)	2.030(4)
Ni(1)	O(1)	2.121(3)
Ni(1)	N(2)	2.142(3)
Ni(1)	N(1)	2.150(3)
S(1)	C(5)	1.607(5)
S(2)	C(10)	1.642(5)
N(3)	C(5)	1.186(5)
N(4)	C(10)	1.164(5)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(6)	Ni(1)	N(4)	95.1(2)
N(6)	Ni(1)	O(1)	85.8(1)
N(6)	Ni(1)	N(2)	76.0(1)
N(6)	Ni(1)	N(1)	76.8(1)
N(3)	Ni(1)	N(4)	94.7(2)
N(3)	Ni(1)	O(1)	84.6(2)
N(3)	Ni(1)	N(2)	106.2(1)
N(3)	Ni(1)	N(1)	100.9(1)
N(4)	Ni(1)	O(1)	173.5(2)
N(4)	Ni(1)	N(2)	87.1(1)
N(4)	Ni(1)	N(1)	93.5(1)
O(1)	Ni(1)	N(2)	86.9(1)
O(1)	Ni(1)	N(1)	93.0(1)
N(2)	Ni(1)	N(1)	152.8(1)

3.1.1.6 Crystal structure of (pyridine-2,6-dicarboxylato-k^3 *N,O,O´*) (2,4,6-Tris(2-pyridyl)-1,3,5-triazine-k^3 *N,N,N´*) nickel(II) pentahydrate, $[Ni(2,6\ pda)(tptz)](H_2O)_5$ (6)

$[Ni(2,6\text{-}pda)(tptz)](H_2O)_5$ **(6)** crystallizes in the triclinic space group P-1 (2) with a = 9.442(2) Å, b = 10.230(2) Å, c = 16.658(4) Å, α = 74.53(2)°, β = 83.95(2) °, γ = 66.17(2) °, V = 1418.4(6) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below, in Tables 4.1 and 4.2. The structure of **(6)** consists of one neutral complex [Ni(2,6-pda)(tptz)] and five lattice water molecules. The coordination geometry around the metal center is distorted octahedral (Fig. 5.3).

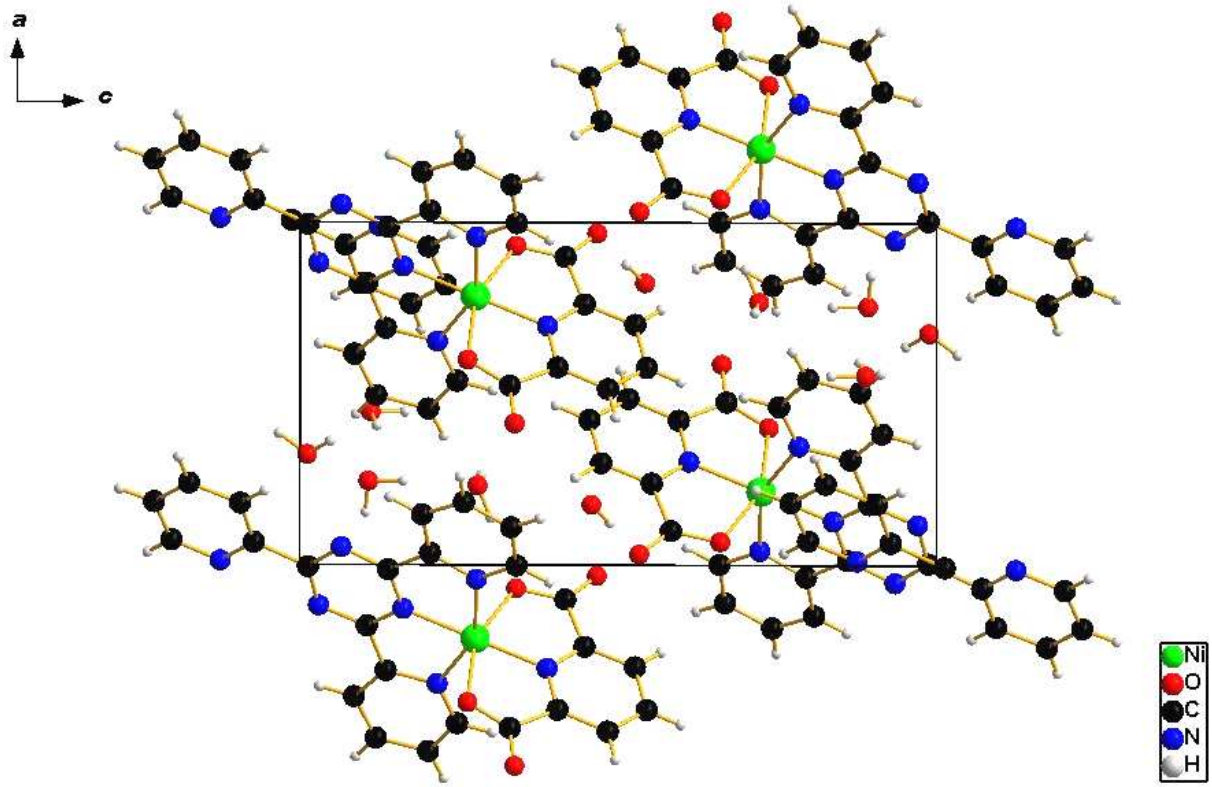


Fig. 5.2: Projection of the unit cell of $[Ni(2,6\text{-}pda)(tptz)](H_2O)_5$ along the crystallographic b-axis.

In (**6**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode. It coordinates through N(6) from the triazine ring and through N(3) and N(7) from two adjacent pyridyl substituents.

Because of the *trans* effect**,** the Ni(1)-N(3) and Ni(1)-N(7) distances are ca. 0.17 Å longer than the Ni(1)-N(6) distance (Table 4.2). The Ni(II) metal center is also coordinated to a 2,6-pda pincer ligand, which is bound to the metal center in a *k*-N,*O,O*' mode. It coordinates through N(2), O(1) and O(2) with O atoms *trans* to each other. The distorted octahedral coordination at the Ni(II) metal center is due to the differences in the donor strengths of the coordinating ligands. The 2,6-pda and tptz ligands are perpendicular to each other, the angle between the two planes is 90.25(4)°.

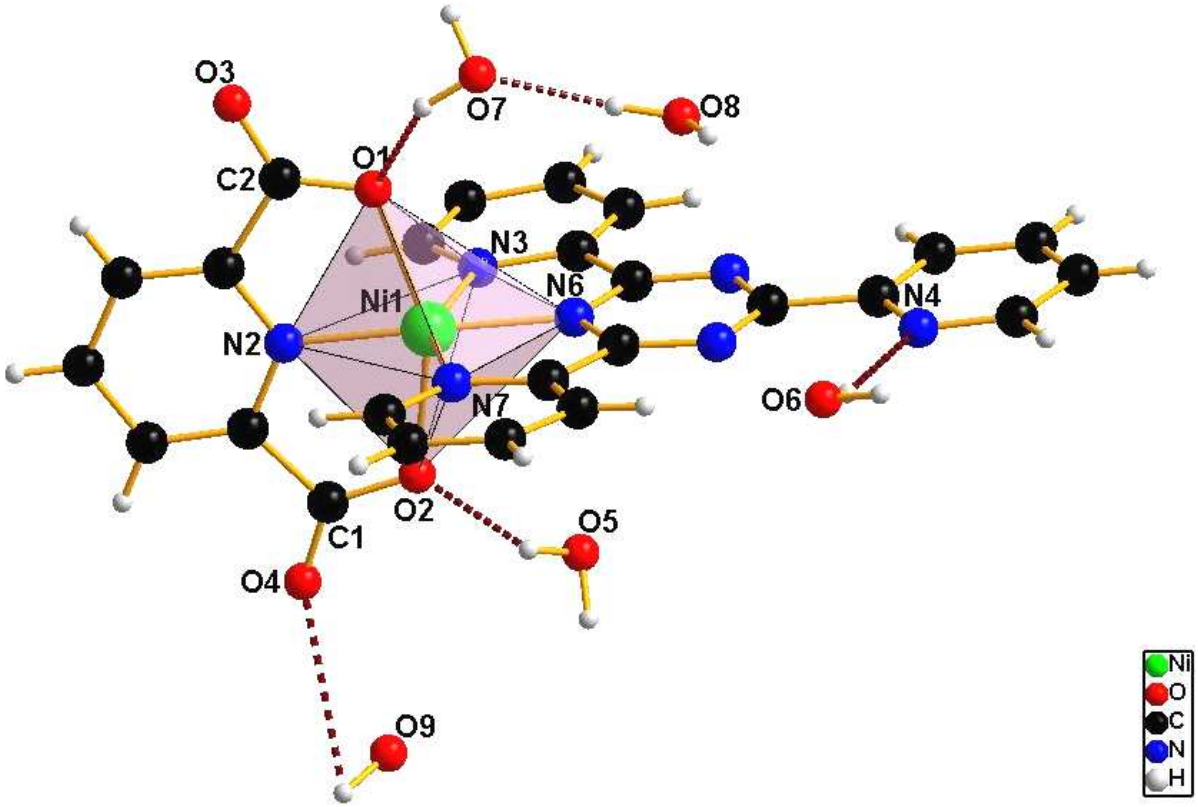


Fig.5.3: The asymmetric unit of [Ni(2,6-pda)(tptz)]$(H_2O)_5$

The Ni-N distances range from 1.964(4) to 2.152(4) Å, the Ni-O distances are with 2.123(4) Å for Ni(1)-O(2) and 2.139(4) Å for Ni(1)-O(1) pretty similar. The Ni-N(pda) atom distances are shorter than Ni-N(tptz), what is consistent with such distances found for other similar compounds represented in this work. Both carboxylic groups are deprotonated, the C-O distances range from 1.219(7) to 1.282(6) Å (Table 4.2). The C(2)-O(1) and C(1)-O(2) distances are 1.264(6) and 1.282(6) Å, respectively; the C(1)-O(4) and C(2)-O(3) distances are 1.219(7) and 1.243(6) Å, respectively. Typical

values for single C-O bonds in carboxylic groups of 2,6-pda range from 1.27-1.30 Å and for C-O double bonds from 1.20-1.23 Å [33]. The hydrogen atom could not be localized on either of these groups; the charge on both carboxylic groups is delocalized. There are five lattice water molecules present. Three of them are linked through hydrogen bonds with O atoms of carboxylic groups, one with the N atom of the terminal pyridyl ring and one with another lattice water molecule.

The motif in the packing represents independent monomers running along the crystallographic b axis (Fig. 5.2).

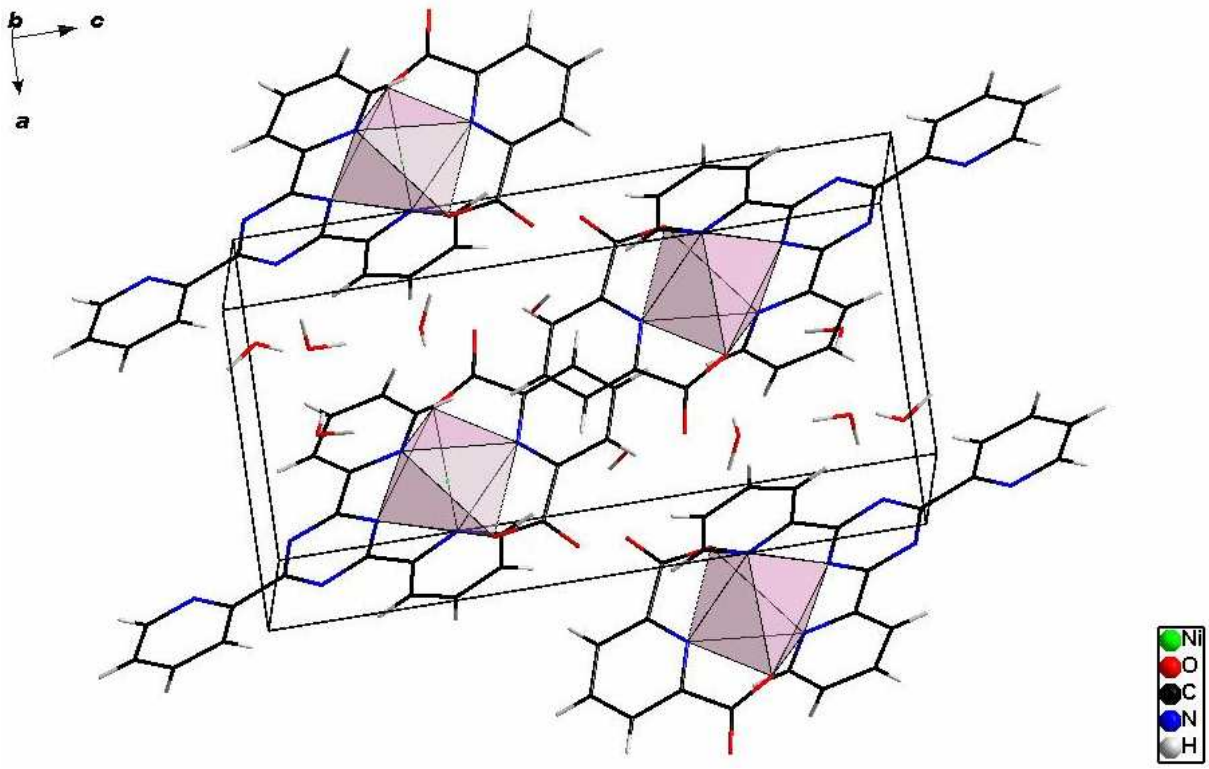


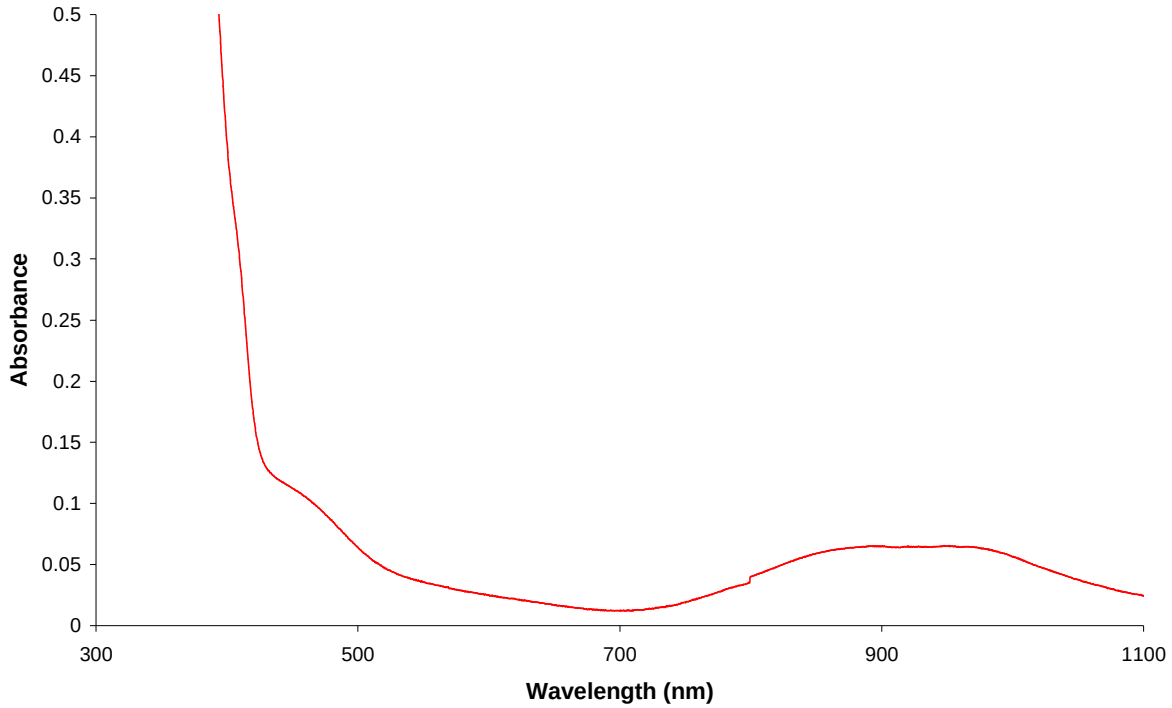
Fig. 5.4: Projection of the unit cell of [Ni(2,6-pda)(tptz)]$(H_2O)_5$.

3.1.1.6 Experimental

Preparation of $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$ (6)

20 ml of a 0.01-molar (0.050 g) aqueous nickel acetate solution were mixed with one equivalent 20 ml of a 0.01-molar (0.125 g) ethanolic tptz solution and one equivalent 20 ml of a 0.01-molar (0.033 g) ethanolic 2,6-pda solution. The mixture was stirred at approximately 60 ℃ for 45 min in a beaker. By evapo ration the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After five days yellow crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS Spectrum of $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$ (6)



The absorption in the visible area of the spectrum at approximately 480 nm is responsible for the dark yellow color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 4.1: Crystallographic and refinement details for [Ni(2,6-pda)(tptz)]$(H_2O)_5$.

Empirical formula	$C_{25}H_{28}N_7Ni_1O_9$
Formula weight	529.10 g·mol^{-1}
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	yellow
Unit cell dimensions	a = 9.442(2) Å
	b = 10.230(2) Å
	c = 16.658(4) Å
	α = 74.53(2), β = 83.95(2), γ = 66.17(2)
Cell volume	1418.4(6) Å^3
Z	2
Density (calculated)	1.239 g·cm^{-3}
Absorption coefficient	0.728 mm^{-1}
F (000)	538
Diffractometer	STOE Image Plate Diffraction System I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	4.50°- 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-11 / 12, -13/ 13, -21/ 21
Reflections collected	11006
Independent reflections	5780
R_{int}	0.0545
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	416
GooF(S)	0.844
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0565, wR_2[b] = 0.1415
R indices (all data)	R_1 = 0.1227, wR_2 = 0.1659

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a)] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b)] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c)] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 4.2: Selected distances/Å and angles/° in [Ni (2,6-pda)(tptz)]$(H_2O)_5$.

Distances/Å

Atoms 1	Atoms 2	d [1,2]
Ni(1)	N(2)	1.964(4)
Ni(1)	N(6)	1.977(4)
Ni(1)	O(2)	2.123(4)
Ni(1)	N(3)	2.141(4)
Ni(1)	O(1)	2.139(4)
Ni(1)	N(7)	2.152(4)
C(2)	O(1)	1.264(6)
C(1)	O(4)	1.219(7)
C(1)	O(2)	1.282(6)
C(2)	O(3)	1.243(6)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(2)	Ni(1)	N(6)	179.1(1)
N(2)	Ni(1)	O(2)	78.2(1)
N(2)	Ni(1)	O(1)	77.3(2)
N(2)	Ni(1)	N(3)	103.8(2)
N(2)	Ni(1)	N(7)	103.0(2)
N(6)	Ni(1)	O(2)	101.2(1)
N(6)	Ni(1)	O(1)	103.2(2)
N(6)	Ni(1)	N(3)	76.8(2)
N(6)	Ni(1)	N(7)	76.4(2)
O(2)	Ni(1)	O(1)	155.6(2)
O(2)	Ni(1)	N(3)	92.0(2)
O(2)	Ni(1)	N(7)	93.8(2)
O(1)	Ni(1)	N(3)	93.3(2)
O(1)	Ni(1)	N(7)	92.1(2)
N(3)	Ni(1)	N(7)	153.2(2)

3.1.1.7(μ_2-4,4'-Bipyridyl)-tetra-aqua-bis(2,4,6-Tris(2-pyridyl)-1,3,5-triazine-k^3 *N,N,N´*)-di-nickel dihydrate, $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ (7)

$[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ **(7)** crystallizes in the monoclinic space group C2/c (2), with a = 18.479(4) Å, b = 14.490(4) Å, c = 23.256(6) Å, β = 107.18(2), V = 5949.0(3) $Å^3$ and Z = 4. Crystallographic and refinement details are listed below in Tables 4.3 and 4.4. The structure of **(7)** consists of two $[Ni(H_2O)_2(tptz)(\ 4,4'\text{-bipy})_{1/2}]^{2+}$ cations, which are linked via the 4,4'-bipy with each other. The four nitrate anions counterbalance the charges of the cations, there are also two lattice water molecules present. Both cations contain 6-coordinate Ni(II), coordinated to one tptz ligand, two aqua ligands and one 4,4'-bipy ligand via the N and O atoms in a distorted octahedral arrangement (Fig. 5.6).

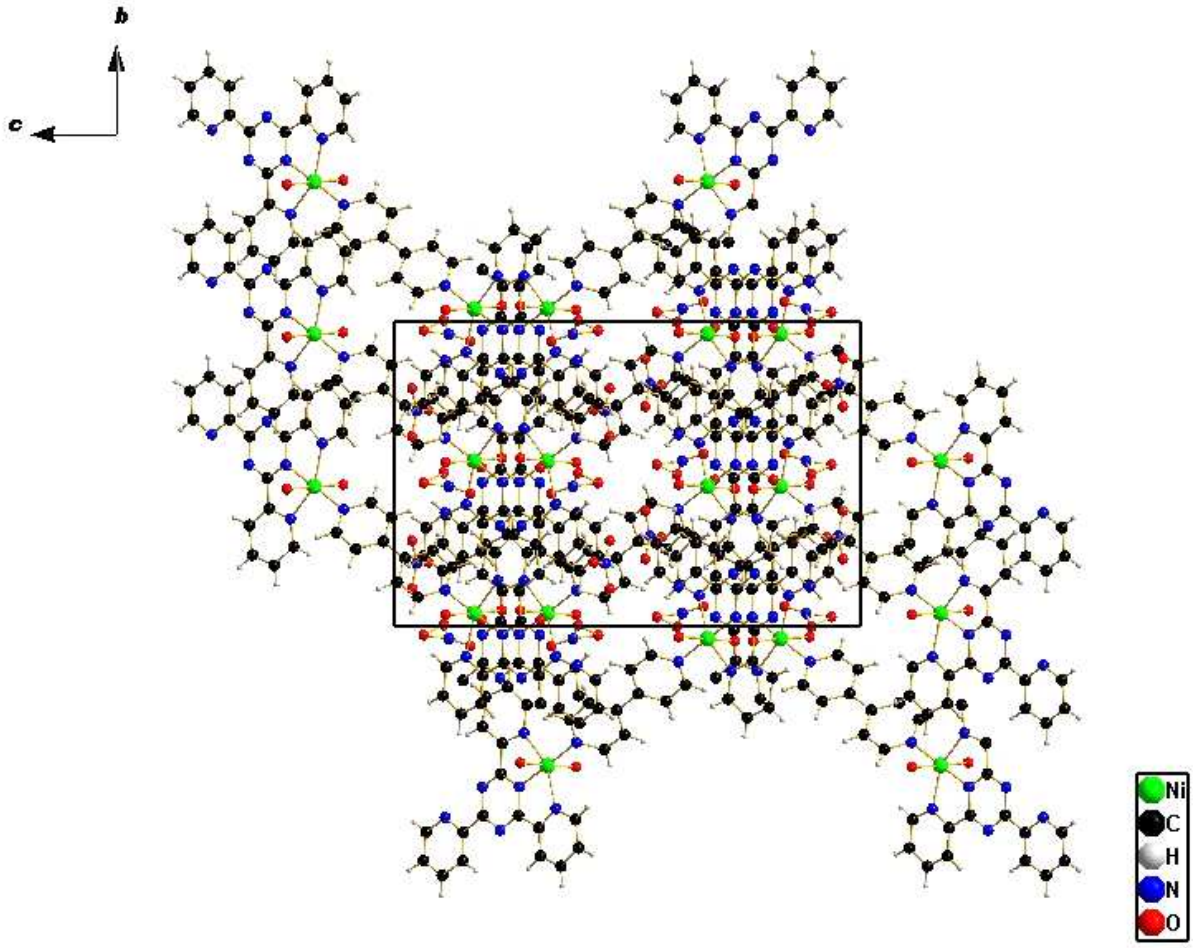


Fig. 5.5: Projection of the unit cell of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ along the crystallographic a-axis.

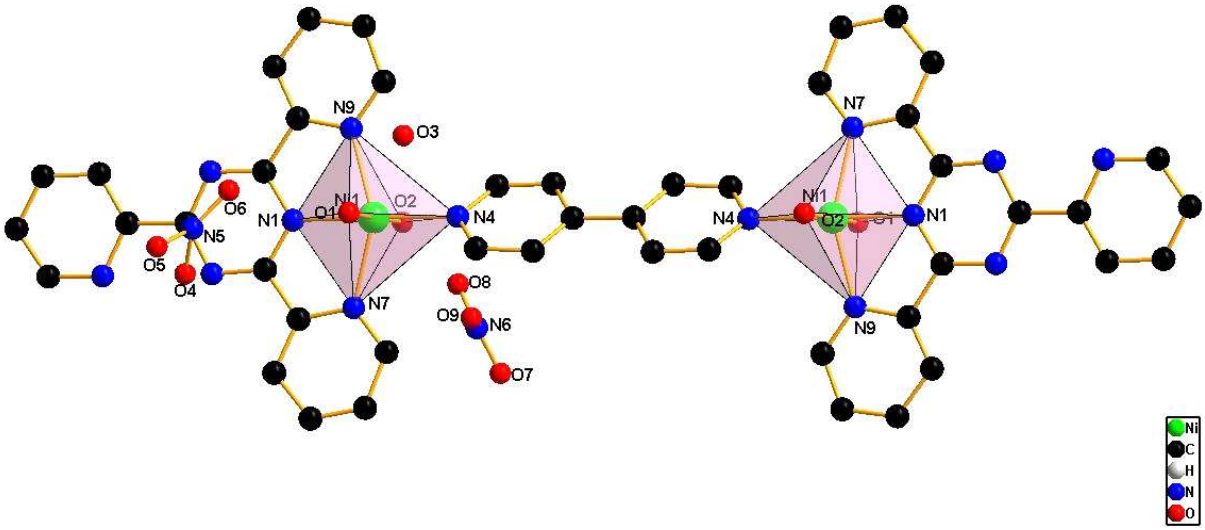


Fig. 5.6: The asymmetric unit of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

The distorted octahedral arrangement around both Ni(II) metal centers is formed by coordination to three N atoms from one tptz molecule, two O atoms of the aqua ligands and to one N atom of the linking 4,4'-bipy molecule (Fig. 5.6). In (**7**) tptz acts as a tridentate ligand, adopting the terpy-like binding mode**;** it coordinates through N(1) from the triazine ring and through N(7) and N(9) from the two adjacent pyridyl substituents. The terminal pyridyl groups are rotated from the main least squares plane (one triazine ring and two adjacent pyridyl rings, which coordinate to the nickel metal center) by 2.09(3)°. The N-Ni-N angles range from 76.47(3) to 178.9(3)°, while the Ni-N bond lengths range from 1.98(2) to 2.16(8) Å. Because of the *trans effect***,** the Ni(1)-N(7) and Ni(1)-N(9) distances are ca. 0.17 Å longer than Ni(1)-N(1) distances (Table 4.4). The Ni(1)-N(4) distances are with 2.07(9) Å longer than the Ni(1)-N(1) and shorter than the Ni(1)-N(7) and Ni(1)-N(9) distances. The two tptz ligands lie in the same plane, the linking 4,4'-bipy is pointing out of the plane (Fig. 5.7), the angle between the two tptz ligands and 4,4'-bipy is 45.19(2)°. The motif in the packing (Fig. 5.5) represents independent monomers running along the a-axis with nitrate anions occupying the holes in the structure. There are N-H bonds, which connect the monomers of neighbouring layers with each other (Fig. 5.9). The hydrogen atoms of the aqua ligands could not be localized, therefore the N-O distance of 2.72(1) Å was taken.

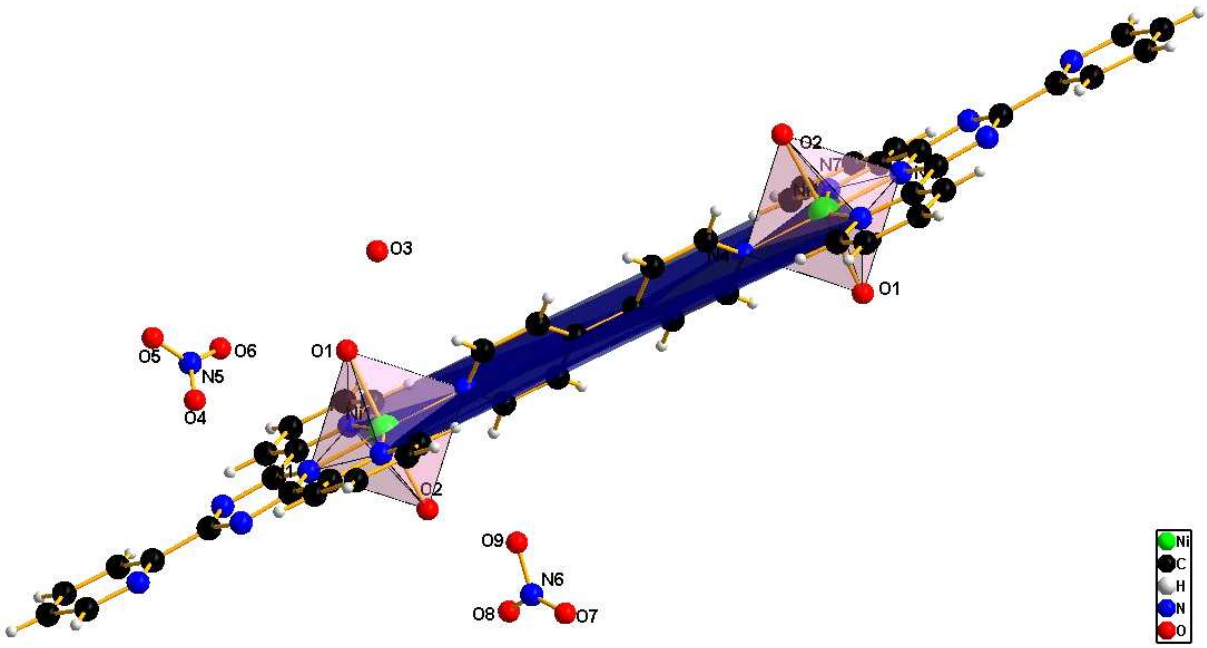


Fig. 5.7: Depiction of the plane in the asymmetric unit of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

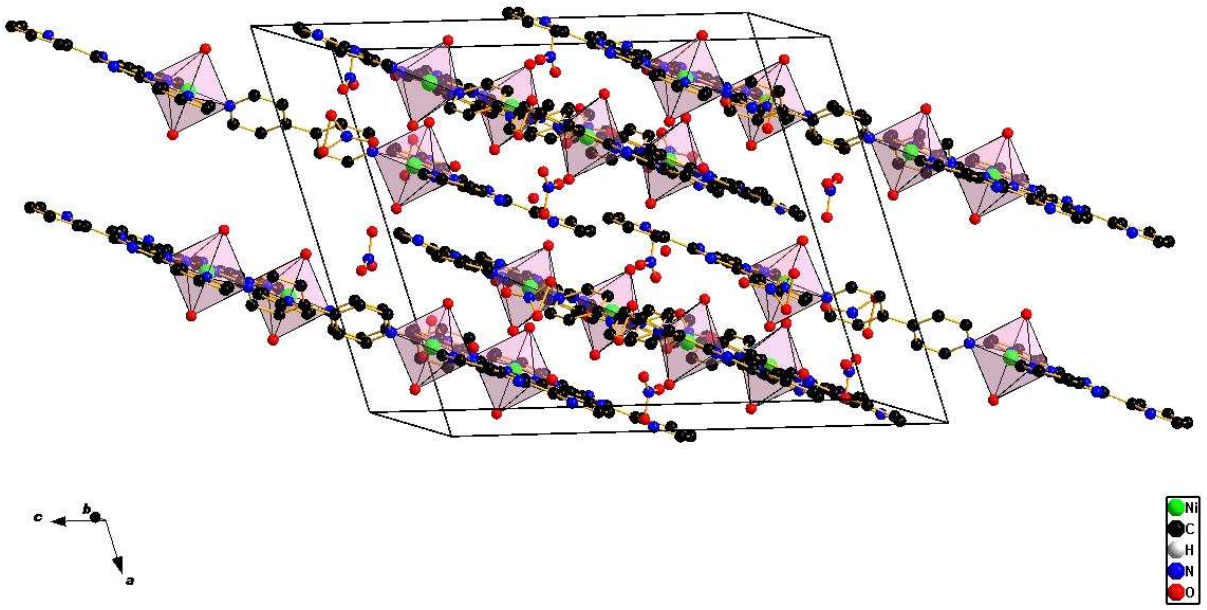


Fig. 5.8: Projection of the unit cell of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

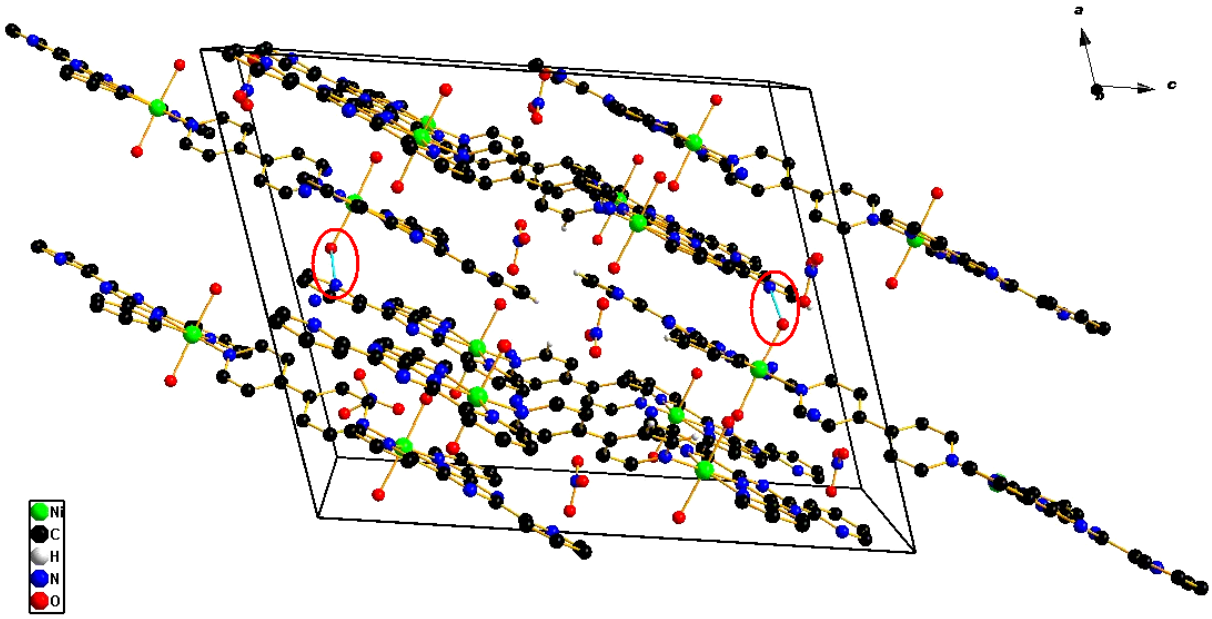


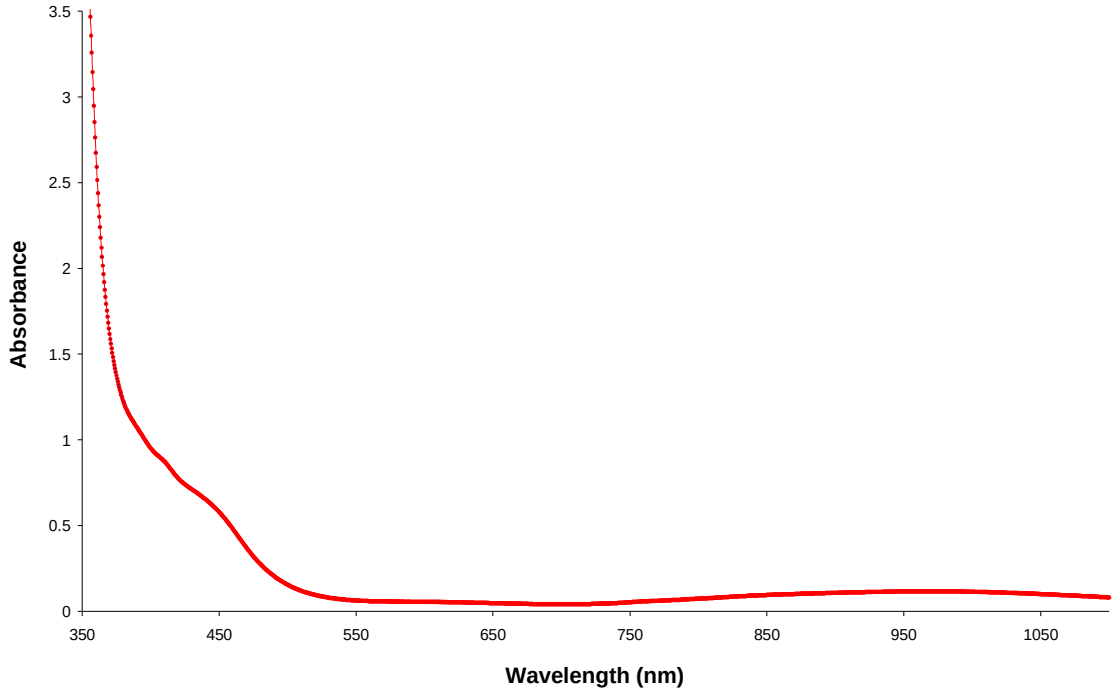
Fig. 5.9: H-bonding in $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

3.1.1.7 Experimental

Preparation of $[Ni_2(H_2O)_4(4,4'\text{-bipy})(tptz)_2](NO_3)_4(H_2O)_2$ (7)

20 ml of a 0.01-molar (0.059 g) aqueous nickel nitrate solution were mixed with one equivalent (20 ml) of a 0.01-molar (0.063 g) ethanolic tptz solution and one equivalent (20 ml) of a 0.01-molar (0.031 g) ethanolic 4,4'-bipy solution. The mixture was stirred at approximately 60 ℃ for 60 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After ten days yellow-orange crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS Spectrum of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ (7)



The absorption in the visible area of the spectrum at approximately 470 nm is responsible for the yellow color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 4.3: Crystallographic and refinement details for $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

Empirical formula	$C_{46}H_{50}N_{18}Ni_2O18$
Formula weight	1260.46 $g \cdot mol^{-1}$
Crystal system	monoclinic
Space group	C2/c (2)
Crystal color	yellow
Unit cell dimensions	a = 18.479(4) Å
	b = 14.490(4) Å
	c = 23.256(6) Å
	β = 107.18(2)
Cell volume	5949.0(3) $Å^3$
Z	4
Density (calculated)	1.407 $g \cdot cm^{-3}$
Absorption coefficient	0.72 mm^{-1}
F (000)	2608.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem II
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	170 (2) K
2θ range	5.62°- 56.16°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-24 / 24, -18 / 19, -29 / 29
Reflections collected	22680
Independent reflections	7010
R_{int}	0.1869
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	380
GooF(S)	0.846[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.1080, wR_2[b] = 0.2568
R indices (all data)	R_1 = 0.2507, wR_2 = 0.3238

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.
$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 4.4: Selected distances/Å and angles/° in $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	1.984(9)
Ni(1)	N(4)	2.071(9)
Ni(1)	N(7)	2.164(9)
Ni(1)	N(9)	2.165(8)
Ni(1)	O(1)	2.084(7)
Ni(1)	O(2)	2.088(6)
N(5)	O(4)	1.245(9)
N(5)	O(5)	1.261(6)
N(5)	O(6)	1.235(6)
N(6)	O(7)	1.240(4)
N(6)	O(8)	1.236(3)
N(6)	O(9)	1.241(4)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1.2.3]
Ni(1)	N(1)	N(4)	178.9(3)
Ni(1)	N(1)	O(1)	91.2(3)
Ni(1)	N(1)	O(2)	91.5(3)
Ni(1)	N(1)	N(7)	76.4(3)
Ni(1)	N(1)	N(9)	76.6(3)
Ni(1)	N(4)	O(1)	89.2(3)
Ni(1)	N(4)	O(2)	88.1(3)
Ni(1)	N(4)	N(7)	102.6(3)
Ni(1)	N(4)	N(9)	104.4(3)
Ni(1)	O(1)	O(2)	177.2(2)
Ni(1)	O(1)	N(7)	89.6(3)
Ni(1)	O(1)	N(9)	89.2(3)
Ni(1)	O(2)	N(7)	91.1(3)
Ni(1)	O(2)	N(9)	91.4(3)
Ni(1)	N(7)	N(9)	152.9(3)

3.2.1 Nickel(II) complexes with 1,10'-Orthophenanthroline

3.2.1.1 Crystal structure of tris(1,10-Phenanthroline-*N,N'*) nickel(II) bis(tetrafluoroborate) monohydrate, $[Ni(Phen)_3](BF_4)_2(H_2O)$ (8)

$[Ni(Phen)_3](BF_4)_2(H_2O)$ (**8**) crystallizes in the triclinic space group P-1 (2) with a = 9.085(2) Å, b = 12.764(2) Å, c = 15.099(3) Å, α = 95.84(1)°, β = 90.48(1)°, γ = 95.23 (1)°, V = 1734.1(1) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below in Tables 4.5 and 4.6. The structure of (**8**) consists of a $[Ni(phen)_3]^{2+}$ cation, two tetrafluoroborate anions, one of which is disordered, and one lattice water molecule. The $[Ni(phen)_3]^{2+}$ cation contains 6-coordinate Ni(II), coordinated to three phen ligands via the N atoms in a slightly distorted octahedral arrangement (Fig. 6.1).

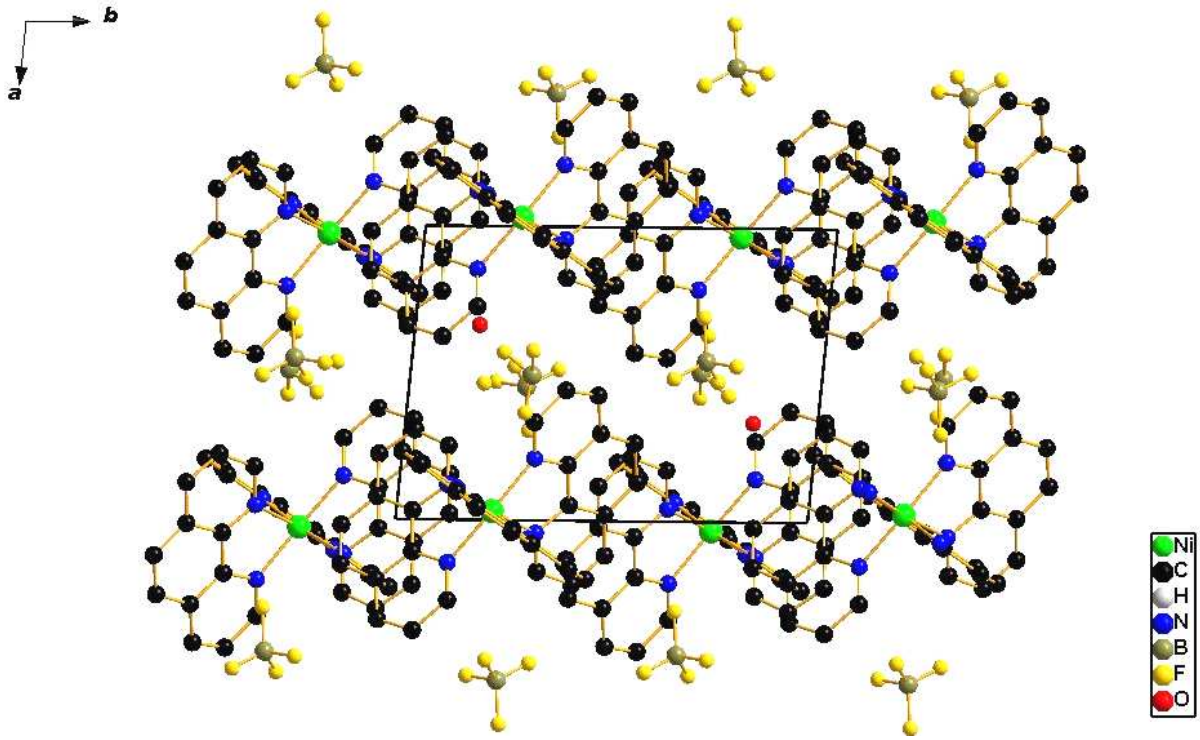


Fig. 6.0: Projection of the unit cell of $[Ni(phen)_3](BF_4)_2(H_2O)$ along the crystallographic c-axis.

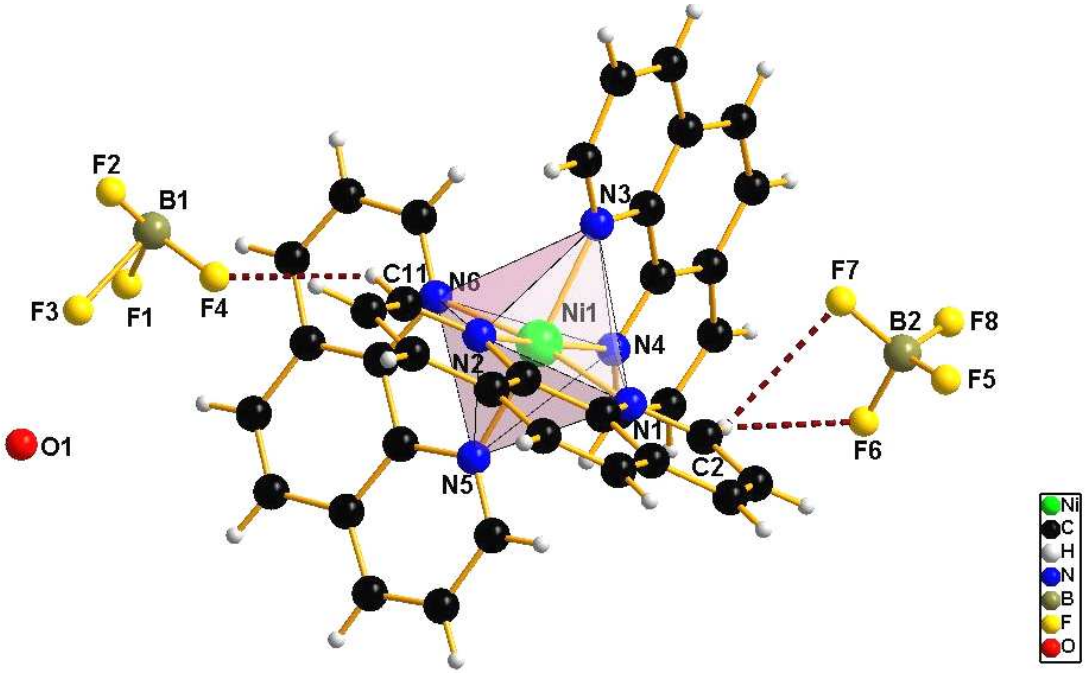


Fig. 6.1: The asymmetric unit of $[Ni(phen)_3](BF_4)_2(H_2O)$.

The Ni-N distances show very little differences, they range from 2.084(4) Å to 2.107(4) Å. The Ni-N angles range from 79.29(2) to 172.71(2)° and thus deviate from ideal octahedral angles by approximately 5-12%. As a result the octahedral geometry around the Ni(II) atom is slightly distorted.

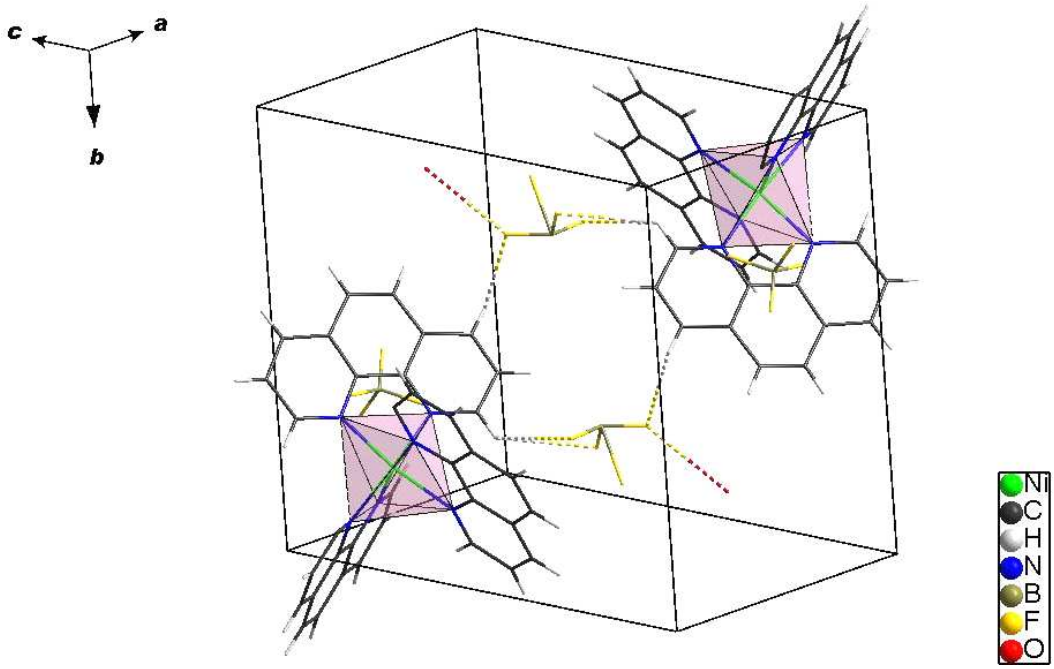


Fig. 6.2: Interconnection of monomers via H-bonds in $[Ni(phen)_3](BF_4)_2(H_2O)$.

One of the tetrafluoroborate anions is linked to a lattice water molecule via a hydrogen bond, the wO(1)-F(3) distance is about 3.00 Å. The tetrafluoroborate anions also exhibit a linking role, involving aromatic H atoms and fluorine atoms of the anion. They connect the monomers in the unit cell via H···F hydrogen bonds (Fig. 6.2), with bond lengths ranging from 2.58 to 2.71 Å. The motif in the packing represents independent monomers running along the c-axis with tetrafluoroborate anions between them. One of the two tetrafluoroborate molecules is disordered (Fig. 6.0 and 6.3).

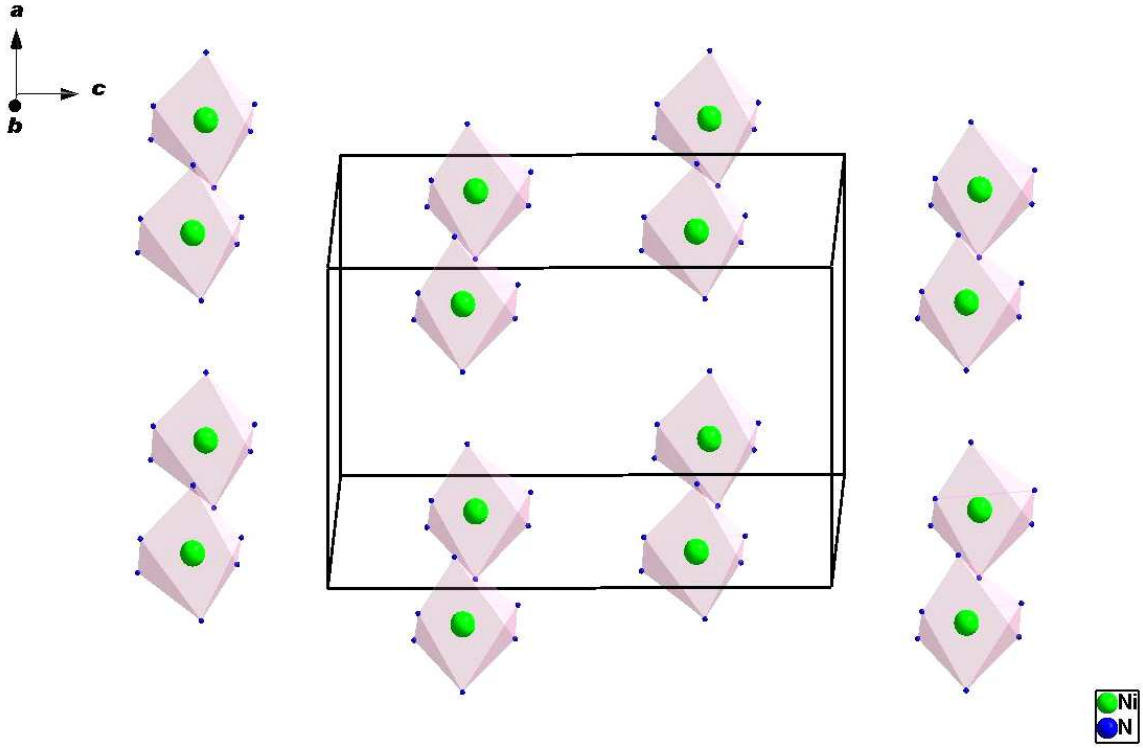


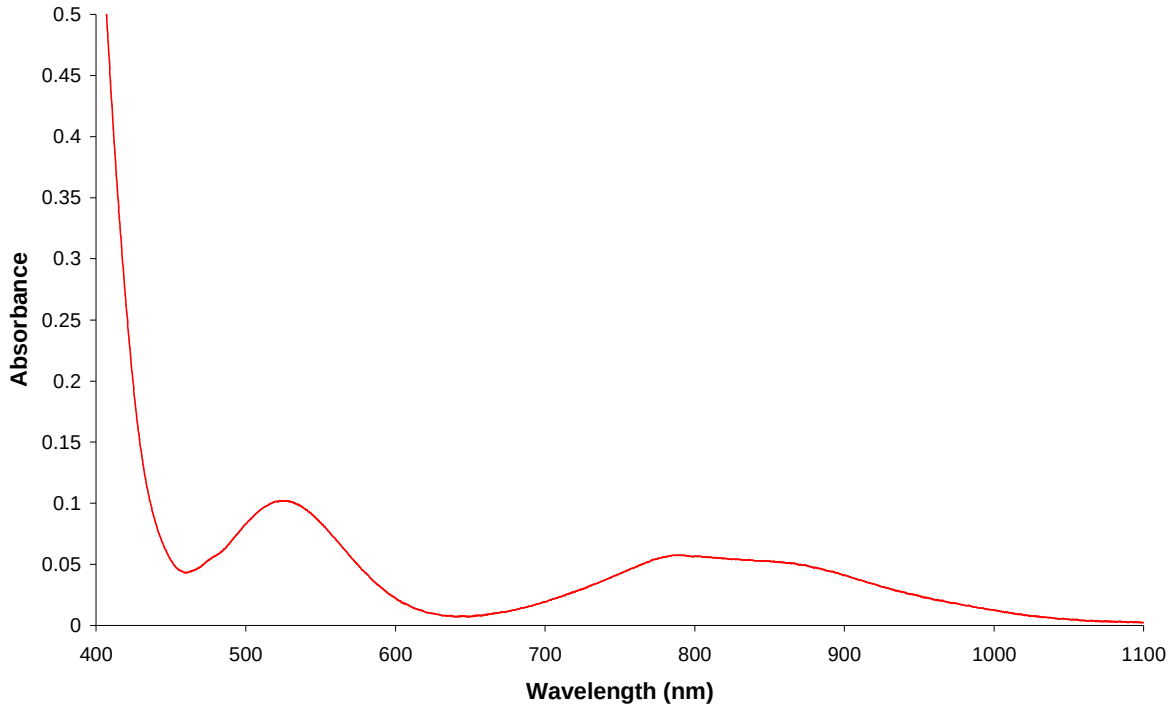
Fig. 6.3: Projection of the unit cell of $[Ni(Phen)_3](BF_4)_2(H_2O)$, atoms other than Ni and N are omitted for better perspective.

3.2.1.1 Experimental

Preparation of $[Ni(phen)_3](BF_4)_2(H_2O)$ (8)

20 ml of a 0.01-molar aqueous nickel tetrafluoroborate solution were mixed with three equivalents (60 ml) of a 0.01-molar (0.127 g) ethanolic phen solution. The mixture was stirred at approximately 60 ℃ for 70 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After six days pale red colored crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS Spectrum of $[Ni(phen)_3](BF_4)_2(H_2O)$ (8)



The absorption in the visible area of the spectrum at approximately 510 nm is responsible for the bright orange-red color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}$ (*F*) transition.

Table 4.5: Crystallographic and refinement details for $[Ni(Phen)_3](BF_4)_2(H_2O)$.

Empirical formula	$C_{36}\,H_{24}\,N_6\,Ni_1\,O_1\,F_8$
Formula weight	790.96 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	red
Unit cell dimensions	a = 9.085(2) Å
	b = 12.764(2) Å
	c = 15.099(3) Å
	α = 95.84(1)°, β = 90.48(1)°, γ = 95.23 (1)°
Cell volume	1734.1(1) $Å^3$
Z	2
Density (calculated)	1.515 $g \cdot cm^{-3}$
Absorption coefficient	0.643 mm^{-1}
F (000)	804
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	2.76° - 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-11 / 11, -15 / 15, -19 / 19
Reflections collected	18927
Independent reflections	7628
R_{int}	0.053
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	487
GooF(S)	1.056 [c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.058, wR_2[b] = 0.1822
R indices (all data)	R_1 = 0.0734, wR_2 = 0.2013

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 4.6: Selected distances/Å and angles/° in [Ni (Phen)$_3$](BF$_4$)$_2$(H$_2$O).

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	2.089(4)
Ni(1)	N(2)	2.107(4)
Ni(1)	N(3)	2.084(4)
Ni(1)	N(4)	2.087(4)
Ni(1)	N(5)	2.099(4)
Ni(1)	N(6)	2.096(3)
wO(1)	F(3)	3.002(1)
H(C2)	F(6)	2.581(7)
H(C2)	F(7)	2.709(5)
H(C11)	F(4)	2.547(9)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
Ni1	N3	N4	79.6(2)
Ni1	N3	N1	95.6(2)
Ni1	N3	N6	92.2(1)
Ni1	N3	N5	170.6(2)
Ni1	N3	N2	96.6(2)
Ni1	N4	N1	94.8(2)
Ni1	N4	N6	90.5(2)
Ni1	N4	N5	95.3(2)
Ni1	N4	N2	172.7(2)
Ni1	N1	N6	171.3(2)
Ni1	N1	N5	92.7(2)
Ni1	N1	N2	79.3(2)
Ni1	N6	N5	79.9(2)
Ni1	N6	N2	95.9(2)
Ni1	N5	N2	89.3(2)

3.2.1.2 Crystal structure of aquachlorido bis(1,10'-phenanthroline-*N,N'*) nickel(II) monochloride dihydrate, $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ (9)

$[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ **(9)** crystallizes in the triclinic space group P-1 (2) with a = 9.632(1) Å, b = 11.475(2) Å, c = 12.863(2) Å, α = 63.87(1)°, β = 84.71(1)°, γ = 79.40(1)°, V = 1254.5(3) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below, in Tables 4.7 and 4.8. The structure of **(9)** consists of a mixed $[Ni(Cl)(phen)_2(H_2O)]^+$ cationic complex, a chloride counterion and two lattice water molecules.

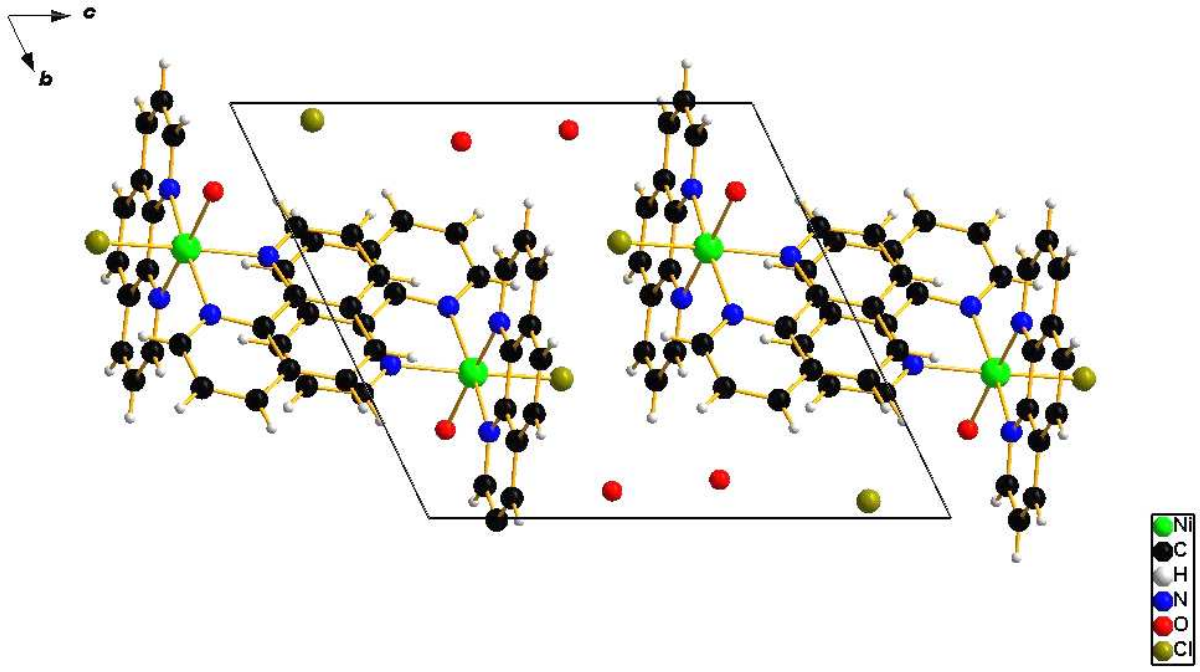


Fig. 6.4: Projection of the unit cell of $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ along the crystallographic a-axis.

A distorted octahedral coordination at the metal center (Fig. 6.5) is due to the differences in the donor strengths of the three different types of ligands which are coordinated to the metal center. The octahedron is formed by one aqua ligand, one chlorine ligand and four N atoms from two bidentate phen ligands, which lie in different planes and are nearly perpendicular to each other with an angle of 89.65(1)° between the two planes (Fig. 6.5). The aqua and chlorine ligands are *cis* to each other.

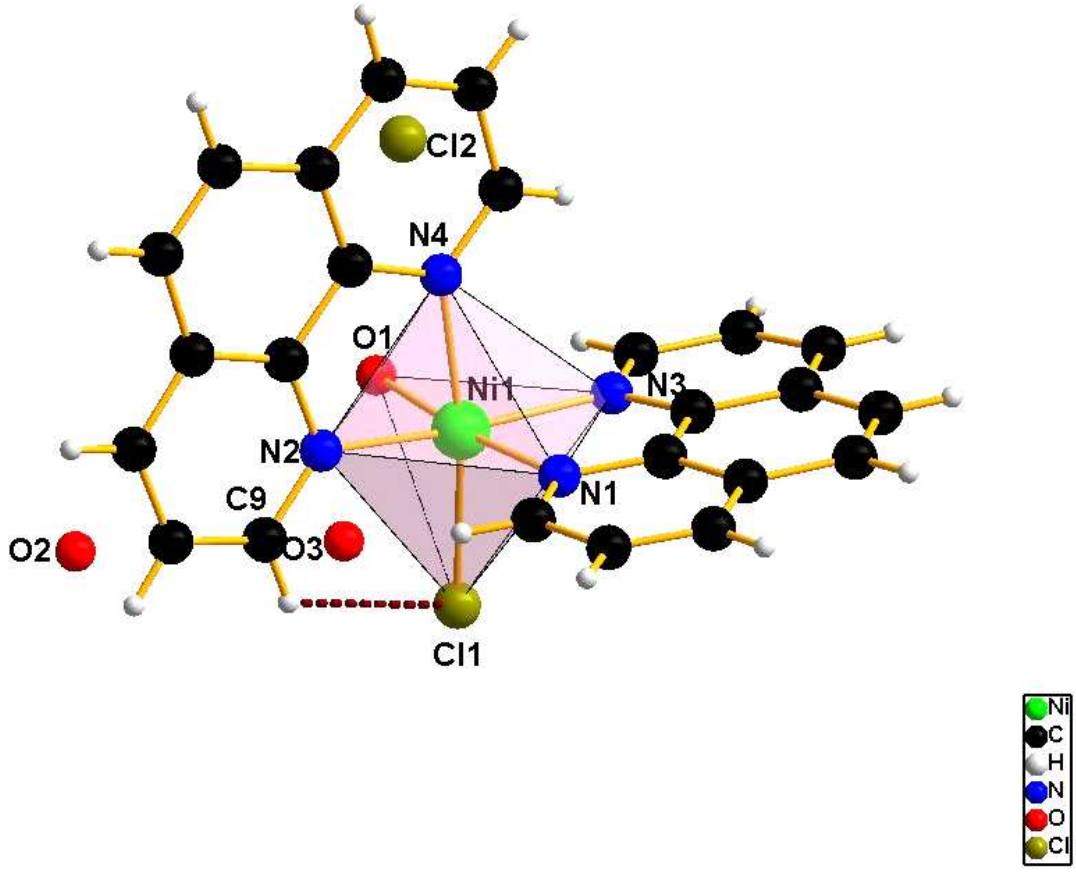


Fig. 6.5: The asymmetric unit of $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$.

The Ni-N bond lengths show little differences, they range from 2.093(3) to 2.118(3) Å, the N-Ni-N angles range from 79.0(1) to 173.8(1)° and deviate thus from ideal octahedral angles, resulting in a slightly distorted octahedral geometry around the Ni(II) metal center. The Ni-O bond length of 2.092(3) Å is very similar to Ni-N bond lengths. The Ni-Cl bond length is 2.382(1) Å, what is typical for Ni-Cl bond lengths found in the literature [33]. The coordination of a negatively charged chlorine ligand by the metal center produces a singly charged $[Ni(Cl)(phen)_2(H_2O)]^+$ cationic complex. This chloride is linked via weak hydrogen bonds to the chelating phen ligand. Atomic distances are listed in Tab. 4.8. Each lattice water molecule lies within a range of approximately 3 Å to one of the aromatic H atoms of the phen ligand. These distances are too long for regular hydrogen bonds and hence can hardly be seen as a very weak interaction. The motif in Fig. 6.6 represents a chain of independent monomers running along the c-axis in a zigzag pattern.

The aromatic rings of the phen ligands show the face-to-face π–π stacking interactions with centroid to centroid distances of about 3.67 Å, here most of the ring-

plane-area overlaps, thus stabilizing the structure and resulting in a zigzag translation pattern of the monomers running along the c-axis.

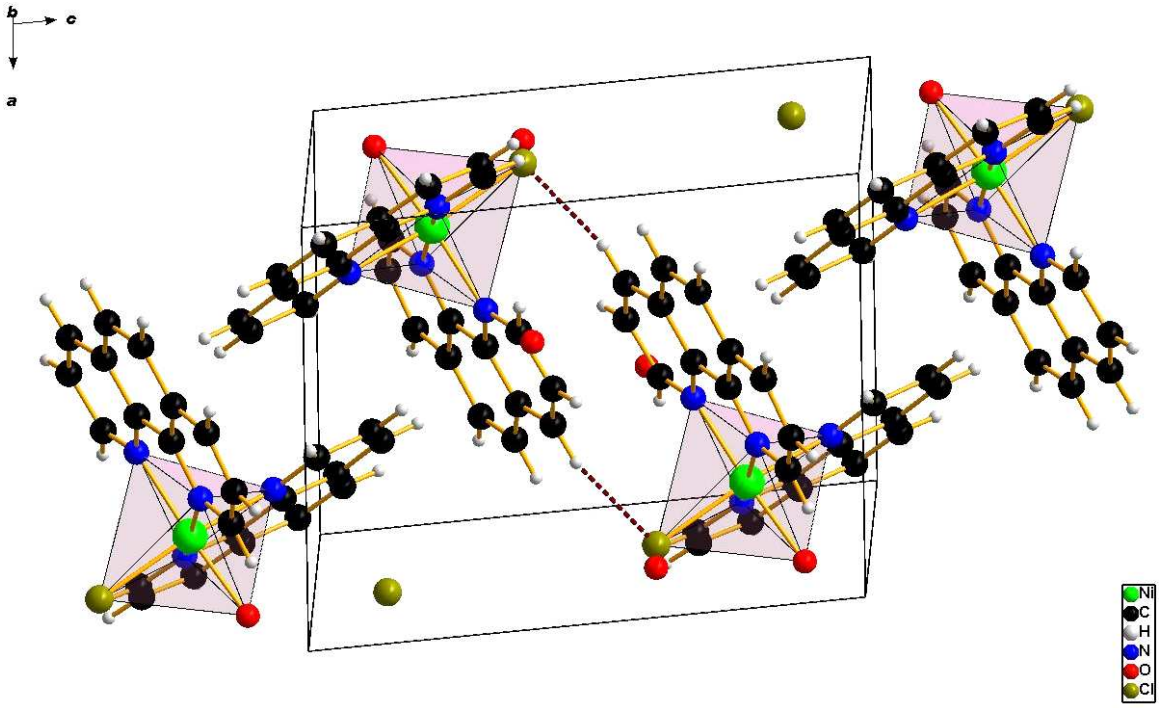


Fig. 6.6: Projection of the unit cell of $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$.

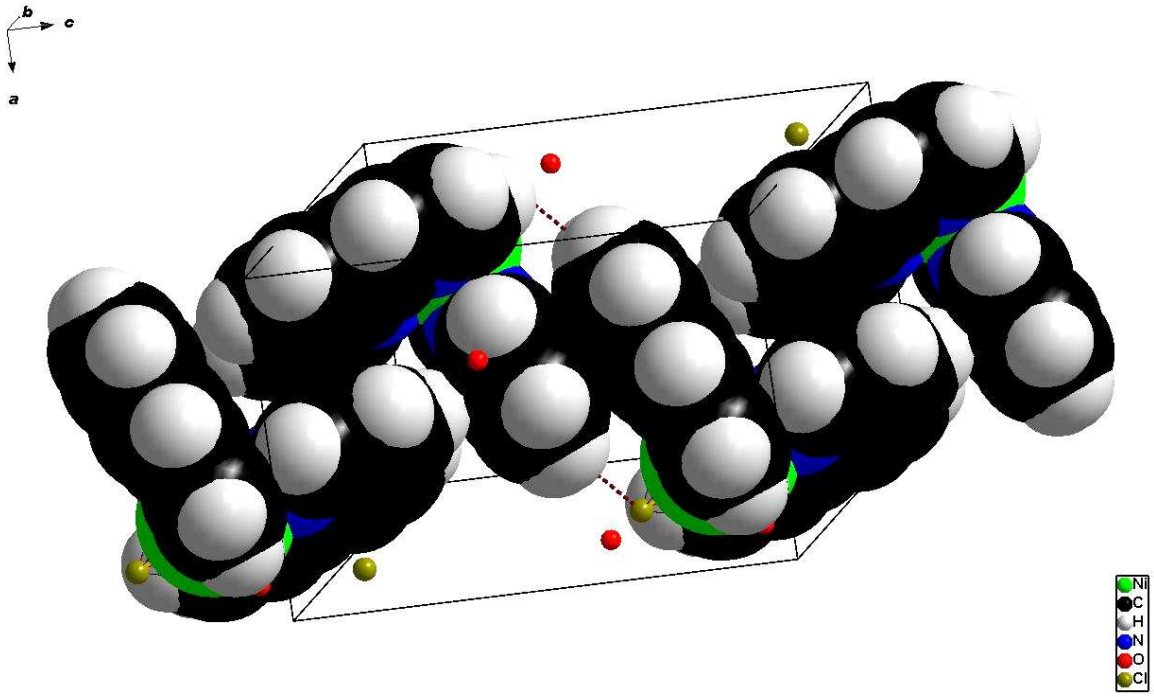


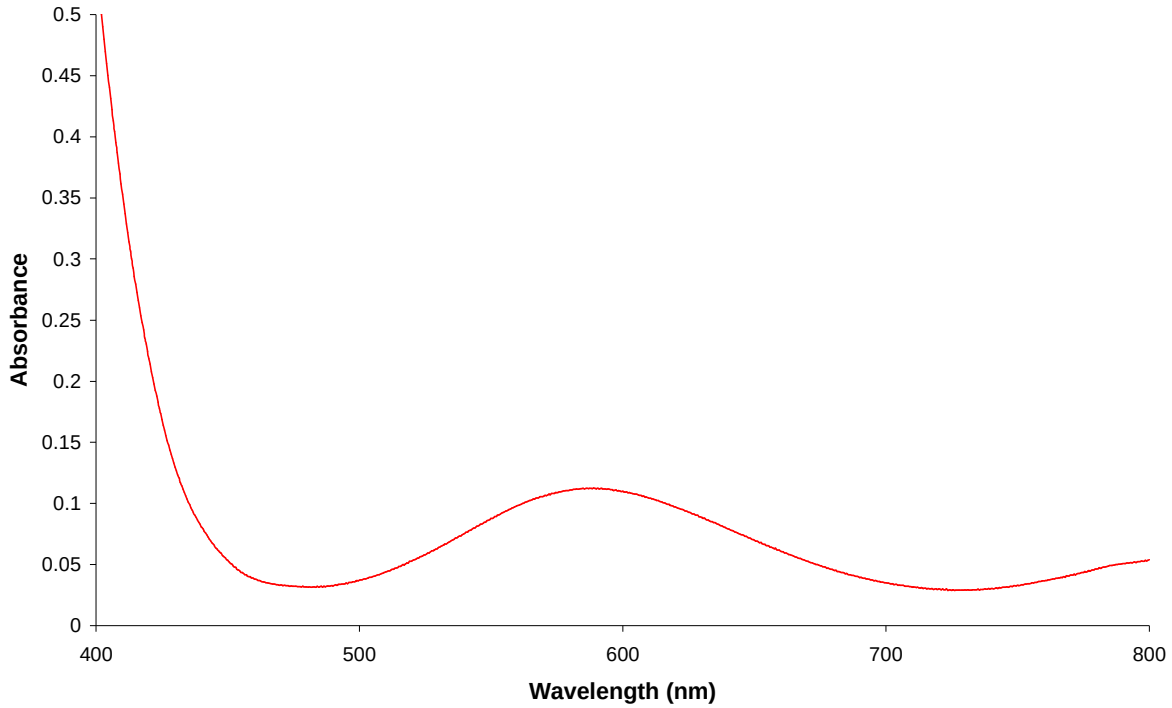
Fig. 6.7: π–π stacking interactions in $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$.

3.2.1.2 Experimental

Preparation of $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ (9)

20 ml of a 0.01-molar (0.047 g) ethanolic nickel chloride solution were mixed with one equivalent 20 ml of a 0.01-molar (0.036 g) acetonitrilic phen solution and one equivalent (20 ml) of a 0.01-molar (0.033 g) acetonitrilic 2,6-pda. Solution mixture was stirred at approximately 60 ℃ for 60 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After ten days green crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS measurements were conducted.

UV-VIS Spectrum of $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$ (9)



The absorption in the visible area of the spectrum at approximately 570 nm is responsible for the bright green color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 4.7: Crystallographic and refinement details for $[Ni(Cl)(phen)_2(H_2O)](Cl)(H_2O)_2$.

Empirical formula	$C_{24}H_{22}Cl_2N_4Ni_1O_3$
Formula weight	544.07 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal colour	green
Unit cell dimensions	a = 9.632(1) Å
	b = 11.475(2) Å
	c = 12.863(2) Å
	α = 63.87(1), β = 84.71(1), γ = 79.40(1)
Cell volume	1254.5(3) $Å^3$
Z	2
Density (calculated)	1.436 $g \cdot cm^{-3}$
Absorption coefficient	1.019 mm^{-1}
F (000)	560
Diffractometer	STOE Image Plate Diffraction System I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	2.76°- 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-11 / 11, -15 / 15, -16 / 16
Reflections collected	14673
Independent reflections	5475
R_{int}	0.0291
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	308
GooF(S)	1.046[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] =0.0512, wR_2[b] = 0.1555
R indices (all data)	R_1 = 0.0688, wR_2 = 0.1659

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 4.8: Selected distances/Å and angles/° in [Ni (Cl)(phen)$_2$(H_2O)](Cl)(H_2O)$_2$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	O(1)	2.092(3)
Ni(1)	N(2)	2.093(3)
Ni(1)	N(1)	2.096(3)
Ni(1)	N(3)	2.100(3)
Ni(1)	N(4)	2.118(3)
Ni(1)	Cl(1)	2.382(1)
H(C9)	Cl(1)	2.804(1)
H(C15)	Cl(1)	2.743(1)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3] [°]
N(2)	Ni(1)	O(1)	92.6(1)
N(1)	Ni(1)	O(1)	173.8(1)
N(3)	Ni(1)	O(1)	94.5(1)
N(4)	Ni(1)	O(1)	86.9(1)
Cl(1)	Ni(1)	O(1)	88.8(7)
N(1)	Ni(1)	N(2)	93.0(1)
N(3)	Ni(1)	N(2)	168.9(1)
N(4)	Ni(1)	N(2)	79.0(1)
Cl(1)	Ni(1)	N(2)	94.7(1)
N(3)	Ni(1)	N(1)	79.6(1)
N(4)	Ni(1)	N(1)	91.6(1)
Cl(1)	Ni(1)	N(1)	93.4(1)
N(4)	Ni(1)	N(3)	92.7(1)
Cl(1)	Ni(1)	N(3)	94.1(1)
Cl(1)	Ni(1)	N(4)	172.2(1)

3.2.1.3 Crystal structure of tris(1,10-phenanthroline-*N,N'*)-nickel(II) bis-(triiodide) monohydrate, $[Ni(phen)_3](I_3)_2(H_2O)$ (10)

$[Ni(phen)_3](I_3)_2(H_2O)$ **(10)** crystallizes in the triclinic space group P-1 (2) with a = 10.035(1) Å, b = 12,698(2) Å, c = 18.091(2) Å, α = 79.77(2)°, β = 87.04(2)°, γ = 67.253(2)°, V = 2091.8(7) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below, in Tables 4.9 and 5.0. The structure of **(10)** consists of a cationic $[Ni(phen)_3]^{2+}$ complex, two triiodide anions and one lattice water molecule. The $[Ni(phen)_3]^{2+}$ cation contains a 6-coordinate Ni(II) atom coordinated to three phen ligands via the N-atoms in a slightly distorted octahedral arrangement (Fig. 6.9).

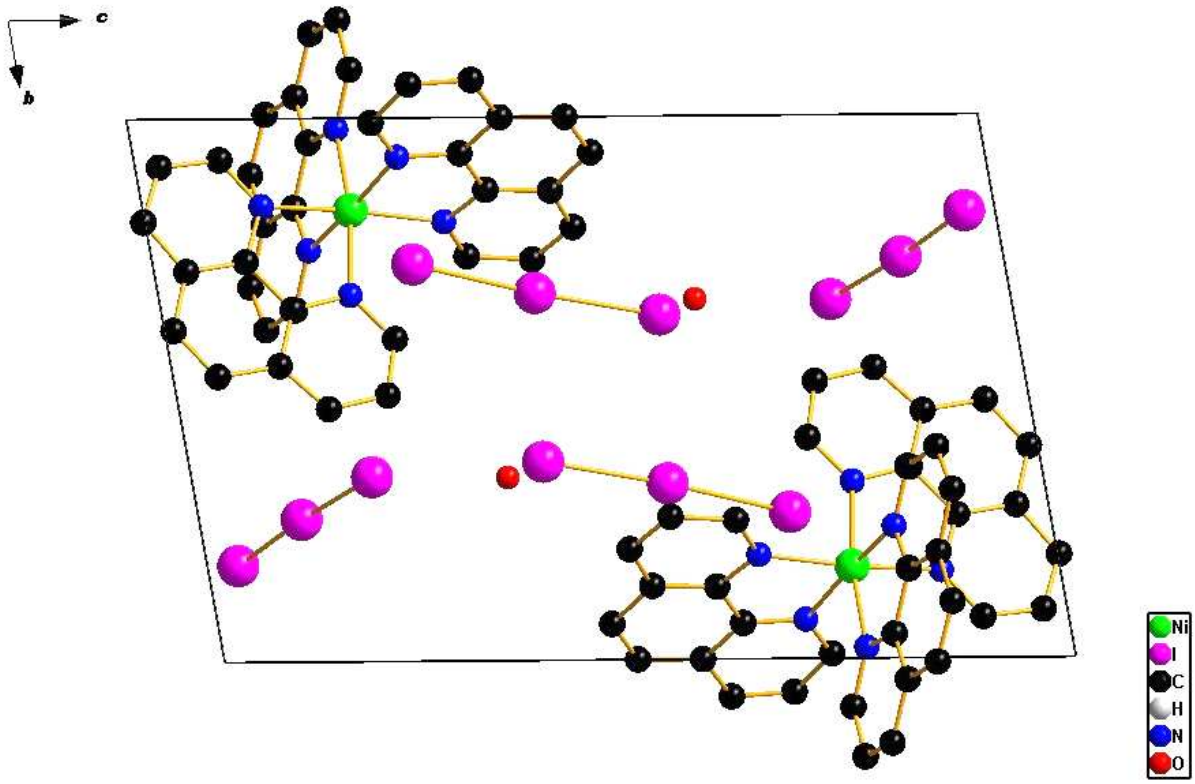


Fig. 6.8: Projection of the unit cell of $[Ni(phen)_3](I_3)_2(H_2O)$ along the crystallographic a-axis.

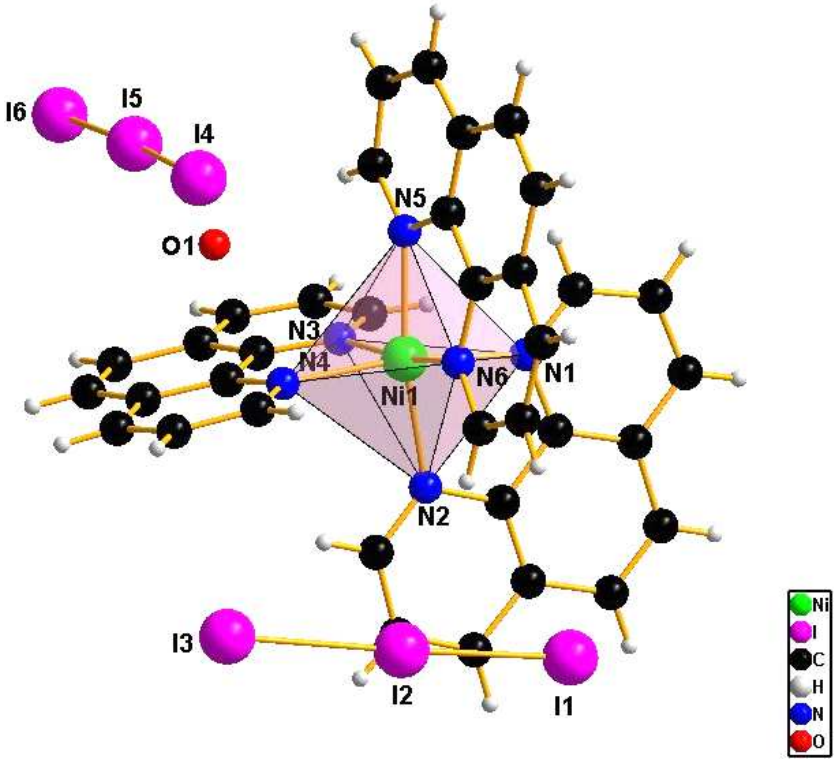


Fig. 6.9: The asymmetric unit of $[Ni(phen)_3](I_3)_2(H_2O)$.

The Ni-N distances range from 2.078(7) Å to 2.117(6) Å and the N-Ni-N angles range from 79.29(2) to 172.71(2)° and deviate thus from a n ideal octahedral arrangement. Two triiodide anions counter-balance the positive charge of the $[Ni(phen)_3]^{2+}$ cation. The I-I bond length ranges are 2.895(11) and 2.945(12) Å for I(1)-I(2) and I(2)-I(3) respectively, and are typical for I-I bond lengths in triiodides [34]. The I_3^- anions lie isolated, and do not exhibit H-bonding with H-atoms of the coordinating phen ligands. The lattice water molecule also shows no H-bonding.

The motif in Fig. 6.8 represents independent monomers running along the a-axis with triiodide anions occupying space between them. The two asymmetric units lie far from each other, where the Ni-Ni distance is 18.335(3) Å. Obviously, for this reason, there is no π–π stacking observed in this structure.

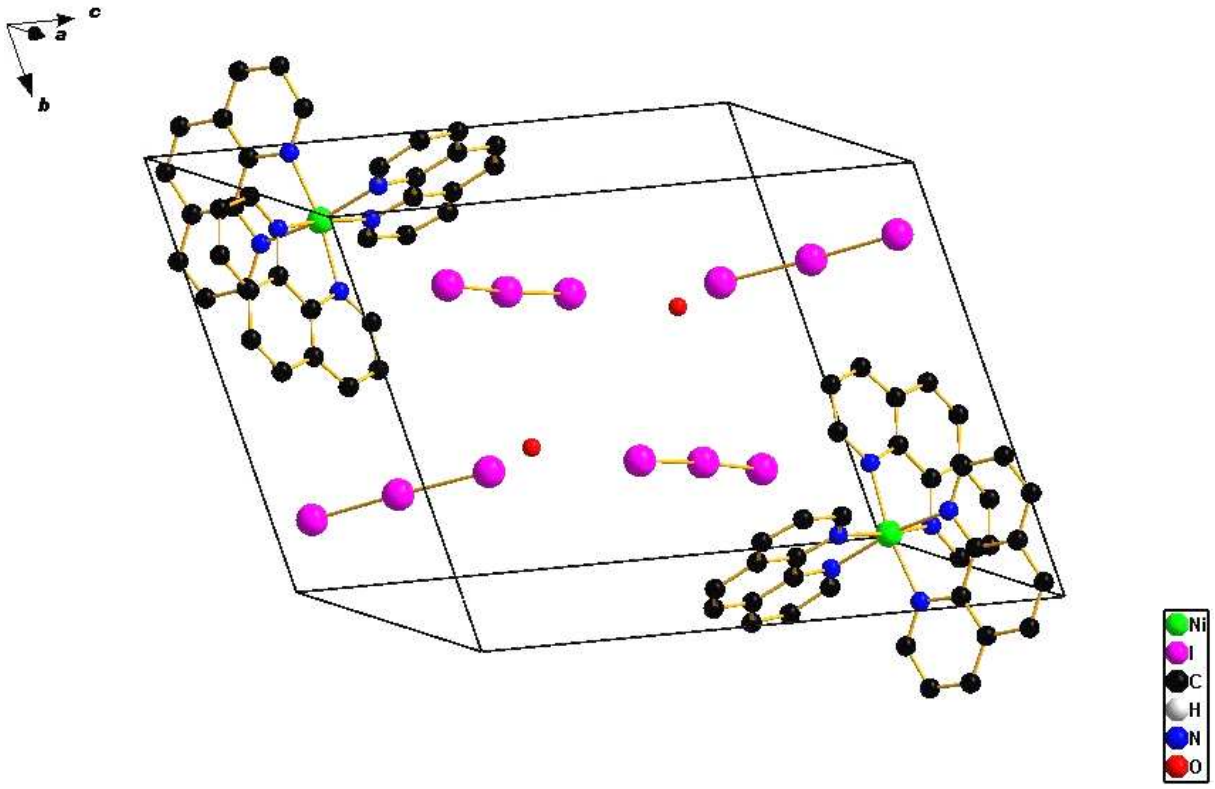


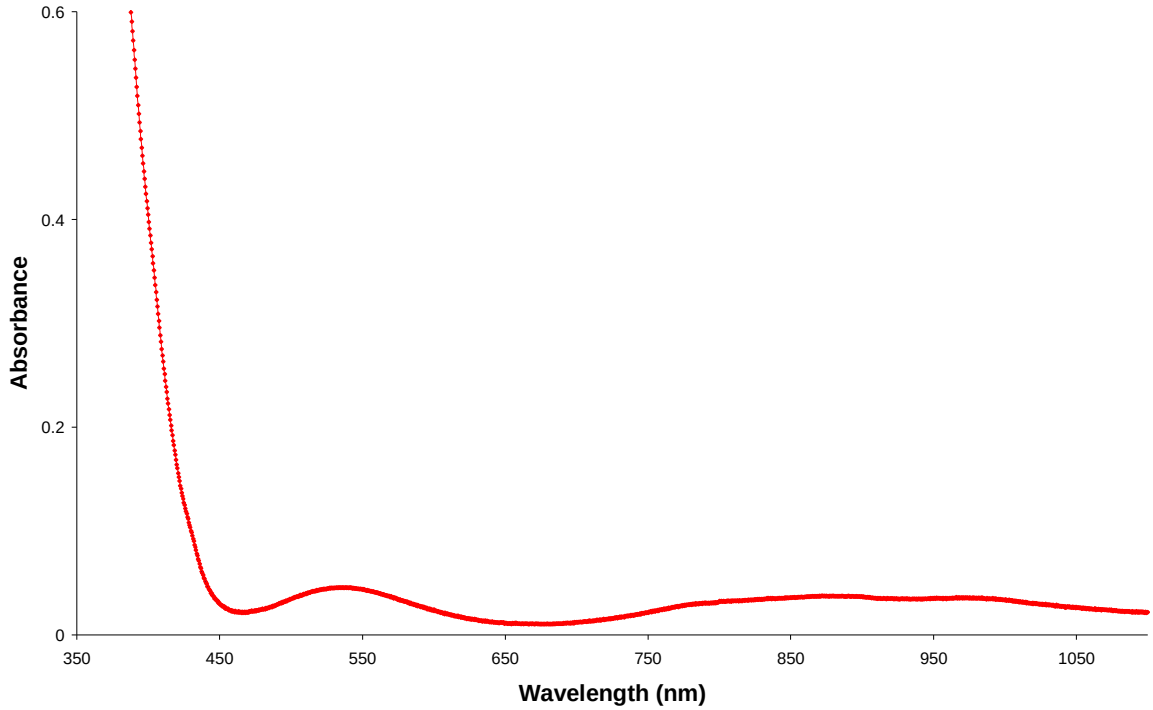
Fig. 7.0: Projection of the unit cell of $[Ni(phen)_3](I_3)_2(H_2O)$.

3.2.1.3 Experimental

Preparation of $[Ni(phen)_3](I_3)_2(H_2O)$ (10)

20 ml of a 0.01 M (0.063 g) ethanolic/aqueous nickel iodide solution were mixed with three equivalents (60 ml) of a 0.01 M (0.127 g) ethanolic phen solution. The mixture was stirred at approximately 60 ℃ for 45 min in a be aker. By evaporation, the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After seven days orange-red crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS spectra measurements were conducted.

UV-VIS Spectrum of $[Ni(phen)_3](I_3)_2(H_2O)$ (10)



The absorption in the visible area of the spectrum at approximately 520 nm is responsible for the orange-red color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 4.9: Crystallographic and refinement details of $[Ni(phen)_3](I_3)_2(H_2O)$.

Empirical formula	$C_{36}H_{24}N6Ni_1I_6O_1$
Formula weight	1378.74 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal colour	red
Unit cell dimensions	a = 10.035(1) Å
	b = 12,698(2) Å
	c = 18.091(2) Å
	α = 79.77(2)°, β = 87.04(2)°, γ = 67.253(2)°
Cell volume	2091.8(7) $Å^3$
Z	2
Density (calculated)	2.189 $g \cdot cm^{-3}$
Absorption coefficient	4.93 mm^{-1}
F (000)	1276.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	4.92°- 56.10°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-13 / 13, -16 / 16, -23 / 23
Reflections collected	25006
Independent reflections	9273
R_{int}	0.0832
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	451
GooF(S)	0.739[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0413, wR_2[b] = 0.1727
R indices (all data)	R_1 = 0.1420, wR_2 = 0.1393

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.

$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 5.0: Selected distances/Å and angles/° in $[Ni(phen)_3](I_3)_2(H_2O)$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	2.114(6)
Ni(1)	N(2)	2.117(6)
Ni(1)	N(3)	2.090(7)
Ni(1)	N(5)	2.095(7)
Ni(1)	N(4)	2.078(7)
Ni(1)	N(6)	2.098(6)
I(1)	I(2)	2.895(11)
I(2)	I(3)	2.945(12)
I(4)	I(5)	2.925(12)
I(5)	I(6)	2.888(13)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(2)	Ni(1)	N(4)	78.7(4)
N(2)	Ni(1)	N(3)	170.2(4)
N(2)	Ni(1)	N(5)	88.7(4)
N(2)	Ni(1)	N(1)	95.0(4)
N(3)	Ni(1)	N(5)	97.3(4)
N(3)	Ni(1)	N(1)	93.7(4)
N(4)	Ni(1)	N(3)	93.2(4)
N(4)	Ni(1)	N(5)	92.8(4)
N(4)	Ni(1)	N(1)	170.4(4)
N(6)	Ni(1)	N(3)	78.7(4)
N(6)	Ni(1)	N(5)	169.8(4)
N(6)	Ni(1)	N(1)	91.1(4)

3.2.1.4 Crystal structure of tris(1,10-Phenanthroline-*N,N'*)-nickel(II) pyridine-2,6-dicarboxylate monohydrate, $[Ni(Phen)_3](2,6\text{-pda})(H_2O)_{11}$ (11)

$[Ni(Phen)_3](2,6\text{-pda})(H_2O)_{11}$ **(11)** crystallizes in the monoclinic space group C2/c (15) with a = 28.683(3) Å, b = 19.070(1) Å, c = 21.049(2) Å, β = 129.49(7)°, V = 8885.29 (14) $Å^3$ and Z = 8. Crystallographic and refinement details are listed below, in Tables 5.1 and 5.2. The structure of **(11)** consists of a $[Ni(phen)_3]^{2+}$ cationic complex, a pyridinedicarboxylate anion and eleven lattice water molecules. The $[Ni(phen)_3]^{2+}$ cation contains 6-coordinate Ni(II) coordinated to three phen ligands via the N atoms in a slightly distorted octahedral arrangement (Fig. 7.2).

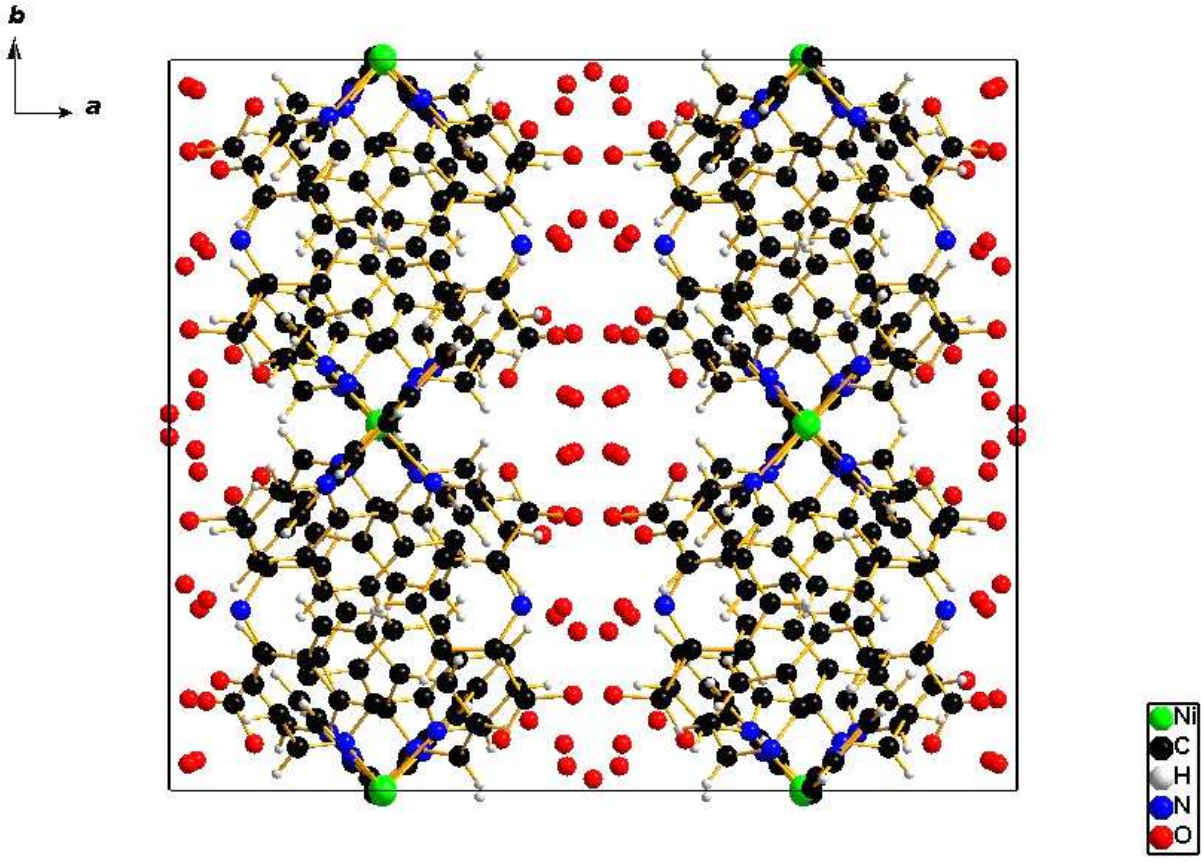


Fig. 7.1: Projection of the unit cell of $[Ni(Phen)_3](2,6\text{-pda})(H_2O)_{11}$ along the crystallographic c-axis.

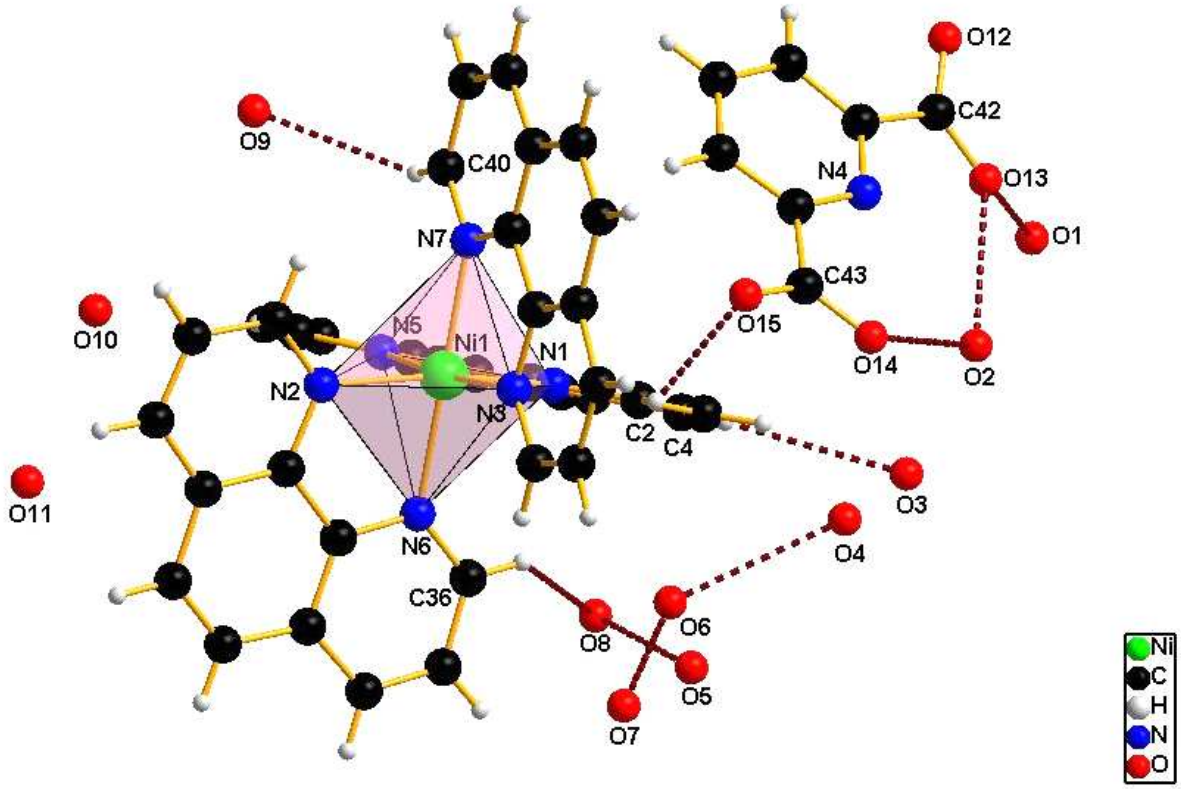


Fig. 7.2: The asymmetric unit of $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$.

The cationic complex consists of one Ni(II) metal center, which is chelated by three bidentate phen ligands. The Ni-N distances show very little difference, they range from 2.079(3) to 2.116(3) Å. The N-Ni-N angles range from 79.20(2) to 174.68° and deviate thus from the ideal octahedral angles; as a result the octahedral geometry around the Ni(II) center is slightly distorted. The 2,6-pda, known as a classical pincer ligand is not coordinated by the metal center in this compound. The 2,6-pda was deprotonated during the reaction of the nickel acetate with phen and 2,6-pda by acetate anions. The C-O atomic distances in the carboxylic groups of 2,6-pda range from 1.241(4) to 1.263(3) Å, the C(43)-O(14) and C(43)-O(15) are 1.262(4) and 1.241(4) Å long, respectively, typical values for single C-O bonds in carboxylic groups of 2,6-pda range from 1.27-1.30 Å and for C-O double bonds from 1.20-1.23 Å [35], so that the bond length of 1.262(4) Å is short for a single C-O bond and 1.241(4) Å is long for a C-O double bond. According to these parameters, the charge on the carboxylic group is delocalized. The same applies to the second carboxylic group, atomic distances are listed below in Table 5.2.

It is therefore double negatively charged and serves as an anion, which counter balances the double positively charged $[Ni(phen)_3]^{2+}$ complex. There are also eleven lattice water molecules present. Nine of them are linked through hydrogen bonds with each other, with the 2,6-pda anion and with the chelating phen ligands. The hydrogen atoms could not be localized, therefore the O-O atomic distances are given, their values are listed in Table 5.2.

The motif in the packing represents independent monomers running along the c-axis with 2,6-pda anions between them (Fig.7.3). There are eight such monomers per one unit cell.

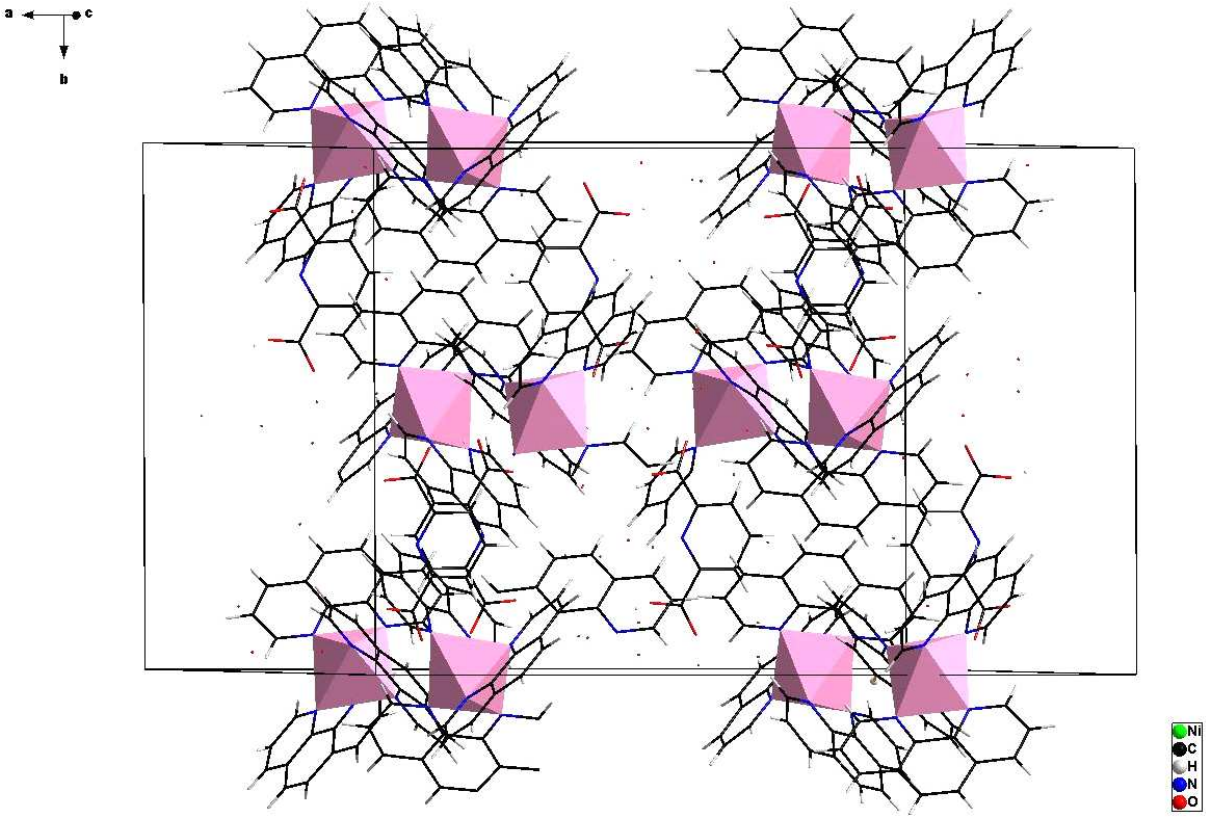


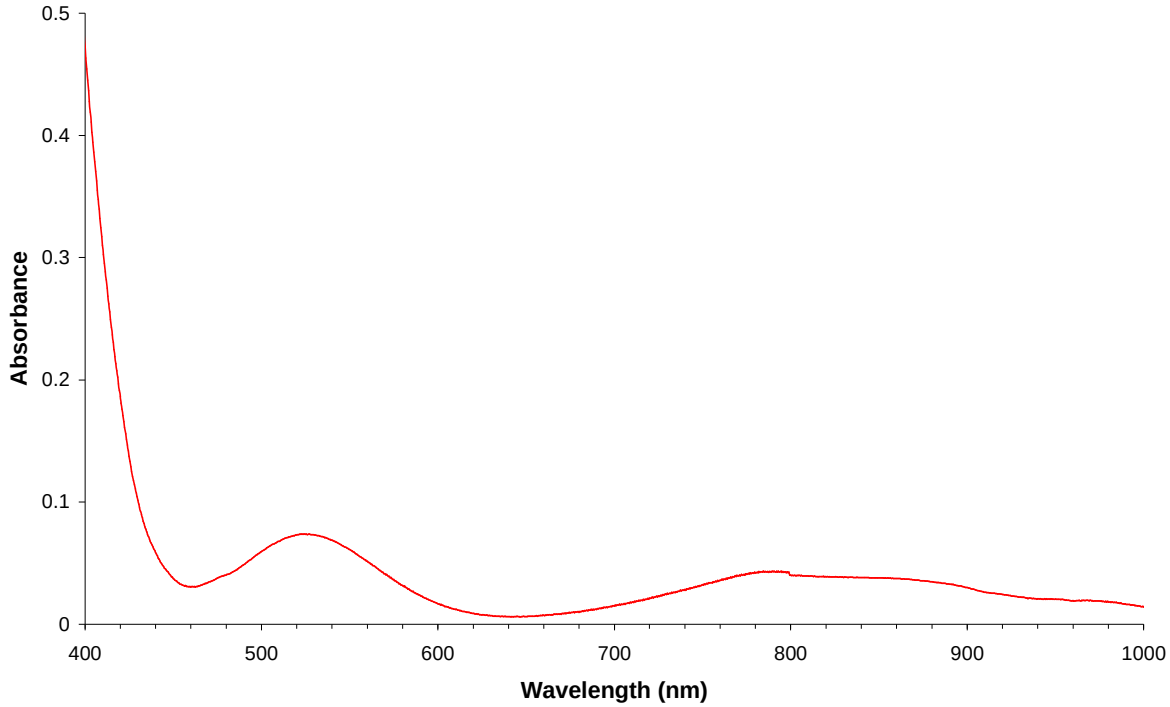
Fig. 7.3: Projection of the unit cell of $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$.

3.2.1.4 Experimental

Preparation of $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$ (11)

20 ml of a 0.01-molar (0.050 g) aqueous nickel acetate solution were mixed with three equivalents (60 ml) of a 0.01-molar (0.108 g) ethanolic phen solution and one equivalent of 2,6-pda. The mixture was stirred at approximately 60 ℃ for 60 min in a beaker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After ten days red crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS spectra measurements were conducted.

UV-VIS Spectrum of $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$ (11)



The absorption in the visible area of the spectrum at approximately 520 nm is responsible for the bright orange-red color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}$ (*F*) transition.

Table 5.1: Crystallographic and refinement details for $[Ni(phen)_3](2,6\text{-pda})(H_2O)_{11}$.

Empirical formula	$C_{43}H_{27}N_7Ni_1O_{15}$
Formula weight	1907.19 $g \cdot mol^{-1}$
Crystal system	monoclinic
Space group	C2/c (15)
Crystal colour	red
Unit cell dimensions	a = 28.683(3) Å
	b = 19.070(1) Å
	c = 21.049(2) Å
	β =129.49(7)°
Cell volume	8885.29 (14) $Å^3$
Z	8
Density (calculated)	1.426 $g \cdot cm^{-3}$
Absorption coefficient	0.510 mm^{-1}
F (000)	3992.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	4.54°- 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-36 / 36, -24 / 22, -27 / 26
Reflections collected	55991
Independent reflections	9926
R_{int}	0.077
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	592
GooF(S)	0.825 [c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0486, wR_2[b] = 0.1235
R indices (all data)	R_1 = 0.1092, wR_2 = 0.1402

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.

$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$

Table 5.2: Selected distances/Å and angles/° in $[Ni(Phen)_3](2,6\text{-pda})(H_2O)_{11}$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(1)	2.079(3)
Ni(1)	N(2)	2.092(3)
Ni(1)	N(3)	2.091(3)
Ni(1)	N(7)	2.103(3)
Ni(1)	N(5)	2.104(4)
Ni(1)	N(6)	2.116(3)
C(43)	O(14)	1.262(4)
C(43)	O(15)	1.241(4)
C(42)	O(12)	1.244(4)
C(42)	O(15)	1.263(3)
H(C2)	O(15)	2.586(4)
H(C4)	O(3)	2.856(5)
H(C36)	O(8)	2.816(4)
wO(13)	wO(1)	2.756(4)
wO(13)	wO(2)	2.803(4)
wO(14)	wO(2)	2.816(4)
wO(8)	wO(5)	2.761(5)
wO(6)	wO(7)	2.983(9)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(1)	Ni(1)	N(3)	97.1(1)
N(1)	Ni(1)	N(2)	167.7(1)
N(1)	Ni(1)	N(7)	93.9(106)
N(1)	Ni(1)	N(5)	79.5(1)
N(1)	Ni(1)	N(6)	91.4(1)
N(3)	Ni(1)	N(2)	91.4(1)
N(3)	Ni(1)	N(7)	79.4(1)
N(3)	Ni(1)	N(5)	174.7(1)
N(3)	Ni(1)	N(6)	93.8(1)
N(2)	Ni(1)	N(7)	96.4(1)
N(2)	Ni(1)	N(5)	92.6(1)
N(2)	Ni(1)	N(6)	79.2(1)
N(7)	Ni(1)	N(5)	96.7(1)
N(7)	Ni(1)	N(6)	171.9(1)
N(5)	Ni(1)	N(6)	90.4(1)

3.2.1.5 Crystal structure of di-bis(pyridine-2,6-dicarboxylato-k^3*N,O,O*) nickelate(II) diaquabis(1,10'-phenanthroline-*N,N*)nickel(II) nonahydrate, $[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ (12)

$[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ (**12**) crystallizes in the triclinic space group P-1 (2) with a = 13.545(2) Å, b = 14.717(2) Å , c = 15.990(1) Å, α = 77.60(1)°, β = 72.86(1)°, γ = 76.32.(1)°, V = 2849.7(6) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below, in Tables 5.3 and 5.4. The structure of (**12**) represents a mixed complex, which consists of one $[Ni(phen)_2(H_2O)_2]^{2+}$ cation, two $[Ni(2,6\text{-}pda)_2]^{1-}$ anions and nine lattice water molecules. All three Ni(II) metal centers are crystallographically independent and adopt a distorted octahedral arrangement (Fig. 7.5).

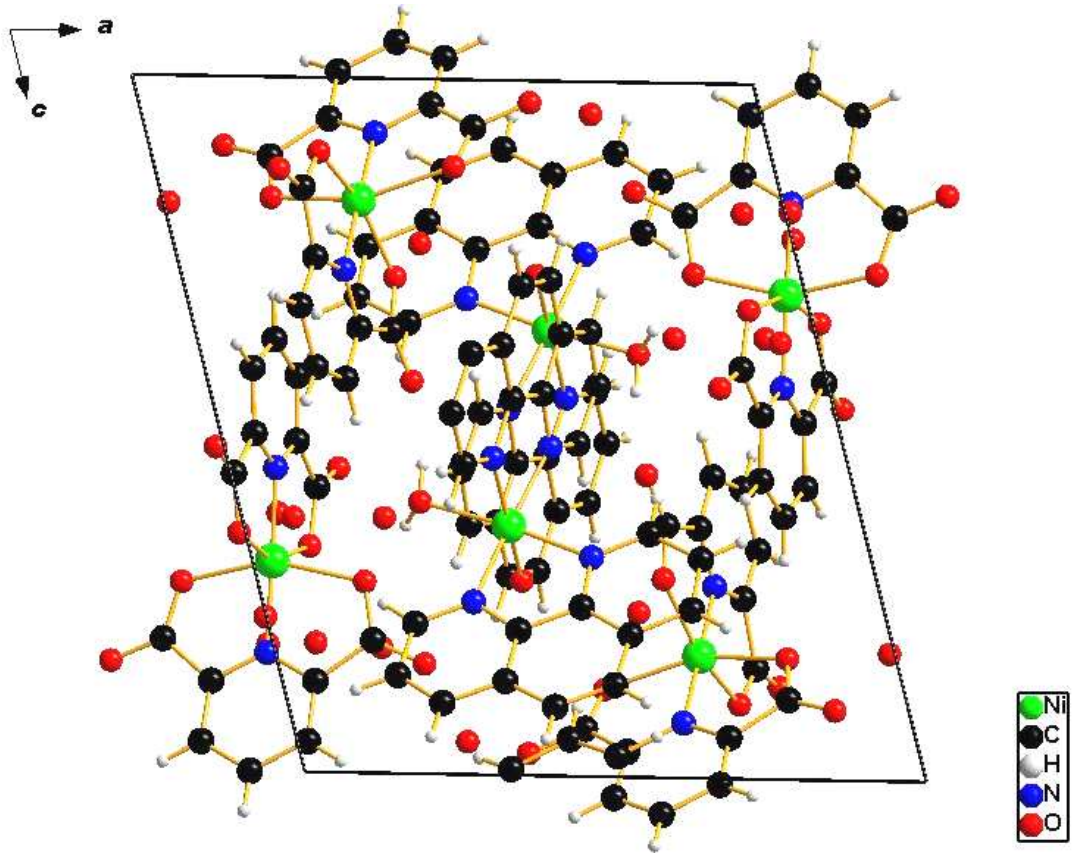


Fig. 7.4: Projection of the unit cell of $[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ along the crystallographic b-axis.

In the cation, Ni(II) is ligated by two phen ligands in addition to two aqua ligands. The ligands are mutually adjacent, the complex represents therefore a *cis* isomer.
The Ni-N distances range from 1.957(4) Å to 2.093(4) Å, the Ni-O bond lengths range from 2.051(4) Å to 2.188(3) Å. The angles range from 78.38(2) to 177.22(1)° and deviate thus from ideal octahedral angles (Tables 5.3 and 5.4). This is due to the differences in the ligand strengths of the coordinating ligands.

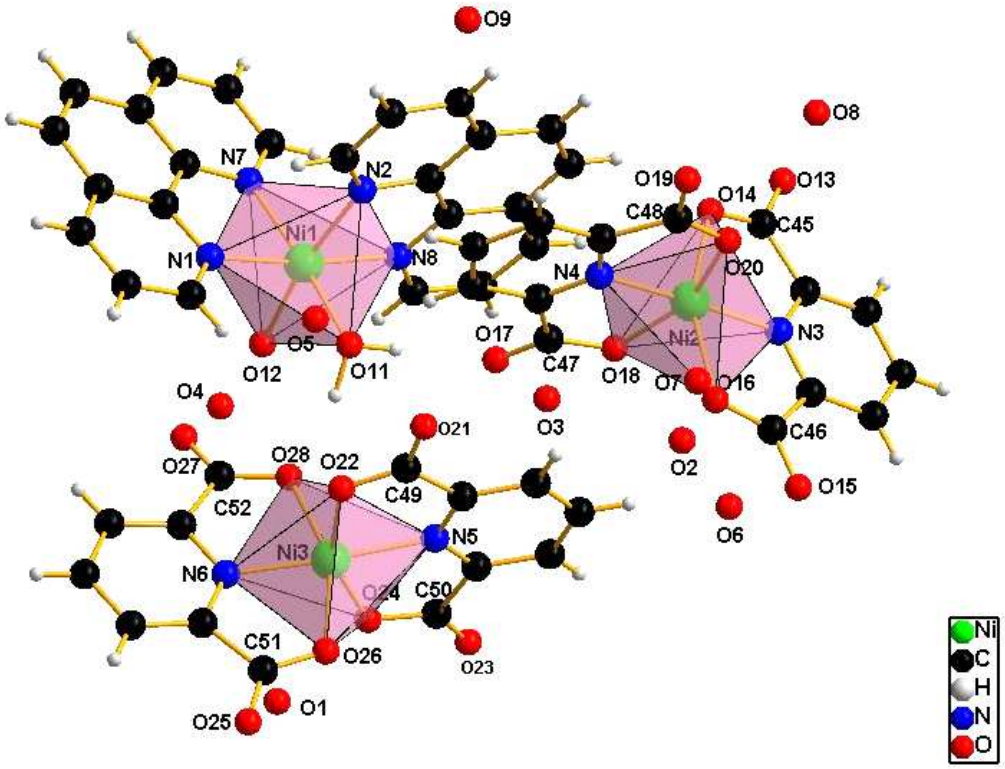


Fig. 7.5: The asymmetric unit of $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$.

The anion represents two structurally identical $[Ni(2,6\text{-pda})]^{1-}$ complexes (Fig. 7.5), where each Ni(II) ion is coordinated to two 2,6-pda ligands in a *k*-N,*O,O'* mode, typical for this 'pincer' ligand [36]. According to the Ni-O distances in both anionic complexes (Table 5.3), three of them have a covalent character and the fourth one is typical for a coordinative Ni-O distance and is similar to other Ni-O atomic distances in Ni(II) complexes [37]**.** The motif in Fig. 7.4 represents a chain of independent monomers along the crystallographic b-axis.

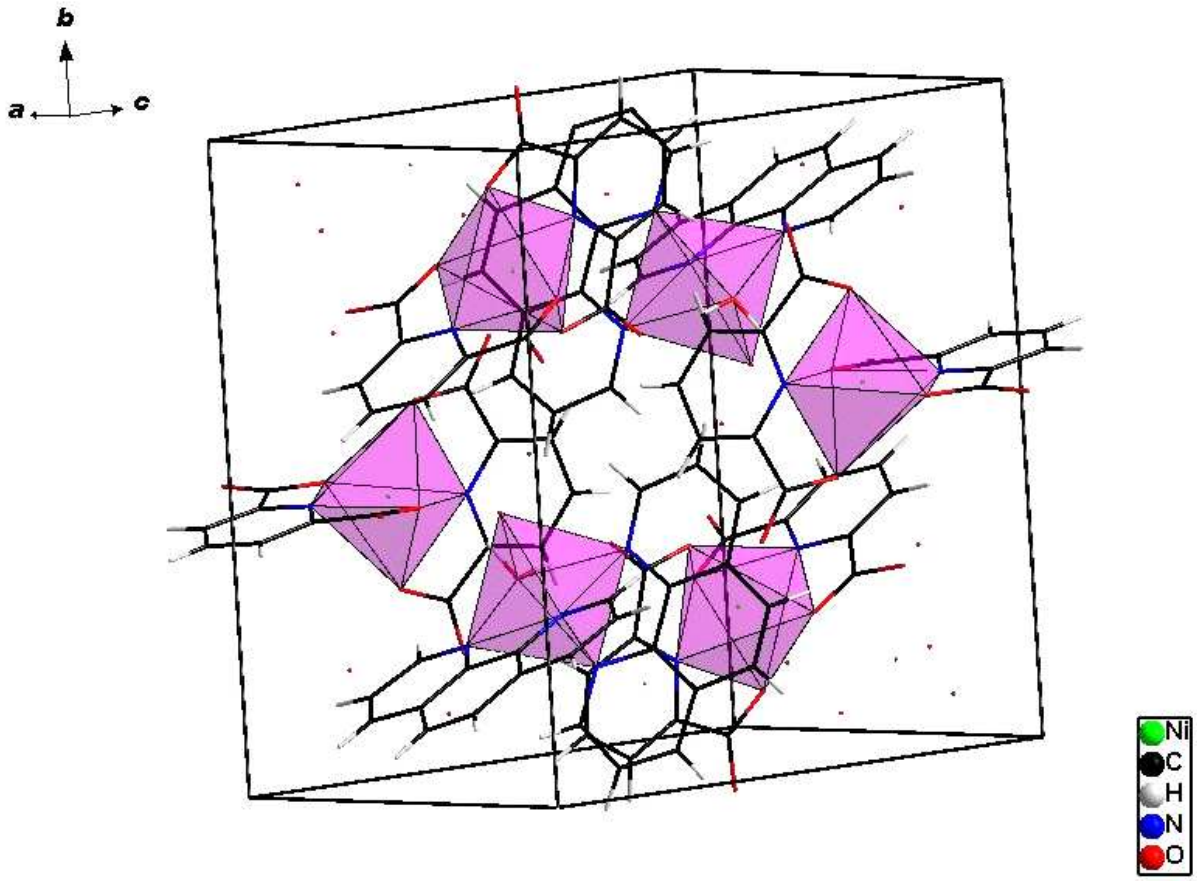


Fig. 7.6: Projection of the unit cell of $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$.

π–π stacking interactions apparently control the packing of the structure. Here the aromatic ring of the phen ligand stacks with the pyridyl ring of 2,6-pda, which is coordinated to the Ni(2) metal center. The rings are slipped in an offset conformation with the hydrogen atoms roughly above the ring centers. The centroid-centroid distance is 3.87 Å, ring normal and the vector between the ring centroids form an angle of around 21°.

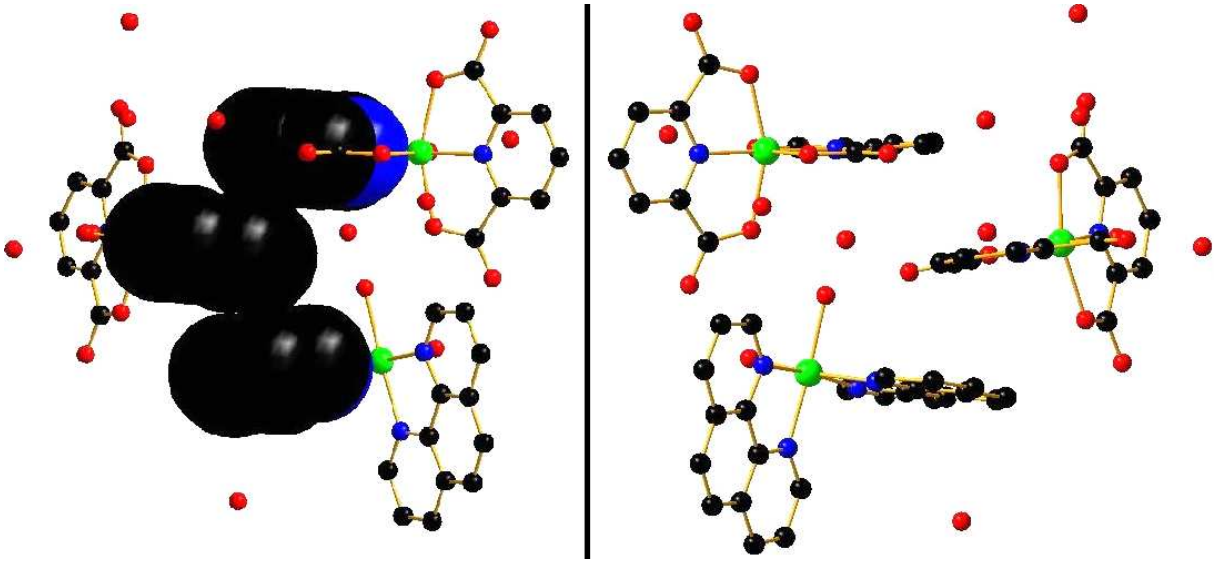


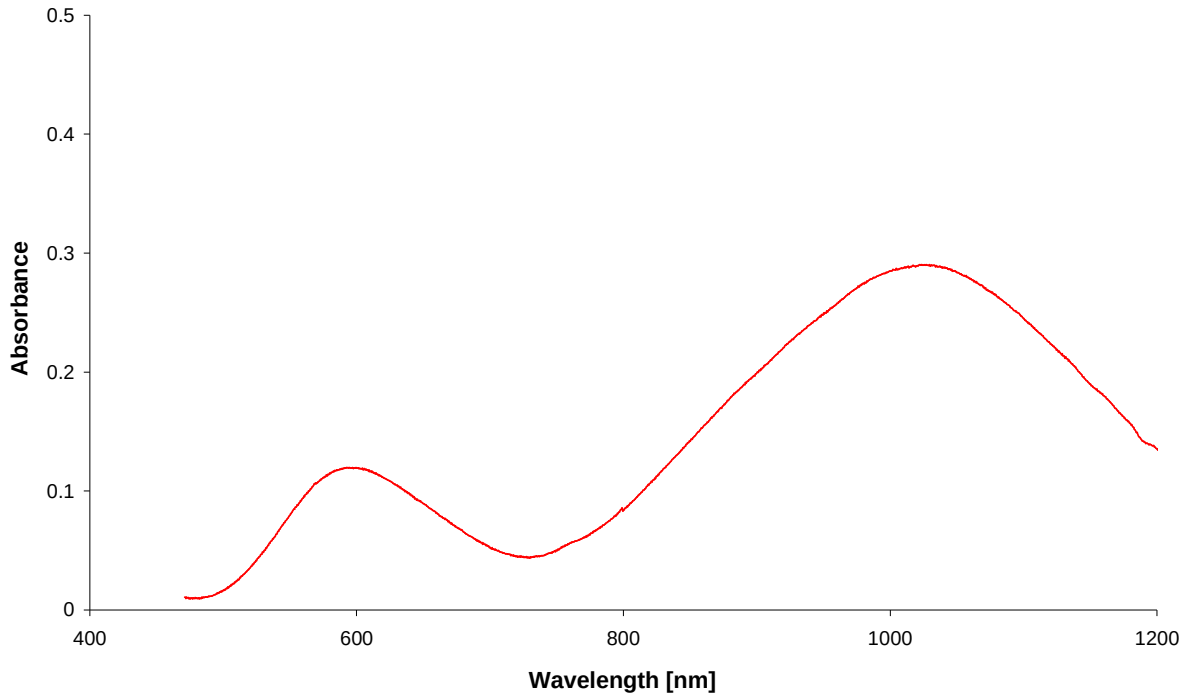
Fig. 7.7: π–π stacking in $[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$.

3.2.1.5 Experimental

Preparation of $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ (12)

20 ml of a 0.01-molar (0.053 g) aqueous nickel sulfate solution were mixed with one equivalent 20 ml of a 0.01-molar (0.034 g) methanolic 2,6-pda solution and two equivalents 40 ml of a 0.01-molar (0.062 g) methanolic phen solution. The mixture was stirred at approximately 60 ℃ for 50 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After five days blue crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS spectra measurements were conducted.

UV-VIS Spectrum of $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$ (12)



The absorption in the visible area of the spectrum at approximately 620 nm is responsible for the bright blue color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 5.3: Crystallographic and refinement details of $[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$.

Empirical formula	$C_{52}H_{52}N_8Ni_3O_{27}$
Formula weight	1397.15 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	blue
Unit cell dimensions	a = 13.545(2) Å
	b = 14.717(2) Å
	c = 15.590(2) Å
	α = 77.60(1)°, β = 72.86(1)°, γ = 76.32.(1)°
Cell volume	2849.7(6) $Å^3$
Z	2
Density (calculated)	1.628 $g \cdot cm^{-3}$
Absorption coefficient	1.079 mm^{-1}
F (000)	1440.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	2.76° - 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-17 / 17, -18 / 18, -20 / 20
Reflections collected	32869
Independent reflections	12609
R_{int}	0.059
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	812
GooF(S)	0.936[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.058, wR_2[b] = 0.1468
R indices (all data)	R_1 = 0.1009, wR_2 = 0.1734

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 5.4: Selected distances/Å and angles/° in $[Ni(2,6\text{-}pda)_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Ni(1)	N(2)	2.089(4)
Ni(1)	N(8)	2.090(3)
Ni(1)	N(1)	2.093(4)
Ni(1)	N(7)	2.093(5)
Ni(1)	O(11)	2.102(3)
Ni(1)	N(4)	1.957(4)
Ni(2)	N(3)	1.967(4)
Ni(2)	O(18)	2.105(3)
Ni(2)	O(20)	2.108(3)
Ni(2)	O(16)	2.133(3)
Ni(2)	O(14)	2.188(3)
Ni(3)	N(6)	1.971(5)
Ni(3)	N(5)	1.979(5)
Ni(3)	O(26)	2.092(3)
Ni(3)	O(22)	2.115(4)
Ni(3)	O(28)	2.135(4)
Ni(3)	O(24)	2.156(4)
C(45)	O(13)	1.305(5)
C(45)	O(14)	1.233(5)
C(46)	O(15)	1.258(6)
C(46)	O(16)	1.267(6)
C(47)	O(17)	1.236(5)
C(47)	O(18)	1.279(5)
C(48)	O(19)	1.260(5)
C(48)	O(20)	1.272(6)
C(49)	O(21)	1.241(7)
C(49)	O(22)	1.275(7)
C(50)	O(23)	1.223(7)
C(50)	O(24)	1.307(6)
C(51)	O(25)	1.238(5)
C(51)	O(26)	1.274(5)
C(52)	O(27)	1.237(7)
C(52)	O(28)	1.293(6)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(8)	Ni(1)	N(1)	173.1(1)
N(8)	Ni(1)	N(7)	95.7(1)
N(8)	Ni(1)	O(11)	90.9(1)
N(1)	Ni(1)	N(7)	79.5(1)
N(1)	Ni(1)	O(11)	93.8(1)
N(7)	Ni(1)	O(11)	173.3(1)
N(4)	Ni(2)	N(3)	177.2(1)
N(4)	Ni(2)	O(18)	78.6(1)
N(4)	Ni(2)	O(20)	78.9(1)
N(4)	Ni(2)	O(16)	101.2(2)
N(4)	Ni(2)	O(14)	103.5(1)
N(3)	Ni(2)	O(18)	98.7(1)
N(3)	Ni(2)	O(20)	103.8(2)
N(3)	Ni(2)	O(16)	78.4(2)
N(3)	Ni(2)	O(14)	77.1(1)
O(18)	Ni(2)	O(20)	157.5(1)
O(18)	Ni(2)	O(16)	94.9(1)
O(18)	Ni(2)	O(14)	92.4(1)
O(20)	Ni(2)	O(16)	91.1(1)
O(16)	Ni(2)	O(14)	155.2(1)
N(6)	Ni(3)	N(5)	174.8(2)
N(6)	Ni(3)	O(26)	78.3(2)
N(6)	Ni(3)	O(22)	96.3(2)
N(6)	Ni(3)	O(28)	78.3(2)
N(6)	Ni(3)	O(24)	108.7(2)
N(5)	Ni(3)	O(26)	102.4(2)
N(5)	Ni(3)	O(22)	78.5(2)
N(5)	Ni(3)	O(28)	101.3(2)
N(5)	Ni(3)	O(24)	76.5(2)
O(26)	Ni(3)	O(22)	93.2(2)
O(26)	Ni(3)	O(28)	156.3(1)
O(26)	Ni(3)	O(24)	93.4(1)
O(22)	Ni(3)	O(28)	93.1(2)
O(22)	Ni(3)	O(24)	154.9(2)
O(28)	Ni(3)	O(24)	90.6(1)

3.2.1.6 Crystal structure of di-bis(pyridine-2,6-dicarboxylato-k^3 *N,O,O*) nickelate(II) diaquabis(2,2'-bipyridine-*N,N'*) nickel(II) hexahydrate, $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ (13)

$[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ **(13)** crystallizes in the triclinic space group P-1 (2) with a = 10.201(2) Å, b = 15.034(3) Å, c = 19.227(1) Å, α = 112.11(1)°, β = 93.14(1)°, γ = 103.25(1)°, V = 2626.7(8) $Å^3$ and Z = 2. Crystallographic and refinement details are listed below, in Tables 5.5 and 5.6. The structure of **(13)** represents a mixed complex, which consists of one $[Ni(2,2'\text{-bipy})_2(H_2O)_2]^{2+}$ cationic complex, two $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]^{1-}$ anionic complexes and six lattice water molecules. The three nickel centers are crystallographically independent. The coordination geometry around the Ni(II) metal centers is distorted octahedral (Fig. 7.9).

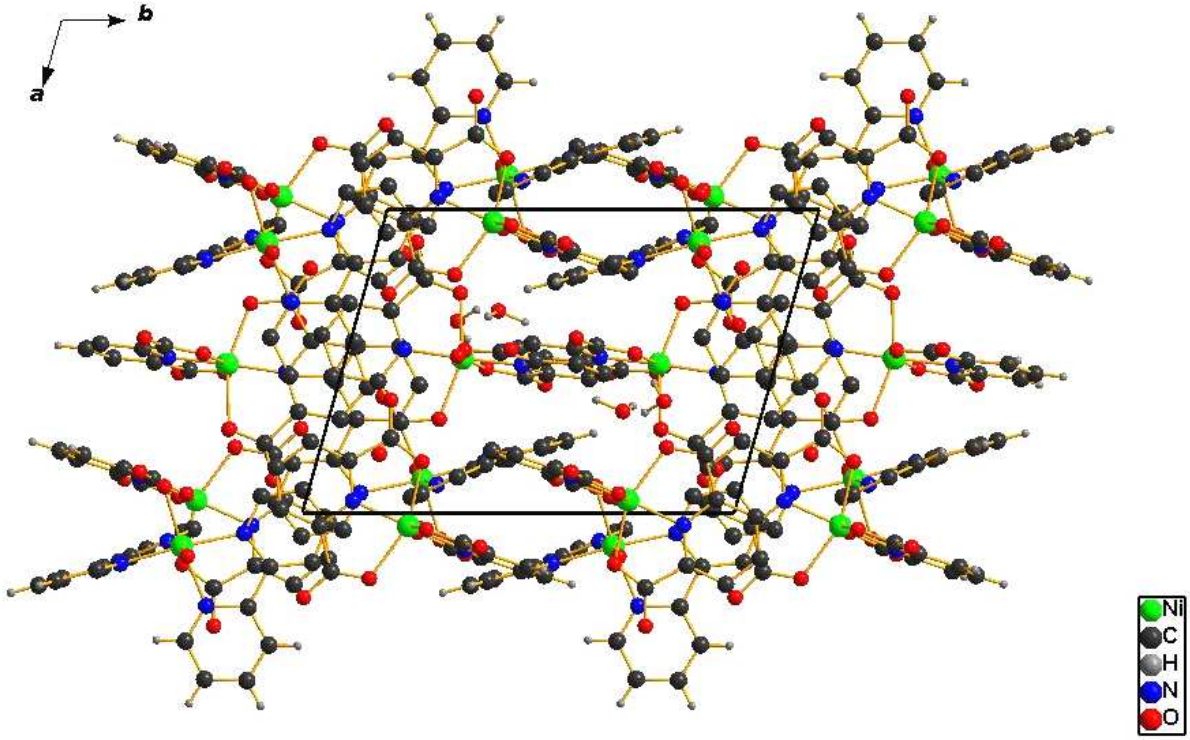


Fig. 7.8: Projection of the unit cell of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ along the crystallographic c-axis.

In the cation, Ni(II) is ligated by two bidentate 2,2'-bipy ligands and further coordinated by two aqua ligands. The aqua ligands are mutually adjacent, and are *cis* to each other. The Ni-N and Ni-O atomic distances range from 2.059(5) to 2.091(4) Å and from 2.063(4) to 2.108(4) Å respectively (Table 5.6). The angles range from 77.02(2) to 176.76(2)°. The coordination geometry around the metal ion is distorted octahedral (Fig. 7.9).

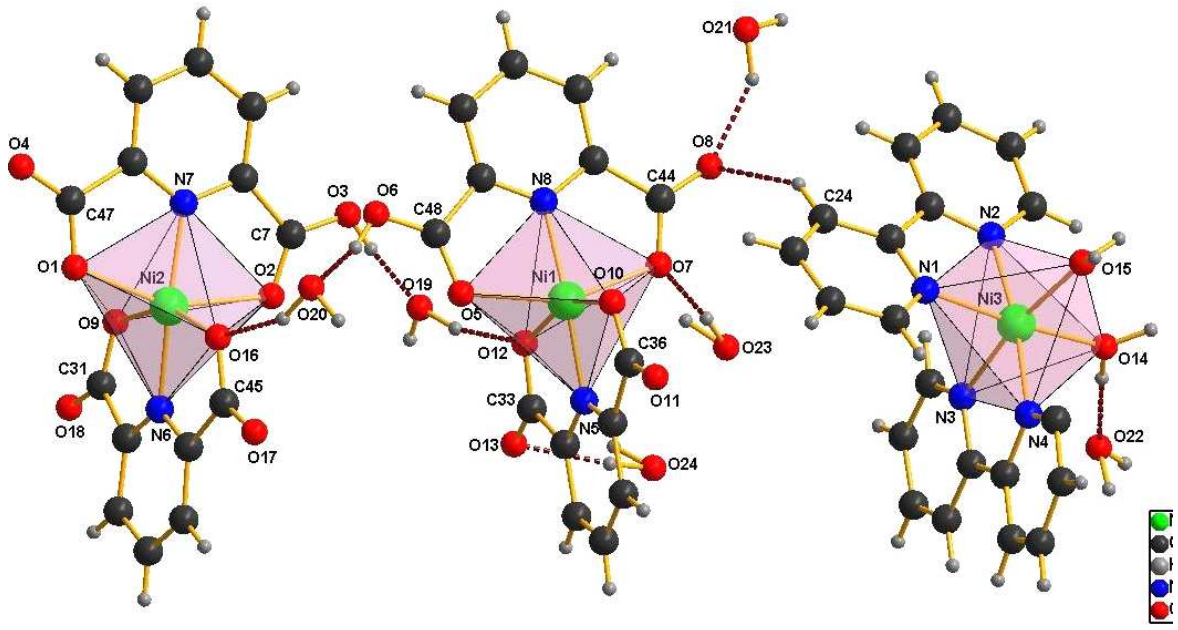


Fig. 7.9: The asymmetric unit of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$.

The anionic part consists of two structurally identical $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]^{1-}$ anionic complexes (Fig. 7.9). Each Ni(II) ion is coordinated to two 2,6-pda ligands in the k^3 N,*O,O'* mode, typical for this 'pincer' ligand. The Ni-O and Ni-N atomic distances range from 2.114(4) to 2.189(4) Å and from 1.942(4) to 1.980(4) Å, respectively (Table 5.5). Similar distances were found in other octahedral Ni(II) complexes [38].

The motif in the packing represents a chain of independent monomers running along the crystallographic c-axis (Fig. 7.8). The six lattice water molecules show extensive H-bonding, what probably stabilizes the crystal structure. The mode of association of water molecules in a crystal hydrate reminds partially some already known water clusters [39].

The two of six lattice water molecules wO(21) and wO(23) and a carboxylic group O7-C-O8 form a cyclic decamer related with two other water molecules and carboxylic group by the center of symmetry (Fig. 8.0).

This decamer connects the two $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]^{1-}$ anions through H-bonding with each other. The $[Ni(2,2'\text{-bipy})_2(H_2O)_2]^{2+}$ cation is connected through H-bonding O(8)-H(C24) with one $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]^{1-}$ anion. wO(19) and wO(20) are bound through H-bonds to carboxylic O-atoms and connect the two $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]^{1-}$ anions with each other (Fig. 8.1).

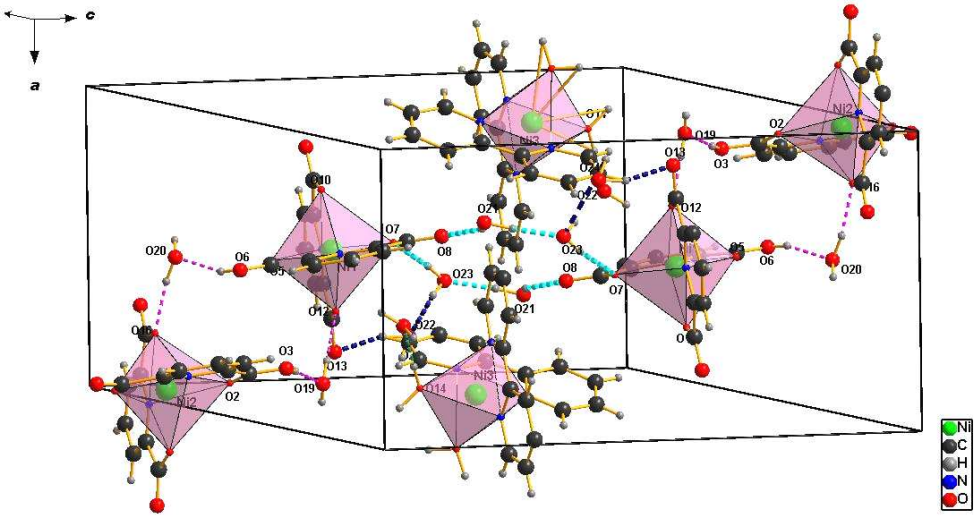


Fig. 8.0: Projection of the unit cell of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$.

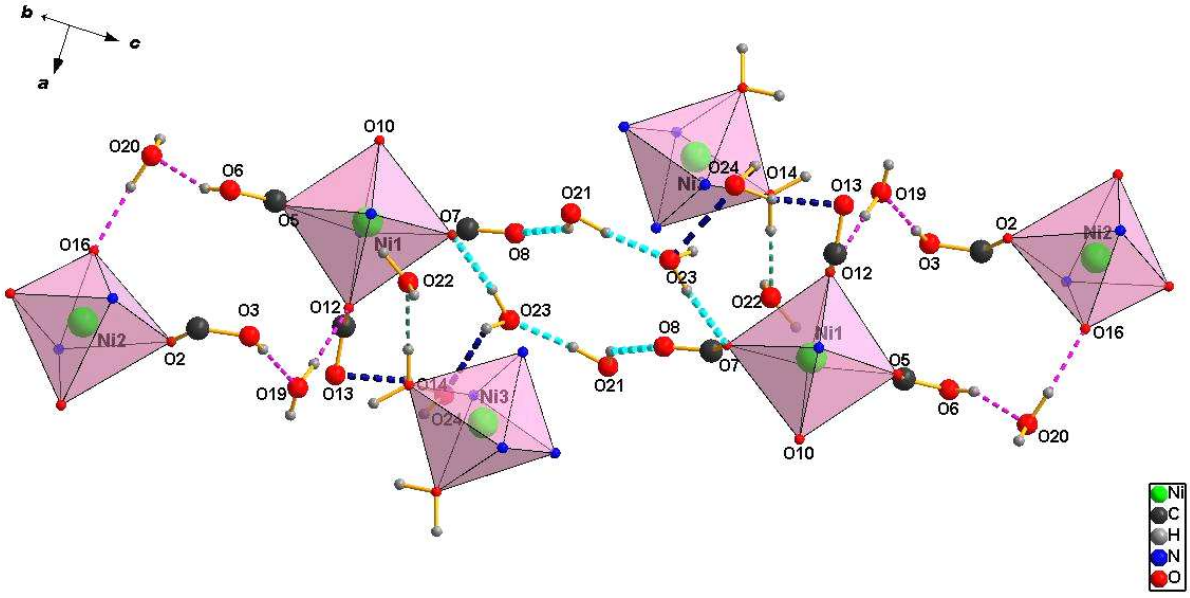


Fig. 8.1: A perspective view of the H-bonding in of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$.

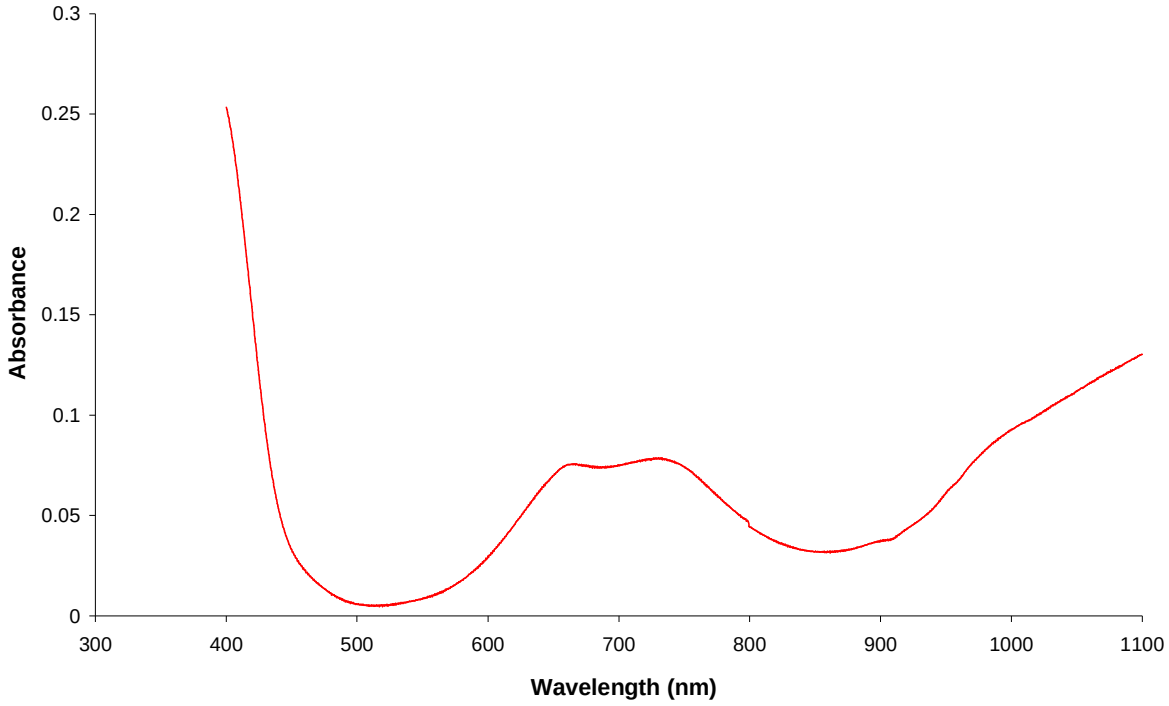
Because of the difficulties to properly orientate water H-atoms the O···O distances were used instead of O-H···O distances and are collected in Table 5.

3.2.1.6 Experimental

Preparation of $[Ni(2,6\text{-}pda)(2,6\text{-}pdaH)]_2[Ni(2,2'\text{-}bipy)_2(H_2O)_2](H_2O)_6$ (13)

20 ml of a 0.01-molar (0.053 g) aqueous nickel sulfate solution were mixed with one equivalent 20 ml of a 0.01-molar (0.034 g) ethanolic 2,6- pda solution and two equivalents 40 ml of a 0.01-molar (0.062 g) ethanolic 2,2'-bipy solution. The mixture was stirred at approximately 60 ℃ for 50 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After five days blue crystals were collected and subjected to X-ray single crystal analysis; afterwards powder diffraction and UV-VIS spectra measurements were conducted.

UV-VIS Spectrum of $[Ni(2,6\text{-}pda)(2,6\text{-}pdaH)]_2[Ni(2,2'\text{-}bipy)_2(H_2O)_2](H_2O)_6$ (13)



The absorption in the visible area of the spectrum at approximately 640 nm is responsible for the blue color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 5.5: Crystallographic and refinement details for $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$.

Empirical formula	$C_{48}H_{46}N_8Ni_3O_{24}$
Formula weight	1295.06 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	blue
Unit cell dimensions	a = 10.201(2) Å
	b = 15.034(3) Å
	c = 19.227(3) Å
	α = 112.11(1)°, β = 93.14(1)°, γ = 103.25(1)°
Cell volume	2626.7(8) $Å^3$
Z	2
Density (calculated)	1.637 $g \cdot cm^{-3}$
Absorption coefficient	1.159 mm^{-1}
F (000)	1332.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	3.36°- 56.04°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-13 / 13, -19 / 19, -25 / 25
Reflections collected	31076
Independent reflections	11556
R_{int}	0.1077
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	812
GooF(S)	0.720[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0465, wR_2[b] = 0.0559
R indices (all data)	R_1 = 0.1520, wR_2 = 0.0736

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.
$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 5.6: Selected distances/Å and angles/° in $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$.

Distances/ Å		
Atom 1	**Atom 1**	**d[1.2]**
Ni(1)	O(10)	2.105(3)
Ni(1)	O(12)	2.121(4)
Ni(2)	N(6)	1.966(4)
Ni(2)	N(7)	1.980(4)
Ni(2)	O(9)	2.114(4)
Ni(2)	O(1)	2.133(4)
Ni(2)	O(2)	2.189(4)
Ni(2)	O(16)	2.117(5)
Ni(3)	O(w14)	2.108(4)
Ni(3)	O(w15)	2.063(4)
Ni(3)	N(1)	2.077(4)
Ni(3)	N(2)	2.059(5)
Ni(3)	N(4)	2.072(4)
C(48)	O(5)	1.243(6)
C(48)	O(6)	1.261(7)
C(44)	O(7)	1.276(6)
C(44)	O(8)	1.225(8)
C(36)	O(10)	1.265(6)
C(36)	O(11)	1.234(7)
C(33)	O(12)	1.258(7)
C(33)	O(13)	1.234(7)
C(47)	O(4)	1.223(6)
C(47)	O(1)	1.279(6)
C(7)	O(3)	1.272(7)
C(7)	O(2)	1.234(5)
C(31)	O(9)	1.260(6)
C(31)	O(18)	1.236(7)
C(45)	O(16)	1.267(8)
C(45)	O(17)	1.224(9)
O(16)	wO(20)	2.692(6)
O(12)	wO(19)	2.796(7)
H(O6)	wO(20)	1.685(5)
H(O3)	O(19)	1.676(3)
O(13)	wO(24)	2.844(7)
O(7)	wO(23)	2.837(6)
O(8)	wO(21)	2.728(6)
O(8)	H(C24)	2.542(4)
H(O14)	O(w22)	1.859(3)

Angles/°

Atom 1	Atom 2	Atom 3	Angle 1.2.3
N(5)	Ni(1)	N(8)	176.8(2)
N(5)	Ni(1)	O(7)	103.6(2)
N(5)	Ni(1)	O(10)	78.7(2)
N(5)	Ni(1)	O(12)	78.6(2)
N(8)	Ni(1)	O(7)	79.0(2)
N(8)	Ni(1)	O(10)	103.3(2)
O(7)	Ni(1)	O(10)	93.4(1)
O(7)	Ni(1)	O(12)	94.1(1)
O(7)	Ni(1)	O(5)	156.3(1)
O(10)	Ni(1)	O(12)	157.2(2)
O(10)	Ni(1)	O(5)	92.4(1)
O(12)	Ni(1)	O(5)	89.4(1)
N(6)	Ni(2)	N(7)	175.5(2)
N(6)	Ni(2)	O(9)	77.7(2)
N(6)	Ni(2)	O(16)	77.9(2)
N(6)	Ni(2)	O(2)	98.8(2)
N(7)	Ni(2)	O(9)	100.8(2)
N(7)	Ni(2)	O(16)	103.6(2)
N(7)	Ni(2)	O(2)	77.0(2)
O(9)	Ni(2)	O(16)	155.6(2)
O(9)	Ni(2)	O(1)	90.4(1)
O(9)	Ni(2)	O(2)	93.1(2)
O(16)	Ni(2)	O(2)	90.7(2)
O(1)	Ni(2)	O(2)	154.8(1)
N(2)	Ni(3)	N(1)	78.9(2)
N(2)	Ni(3)	N(3)	96.9(2)
N(2)	Ni(3)	O(14)	92.5(2)
O15	Ni(3)	N(4)	95.6(1)
O15	Ni(3)	N(1)	94.6(2)
O15	Ni(3)	N(3)	171.1(2)
O15	Ni(3)	O(14)	87.1(2)
N(4)	Ni(3)	N(1)	95.8(2)
N(4)	Ni(3)	N(3)	78.9(2)
N(1)	Ni(3)	N(3)	93.0(2)
N(1)	Ni(3)	O(14)	171.2(2)
N(1)	Ni(3)	O(14)	86.2(2)

3.2.1.7 Crystal structure of aqua(2,2'-bipyridine-k^2N,N')(pyridine 2,6-dicarboxylato-k^3N,O,O) nickel(II) dihydrate, $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$ (14)

$[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)]\cdot 2H_2O$ (**14**) crystallizes in the monoclinic space group $P2_1/c$ (14) with a = 10.652(2) Å, b = 20.624(3) Å, c = 17.699(3) Å, β = 98.21(1)°, V = 3848.4(1) $Å^3$ and Z = 8. Crystallographic and refinement details are listed below, in Tables 5.7 and 5.8. The structure of (**14**) represents a mixed complex, which consists of two $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)]$ complexes and two lattice water molecules. Both Ni(II) metal centers are crystallographically independent and adopt a distorted octahedral arrangement.

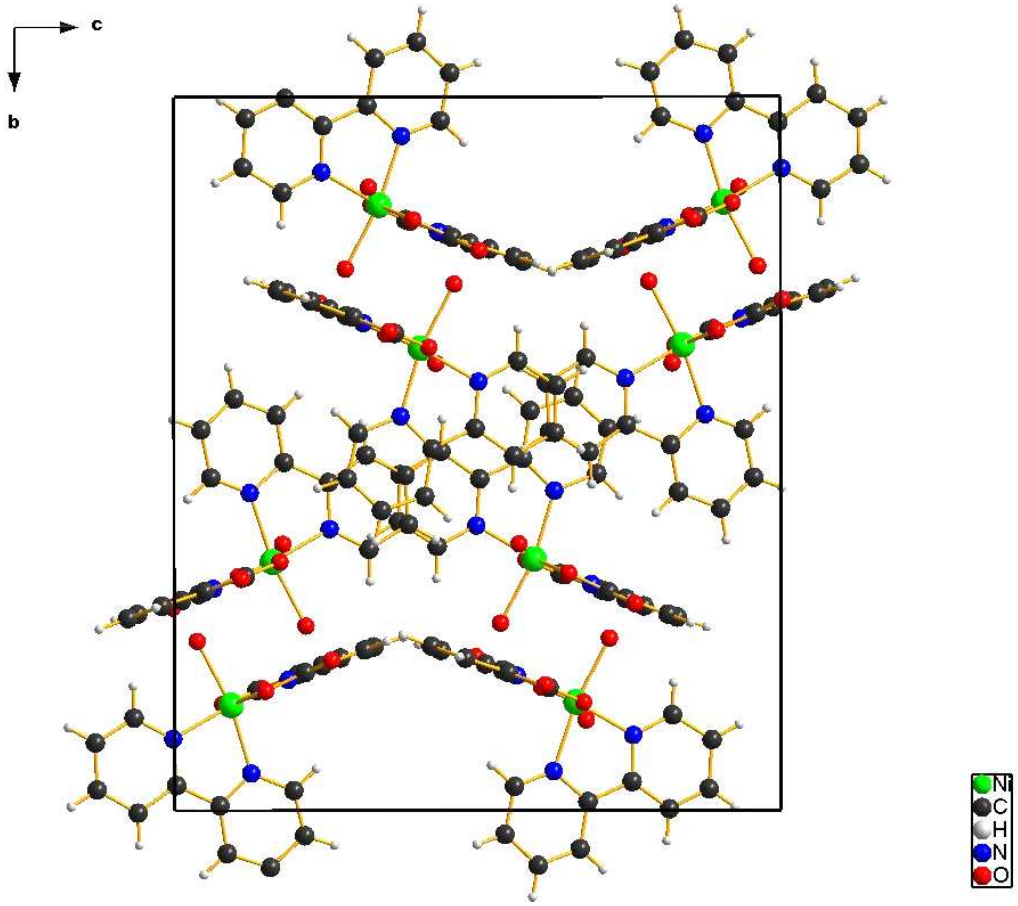


Fig. 8.2: Projection of the unit cell of $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$ along the crystallographic a-axis.

A distorted octahedral coordination at both independent Ni(II) atoms is due to the differences in the donor strengths of the three different ligands, which are coordinated to the metal center. The 2,6-pda pincer ligands are bound to the metal center in a *k*-N,*O,O*' mode with the O atoms *trans* to each other. The 2,2'-bipyridine (bipy) ligand chelates to the metal center in a k^2N,N' mode through N atoms. The Ni-O and Ni-N atomic distances in the two independent but structurally identical complex molecules range from 1.901(1) to 2.149(7) Å and from 1.942(4) to 2.109(9) Å, respectively.

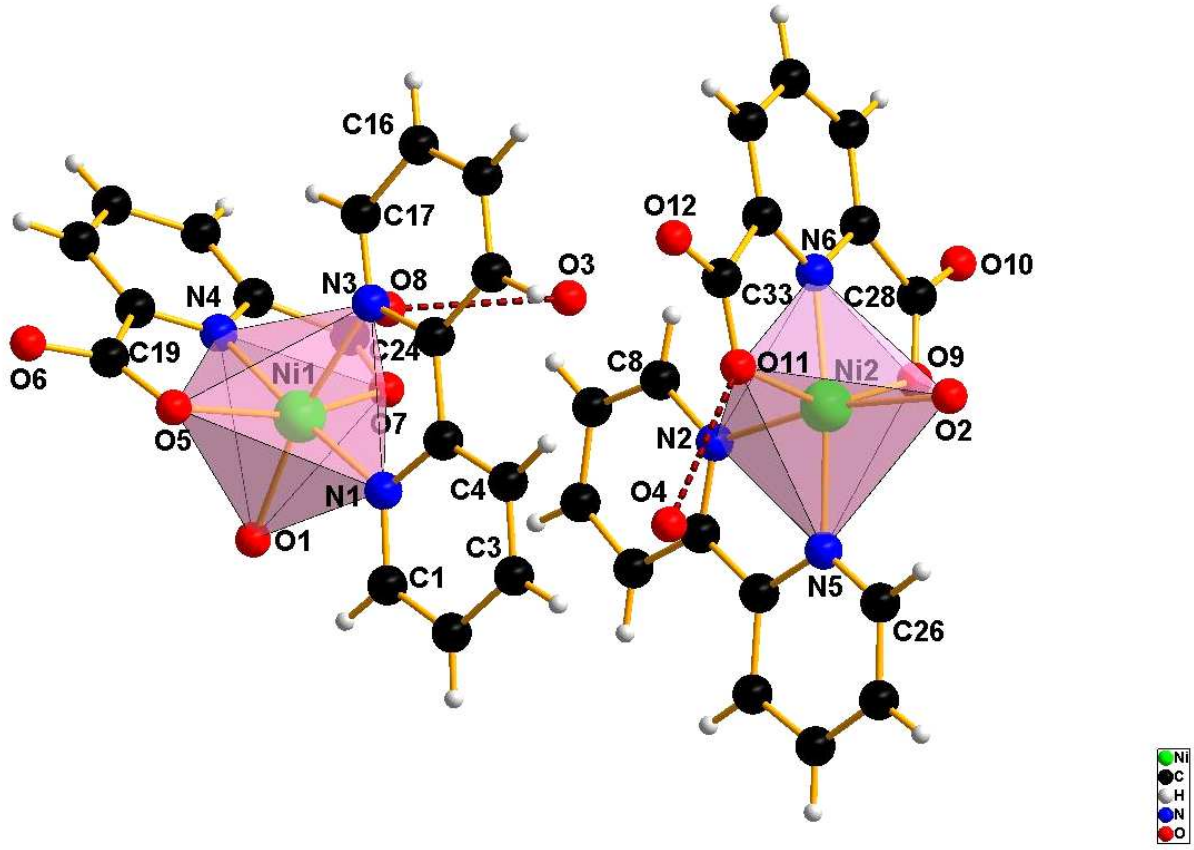


Fig. 8.3: The asymmetric unit of [Ni(H_2O)(2,2'-bipy)(2,6-pda)](H_2O)$_2$.

The Ni-N(2,6-pda) distances are shorter than Ni-N(2,2-bipy), what is consistent with such atom distances found in other similar compounds described in this work. 2,6-pda and 2,2'-bipy ligands in each complex are nearly normal to each other. The torsion angles O(5)Ni(1)N(1)C(1) and O(9)Ni(2)N(5)C(26) are 86.642(9) and 96.285(9)°, respectively, the 2,6-pda/2,2'-bipy dihed ral angle is thus more acute in the complex with the central Ni(1) atom.

All four carboxylic groups are deprotonated, the C-O distances range from 1.243(1) to 1.274(1) Å. The Ni-O(pda) distances range from 2.136(7) to 2.156(7) Å and are longer than the Ni-O(H_2O) distances (Table 5.8).

The two lattice water molecules are connected via hydrogen bonds to the carboxylic oxygen atoms of the coordinating pda ligands. The hydrogen atoms of the lattice water could not be localized. Therefore the O-O atomic distances are given; these range from 2.869(1) to 2.921(1) Å (Table 5.8). The motif of the packing represents a chain of independent monomers running along the crystallographic c-axis (Fig. 8.4).

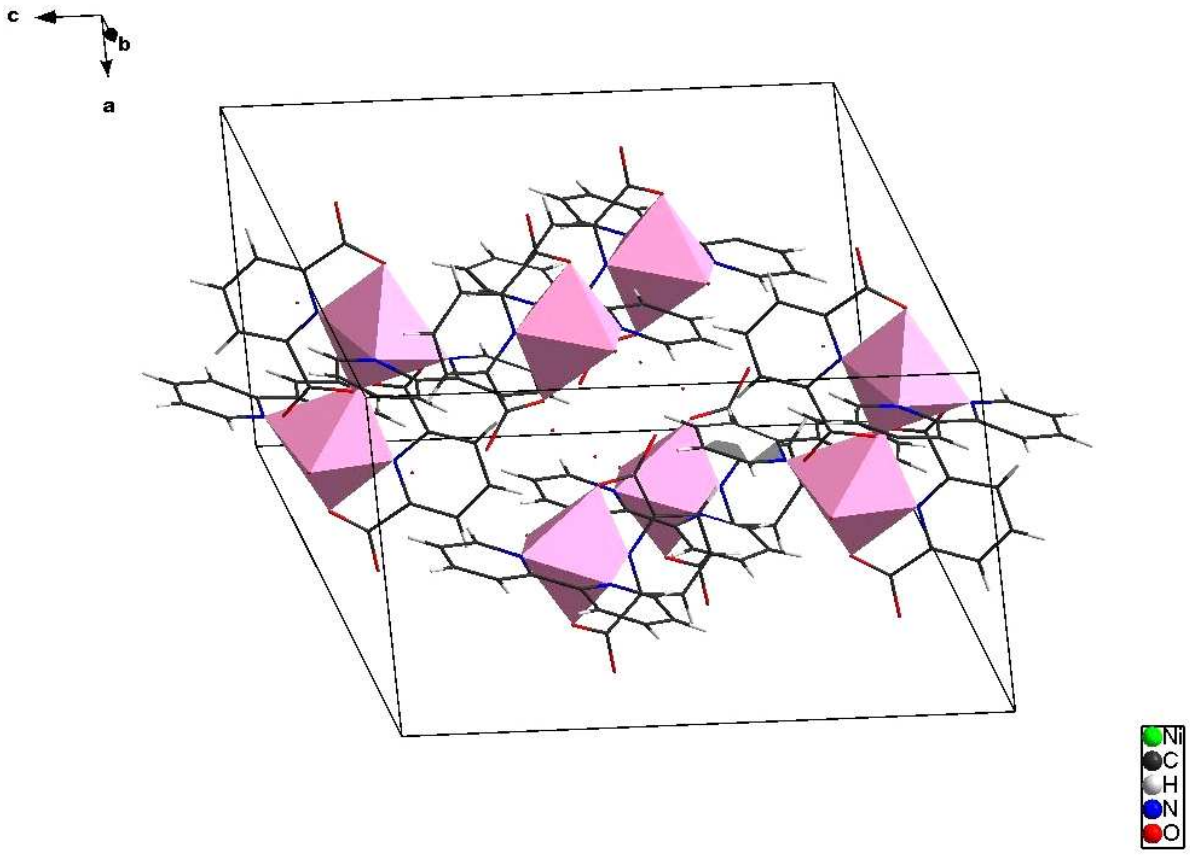


Fig. 8.4: Projection of the unit cell of [Ni(H_2O)(2,2'-bipy)(2,6-pda)](H_2O)$_2$.

There are π–π stacking interactions between the heteroaromatic rings of the bipy ligands chelating both metal centers (Fig. 8.5), in this way the two similar complexes containing independent metal centers interact with each other.

The centroid-centroid distance is 3.58 Å, the pattern of the stacking arrangement represents thus a nearly perfect face-to-face alignment of atoms, where most of the ring-plane area overlaps.

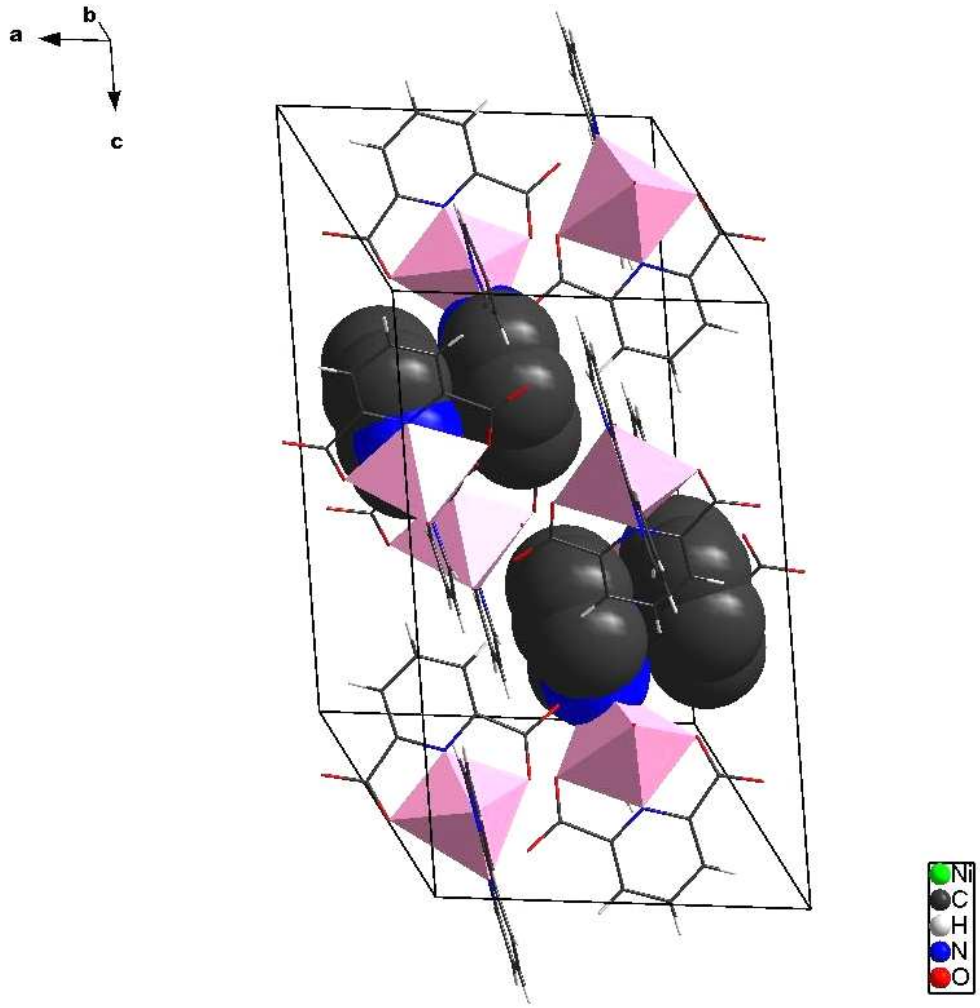


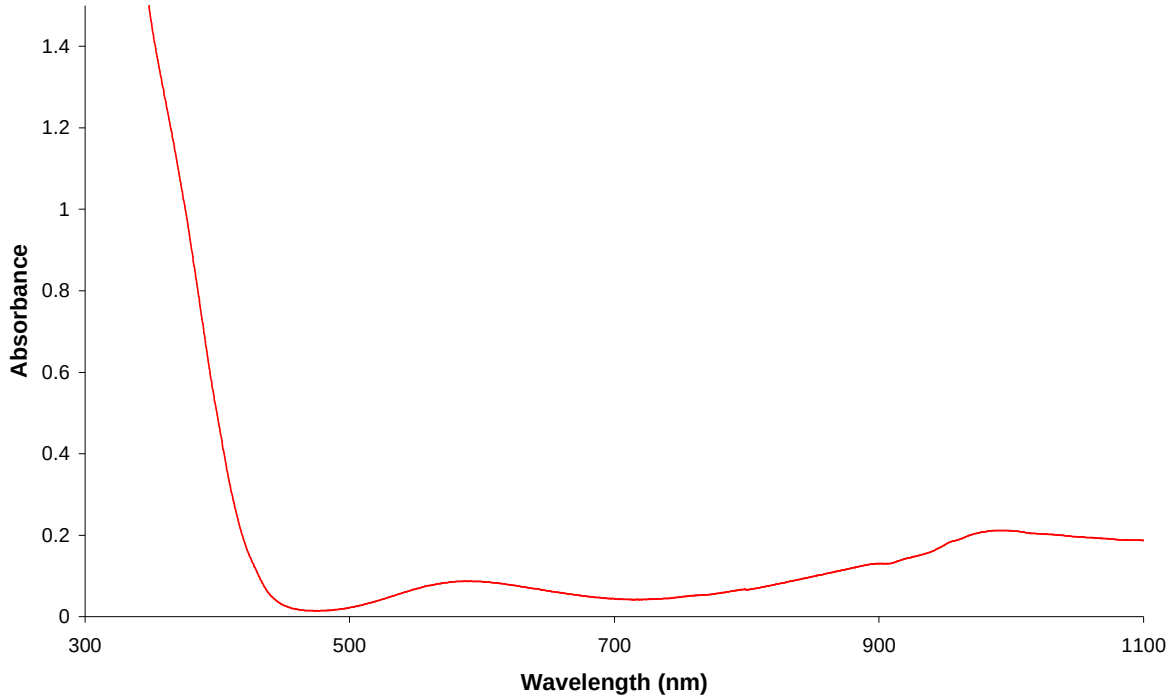
Fig. 8.5: The asymmetric unit of [Ni(H_2O)(2,2'-bipy)(2,6-pda)](H_2O)$_2$.

3.2.1.7 Experimental

Preparation of $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$ (14)

20 ml of a 0.01-molar (0.050 g) aqueous nickel acetate solution were mixed with one equivalent 20 ml of a 0.01-molar (0.125 g) ethanolic 2,6-pda solution and two equivalents 40 ml of a 0.01-molar (0.062 g) ethanolic 2,2'-bipy solution. The mixture was stirred at approximately 60 ℃ for 50 min in a be aker. By evaporation the volume of the mixture was reduced to a half, the beaker was sealed off with parafilm, perforated and kept under a hood. After five days blue colored crystals were collected and subjected to X-ray single crystal analysis, afterwards powder diffraction and UV-VIS spectra measurements were conducted.

UV-VIS Spectrum of $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$ (14)



The absorption in the visible area of the spectrum at approximately 620 nm is responsible for the bright blue color of the compound. This band can be assigned to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

Table 5.7: Crystallographic and refinement details for $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$.

Empirical formula	$C_{17}H_{15}N_3Ni_1O_6$
Formula weight	416.03 $g \cdot mol^{-1}$
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
Crystal colour	blue
Unit cell dimensions	a = 10.652(2) Å
	b = 20.624(3) Å
	c = 17.699(3) Å
	β = 98.21(1)°
Cell volume	3848.4(1) $Å^3$
Z	8
Density (calculated)	1.436 $g \cdot cm^{-3}$
Absorption coefficient	1.045 mm^{-1}
F (000)	1712.0
Diffractometer	STOE Image Plate Diffraction System I
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	293 (2) K
2θ range	5.54°- 54.72°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-14 / 14, -26 / 26, -23 / 23
Reflections collected	37062
Independent reflections	9044
R_{int}	0.2371
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	487
GooF(S)	0.785[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0741, wR_2[b] =0.1571
R indices (all data)	R_1 = 0.2351, wR_2 = 0.2104

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$. $w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 5.8: Selected distances/Å and angles/° in [Ni (H_2O)(2,2'-bipy)(2,6-pda)](H_2O)$_2$.

Distances/Å

Atom 1	Atom 2	d 1,2
Ni(1)	N(4)	1.979(7)
Ni(1)	N(1)	2.034(8)
Ni(1)	O(1)	2.081(7)
Ni(1)	N(3)	2.109(9)
Ni(1)	O(5)	2.138(7)
Ni(1)	O(7)	2.156(7)
Ni(2)	N(6)	1.901(1)
Ni(2)	N(5)	2.039(8)
Ni(2)	N(2)	2.057(9)
Ni(2)	O(2)	2.090(8)
Ni(2)	O(11)	2.136(7)
Ni(2)	O(9)	2.149(7)
C(19)	O(5)	1.249(1)
C(19)	O(6)	1.251(1)
C(24)	O(7)	1.247(1)
C(24)	O(8)	1.259(1)
C(28)	O(1)	1.243(1)
C(28)	O(9)	1.245(1)
C(33)	O(1)	1.246(1)
C(33)	O(1)	1.274(1)
O(8)	wO(3)	2.869(1)
O(11)	wO(4)	2.921(1)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
N(4)	Ni(1)	N(1)	173.9(3)
N(4)	Ni(1)	O(1)	93.4(3)
N(1)	Ni(1)	O(1)	92.4(3)
N(4)	Ni(1)	N(3)	94.3(5)
N(1)	Ni(1)	N(3)	80.2(5)
O(1)	Ni(1)	N(3)	169.9(4)
N(4)	Ni(1)	O(5)	78.0(3)
N(1)	Ni(1)	O(5)	99.6(3)
N(3)	Ni(1)	O(5)	95.9(4)
N(4)	Ni(1)	O(7)	76.9(3)
O(1)	Ni(1)	O(7)	87.7(3)
N(3)	Ni(1)	N(1)	87.7(4)
O(5)	Ni(1)	O(7)	154.9(3)
N(6)	Ni(2)	N(5)	173.7(4)
N(5)	Ni(2)	N(2)	77.7(5)
N(5)	Ni(2)	O(2)	92.3(3)
N(2)	Ni(2)	O(2)	168.7(4)
N(6)	Ni(2)	O(11)	77.4(3)
N(2)	Ni(2)	O(9)	90.6(4)
O(2)	Ni(2)	O(9)	86.8(3)
O(11)	Ni(2)	O(9)	155.0(3)

4. Summary

In the course of this work the influence of co-ligands on structures of new Ni(II) coordination compounds was studied. For this reason eight various Ni(II) salts and five N-donor ligands were used. The co-ligands listed below can be classified in terms of weak and strong coordinating species, their coordinating strength rises from the left to the right:

$$BF_4^-, ClO_4^-, Cl^-, I^-, SCN^-, CH_3COO^-, SO_4^{2-}, NO_3^-$$

It could be shown that the use of various co-ligands has no influence on the coordination mode of the Ni(II) metal center. In all these compounds Ni(II) exhibited, for reasons discussed in the results and discussion section, only the octahedral coordination. Nevertheless, the use of different co-ligands leads to structural changes in the coordination compounds.

By obtaining the new coordination compound $[Ni(SCN)_2(tptz)(H_2O)]$ it was shown that, in contrast to other co-ligands used in this thesis, SCN^- coordinates to the metal center, whereas BF_4^-, I^- and NO_3^- prefer to counter-balance the positive charge of the Ni(II) complex. This resulted in the four new coordination compounds $[Ni(tptz)_2](BF_4)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)$, $[Ni(tptz)_2](I)_2(H_2O)_2$ and $[Ni(tptz)_2](NO_3)_2(H_2O)_7$. They all contain the same $[Ni(tptz)_2]^{2+}$ cationic complex, but three different anions. Though the reaction conditions and stoichiometry were the same for all five above listed compounds, the results obtained are not identical.

For this reason it becomes obvious that the choice of the co-ligand can shape the structure of the coordination compound. Another interesting observation was made while acetate was used as a co-ligand. The reactions of the phen and 2,6-pda ligands (mixed-ligand systems) with different co-ligands and Ni(II) metal center yielded the novel coordination compounds $[Ni(Phen)_3](pda)(H_2O)_{11}$, $[Ni(Phen)_3](BF_4)_2(H_2O)$, $[Ni(Phen)_3](I_3)_2(H_2O)$ and $[Ni(Cl)(phen)_2H_2O)](Cl)(H_2O)_2$. In $[Ni(Phen)_3](pda)(H_2O)_{11}$, in contrast to the other three compounds, one of the N-donor ligands (2,6-pda) was deprotonated by the strong acetate base and acts as an anion.

In the same way the acetate acts in the reaction of 2,6-pda and tptz with nickel(II) acetate, where it deprotonated the 2,6-pda what resulted in the novel coordination compound $[Ni(2,6\text{-pda})(tptz)](H_2O)_5$.

The use of sulfate as a co-ligand in the same reaction sequence yielded the new coordination compound $[Ni(2,6\text{-pda})_2]_2[Ni(phen)_2(H_2O)_2](H_2O)_9$, which is the first example of a mixed 2,6-pda/phen ligand system with three crystallographically independent Ni(II) metal centers. The same pattern was observed with 2,2-bipy, where a similar new Ni(II) coordination compound, $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ was obtained. Another mixed-ligand coordination compound, $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$, was obtained in the reaction of 4,4'-bipy with tptz and nickel(II) nitrate. In this reaction 4,4'-bipy was successfully used as a linker-ligand, what yielded the first tptz containing dimeric coordination compound of such type. This has also clearly shown the difference in the coordination pattern that arises due to the isomerism (4,4'-bipy vs. 2,2'-bipy), which can be observed while comparing the chelating 2,2'-bipy in the novel mixed-ligand coordination compounds $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ and $[Ni(2,6\text{-pda})(2,2'\text{-bipy})(H_2O)](H_2O)_2$ with a linking 4,4'-bipy in $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$. The use of 4,4'-bipy as a linker ligand in combination with such multimodal ligands as tptz and 2,6-pda may give rise to new coordination polymers, what could be very promising and interesting for the supramolecular chemistry. The multimodal 2,6-pda was also extensively used in this work. It was shown that this ligand may act both as an anion or a as chelating tridentate ligand. Since it is a multimodal ligand, other coordination modes were expected and for this reason it was attempted to synthesize a heterometallic coordination compound with Ni(II) and Nd(III). The presence of Nd(III) was expected to change the coordination mode of the 2,6-pda, because of the oxophilicity typical of rare earth metals. Though the attempted synthesis of a bimetallic Ni(II)/Nd(III) complex was not successful, a new coordination compound, $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6](H_2O)_7$, was obtained. Interestingly, the 2,6-pda ligand shows both chelating and bridging coordination modes, linking the three Nd(III) metal centers through the oxygen atoms.

Almost all compounds presented in this thesis show extensive H-bonding and π–π stacking interactions. They are very important because of their stabilizing effect in coordination polymers. The comparison of both coordination compounds $Ni(phen)_3](BF_4)_2(H_2O)$ and $[Ni(tptz)_2](BF_4)_2(H_2O)$ makes it evident, that in both

compounds the anions take part in H-bonding and no π–π stacking interactions occur, whereas in other similar compounds with other co-ligands π–π stacking interactions predominate. It is a very interesting detail, since such an approach might be used in syntheses where other interactions than the H-bonding are undesirable.

All coordination compounds presented in this thesis were analyzed by single-crystal XRD and UV-VIS measurements.

5. Supplementary

5.1 Methods of Product Characterization and Equipment

5.1.1 Preparative Methods

Different techniques were employed in the syntheses of compounds in the present work. The reactions were conducted either in a beaker with subsequent isothermal evaporation or under inert gas conditions. The figures of the apparatus used and their description are given below.

5.1.2 Working under inert gas conditions

Some reactions were performed using a Schlenk line (Fig 8.6), which consists of a double bank manifold with several ports and is connected to a source of an inert gas (nitrogen). It represents a useful tool, which allows safe handling of handling of air and moisture sensitive compounds [40].

Fig.8.6: The Schlenk line

5.1.3 Reactions in beakers with subsequent isothermal evaporation

Because of the redox stability of Ni(II) in aqueous solution, most reactions were conducted in open beakers, where the educts were dissolved in a relevant solvent and stirred at approximately 60 °C. By evaporation th e volume of the mixture was concentrated to one half. The beakers were sealed with parafilm, perforated and kept under a hood until the first crystals were formed.

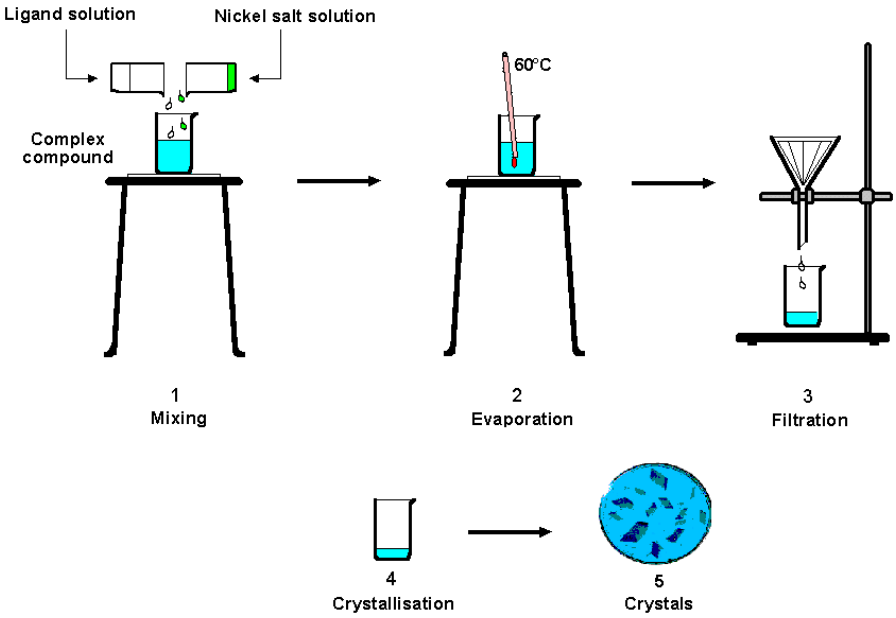


Fig. 8.7: Reactions in beakers.

5.2. X-ray structure Analysis

Several methods have been used for the determination and physical characterization of the new structures synthesized during the course of this work; the single crystal structure determination and powder diffraction were used to determine the new crystal structures and identify the phases. UV-VIS Spectroscopy was then used in order to investigate electronic transitions and understand the color of the compounds.

5.2.1 X- ray tube and X- ray radiation [41-46]

The radiation needed for crystal structure analysis is monochromatic X-ray, which can be produced by X-ray tube (Fig.8.9). The X-ray tube is a vacuum tube, which consists typically of a tungsten cathode that emits electrons into the vacuum and an anode (typically copper or molybdenum) to collect these electrons. This way a flow of electrical current through the tube is being established, it is also known as the beam. The electrons are accelerated by a high voltage of about 30 to 150 kV. Electrons from the cathode collide with the anode, and accelerate other electrons, ions and nuclei within it.

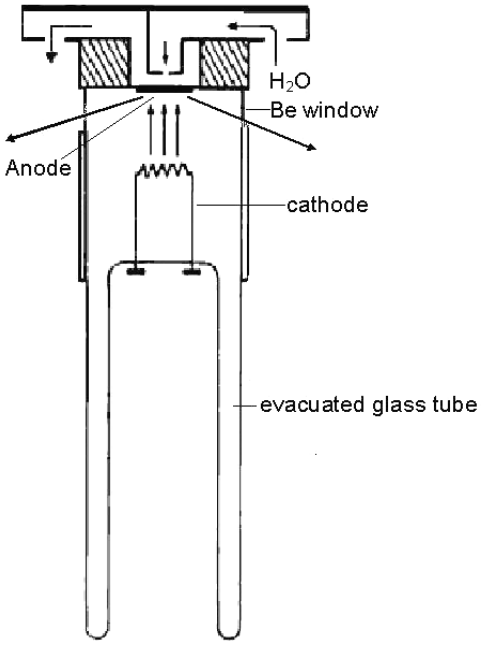


Fig 8.9: X-ray tube.

Depending on the anode material and the accelerating voltage, various X-ray spectra can be generated. Approximately 1% of the energy generated results in two types of X-ray radiation. The rest is released as heat. The first type is called the Bremsstrahlung, it consists of a continuous, broad spectrum, containing many wavelength of radiation and is also called the ‘‘the white’’ radiation. The second type is called the ‘‘the characteristic radiation’’, it is very important for the study of crystal structure. This radiation arises as a result of the electrons getting bounced out of position from atoms of the anode material, in particular from the *K*-shell (quantum number n=1). This is immediately followed by another electron falling back toward the nucleus. The energy differences between electron levels are discreet and the energy released will depend upon the number of protons and neutrons in the nucleus and the shell from which the electron was displaced. The loss in energy appears as an emitted photon with a well defined wave length. Because of the selection rule for transitions between the K- and the L-shells ($\Delta l = \pm 1$), a closely spaced doublet is expected, it is known as $K\alpha 1$ and $K\alpha 2$ radiation. The same rule applies to the electron transition from the *M*-shell to the *K*-shell, where a higher energy doublet known as $K\beta 1$ and $K\beta 2$ is emitted. Nearly all diffraction experiments are carried out with monochromatic radiation, the very strong $K\alpha$ lines are used, and the radiation of other wavelengths is eliminated by using filters.

5.2.2 X-Ray Diffraction [47-49]

It is possible using X-rays to determine the arrangement of atoms within a single crystal and find the geometry or shape of a molecule.The interaction of atoms in crystals with X-ray waves produces interference. Because a crystal structure consists of an orderly arrangement of atoms, the reflections occur from what appears to be the lattice planes. A beam of X-rays enters a crystal with one of these lattice planes oriented at an angle of θ to it. Two such X-rays are shown in Figure 9.1, where the spacing between the lattice planes occurs over the distance *d*. Ray 1 reflects off of the upper atomic plane at an angle equal to its angle of incidence. Similarly, Ray 2 reflects off of the lower atomic plane at the same angle. While Ray 2 is in the crystal, however, it travels a distance of 2a farther than ray 1. If this distance 2a is equal to

an integral number of wavelengths ($n\lambda$), then rays 1 and 2 will be in phase on their exit from the crystal and constructive interference will occur.

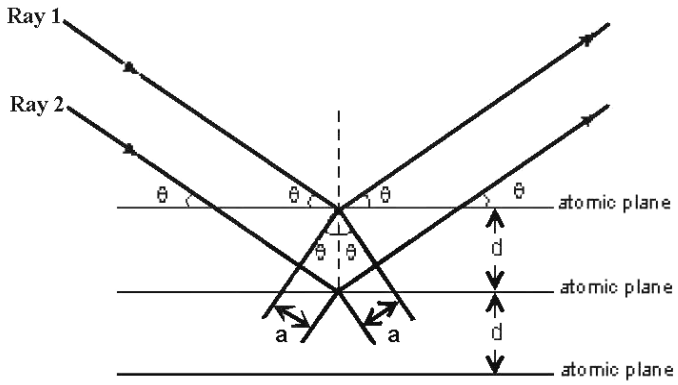


Fig.9.1 Bragg's equation

If the distance 2a is not an integral number of wavelengths, then destructive interference will occur and the waves will not be as strong as when they entered the crystal. Thus, the condition for constructive interference to occur is:

$$n\lambda = 2a$$

With the help of trigonometry the distance 2a can be figured out in terms of the spacing *d* between the atomic planes.

$$a = d \sin\theta$$

$$\text{or } 2a = 2\, d \sin\theta$$

$$\text{thus, } \boldsymbol{n\lambda = 2d \sin\theta} \qquad (2)$$

Equation (2) is known as **Bragg's Law** for X-ray diffraction. It states; if the wavelength λ of the X-rays going in to the crystal is known and the angle ***θ*** of the diffracted X-rays coming out of the crystal can be measured, then the spacing (referred to as ***d-spacing***) between the lattice planes can be .

$$\mathbf{d = n\lambda / 2 \sin\theta}$$

The Bragg's equation links the following parameters together:

- *d* - distance between parallel lattice planes
- λ - wave length of the X-rays going in to the crystal
- *θ* - angle between the X-ray and the lattice plane, the so called Bragg' angle
- *n* – integer (n = 1, 2, 3, etc.)

This diffraction will only occur if the rays are in phase when they emerge, and this will only occur at the appropriate value of *n* (*n* = 1, 2, 3, etc.) and *θ*. Reorientation of the crystal so that another lattice plane is exposed and measurement of the d-spacing between all lattice planes in the crystal is resulting in determination of the crystal structure and the size of the unit cell.

5.3 Imaging Plate Diffraction System (IPDS)

Single crystal structure determination was conducted on the Imaging Plate Diffraction System (IPDS). The diffracted X-rays are registered on the Imaging Plate.

Fig. 9.2: Imaging-Plate-Diffractometer (STOE, IPDS I)

The Imaging Plate is a flexible image sensor, coated with barium fluorobromide containing a trace amount of divalent europium as a luminescence center, $BaFBr/Eu^{2+}$ [50, 51]. It can be regenerated by its exposure to white light and used repeatedly. The collected images can be read by the software supplied to the diffractometer. As a result a raw data set for a crystal structure solution emerges.

5.4 Crystal Structure Solution

In order to solve a crystal structure, phases of enough reflections have to be well known to reveal almost if not all of the atoms in the unique part of the unit cell. The determination of crystal structures is based on the ability to decompose the complex electron density function through Fourier transform into simpler functions, $F_0(hkl)$. If

the Fourier coefficients with the amplitude $|F_{hkl}|$ and the term $e^{i\varphi}$ (the phase) are known, then the crystal structure can be determined through Fourier synthesis [52].

$$\mathrm{F_{hkl}} = \sum_{hkl} f_j \exp[2\pi i(\mathrm{hx} + \mathrm{ky} + \mathrm{lz})] \qquad (3)$$

This equation can be expressed in terms of electron density:

$$\mathrm{F_{hkl}} = \sum_{hkl} \rho_{(xyz)} \exp[2\pi i(\mathrm{hx} + \mathrm{ky} + \mathrm{lz})] \qquad (4)$$

From the Fourier transform results:

$$\rho_{(xyz)} = (1/V)\sum_{hkl} \mathrm{F_{hkl}} \exp[-2\pi i(\mathrm{hx} + \mathrm{ky} + \mathrm{lz})] \qquad (5)$$

Equation (5) can be expressed in cosine terms:

$$\rho_{(xyz)} = 1/V \sum_{hkl} F_{hkl}[\cos(2\pi(hx + ky + lz) + i\sin(2\pi(hx + ky + lz)] \qquad (6)$$

The problem of the X-ray diffraction analysis of crystal structures is that the above described amplitudes and information about the phases are not available. Moreover, only the intensities I_0(hkl), which are proportional to the square of the structure factor, amplitude, can be determined from the Fourier coefficients. There are several methods to solve this „phase problem“.

$$\mathrm{I_0}(hkl) = \left|F_{hkl}\right|^2 \cdot e^{i\varphi} \qquad (7)$$

Crystal structures of small molecule compounds can be solved in several ways [53, 54]. Direct methods can retrieve the lost phases from the corresponding diffraction amplitudes, they are commonly applied. Patterson methods are significantly aided by the presence of one or more heavy atoms in the structure. Some difficult small-molecule structures are sometimes solved either by superposition maps or by rotation and translation functions, these are considered to be very specialized extensions of the Patterson method.

5.4.1 Patterson Methods

It is impossible to measure the relative phases among the diffracted beams, therefore the direct calculation of the electron density function and the resulting atomic positions within the unit cell are unfeasible. In 1934 Patterson introduced a method of solving the phase problem. Patterson modified the electron density function by replacing the amplitudes *F*(hkl) and phases *Φ(hkl)* by the squared amplitudes F^2 whose values are proportional to the diffraction intensities . This makes it possible to directly calculate the Patterson function from the experimental data.

$$\mathrm{P}(u,v,w) = 1/V \sum_{hkl} \mathrm{F}_{\mathrm{hkl}}^2 \cdot (\cos[2\pi(hu+kv+lw)]) + i\sin[2\pi(hu+kv+lw)] \quad (8)$$

As a result a map of position vectors is provided. The value of the function at maximas is proportional to the product of the implied atomic numbers, which provides a clear advantage for detecting vectors between "heavy" atoms (atoms with a large number of electrons).

5.4.2 Direct Methods

Generally statistical methods are used to find correlations between the structure factors and the Miller's indices (hkl), by exploiting the known phase relationships between certain groups of reflections the phase problem is taken into account (avoided). Direct methods are preferred for phasing crystals of small molecules ≤ 1000 atoms in the asymmetric unit. The results are leading to further structure factors. The searched atomic positions are resulting from the Fourier synthesis.

$$\mathrm{R} = \frac{\sum_{hkl} \left\| F_0 \right| - \left| F_c \right\|}{\sum_{hkl} \left| F_0 \right|} \quad (9)$$

(F_0 = observed structure factor, F_c = calculated structure factor)

The solved structure can further be refined using least-squares techniques, which re-calculate the structure using Fourier transformations. Absorption correction, introduction anisotropic temperature factors and adding of weighting factors contribute to a further refinement of the structure.

5.5 X- ray Powder Diffraction [55]

This method represents a quick analytical technique, which is primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The sample is ground up to a fine powder and average bulk composition is determined. Crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. Because of the random orientation of the powdered material, all possible diffraction directions of the lattice should be attained. The diffracted X-rays are detected, processed and counted. After a scan of the sample the X-ray intensity can be plotted against the angle 2θ. Using the Bragg equation, 2θ for each diffraction peak can then be converted to d-spacing. This allows identification of the substance, because each substance has a set of unique d-spacings. This can be achieved by comparison of d-spacings with standard reference patterns. Every compound with the same crystal structure produces an identical powder diffraction pattern, what serves as kind of a "fingerprint" for the substance. Comparing an unknown diffraction pattern with those supplied by the ICDD**,** enables its easy identification. The measurements were conducted on the powder diffractometer (Fig. 9.3).

Fig. 9.3: Powder diffractometer (STOE, Stadi P)

5.6 UV-Vis Spectroscopy [56]

In order to understand why some compounds are colored and others are not measurements of light absorption at different wavelengths in the visible and adjacent UV and near-infrared (NIR) part of the spectrum have to be conducted. The perceived color of the compounds is affected by the light absorption in the visible range of the spectrum. Solutions of transition metal ions often exhibit characteristic colors, this is due to the absorption of visible light and the subsequent excitement of d-electrons within the metal atoms from one electronic state to another. The presence of certain anions, ligands or both of them strongly affects the color of the compound. Since the absorbance of a solution is directly proportional to the concentration of the absorbing species, they are related by the Beer- Lambert law, for a fixed path length UV-Vis spectroscopy can be used to determine the concentration of the absorber in a solution. Because of the significant UV absorption of many organic solvents, not all solvents are suitable for use in UV spectroscopy. Since ethanol absorbs very weakly at most wavelengths, it was therefore solely used for the UV-Vis measurements of the compounds in the present work.

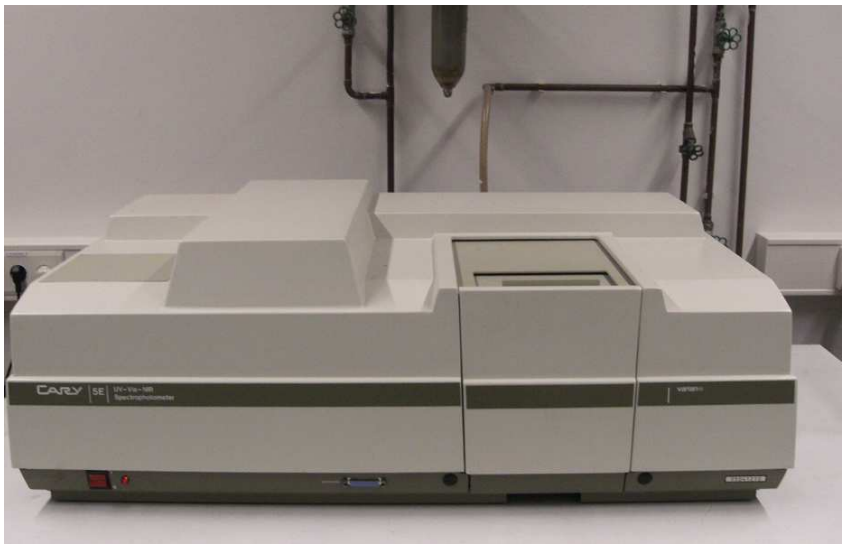


Fig. 9.4: UV-VIS-NIR Spectrophotometer (U-290 Hitachi)

6. Experimental Section

6.1 Index of used chemicals

Name	Chemical Formula	Purity	Origin
Ni(II)-perchlorate-hexahydrate	$Ni(ClO_4)_2 \cdot 6H_2O$	>99%	Fluka
Ni(II)-nitrate-tetrahydrate	$Ni(NO_3)_2 \cdot 4H_2O$	>99%	Fluka
Ni(II)-chloride-hexahydrate	$NiCl_2 \cdot 6H_2O$	>99%	Fluka
Ni(II)-tetrafluoroborate	$Ni(BF_4)_2$	>99%	Fluka
Ni(II)-iodide	NiI_2	>99%	Fluka
Ni(II)-acetate-tetrahydrate	$Ni(AcO)_2 \cdot 4H_2O$	>99%	Fluka
Ni(II)-sulfate-hexahydrate	$NiSO_4 \cdot 6H_2O$	>99%	Fluka
Ni(II)-thiocyanate	$Ni(SCN)_2$	>99%	Fluka
1,10-phenanthroline-hydrate	$C_{12}H_8N_2 \cdot H_2O$	>99%	Fluka
2,6-pyridindicarboxylic acid	$C_7H_5NO_4$	>98%	Fluka
2,4,6-tri(2-pyridyl)-1,3,5-triazine	$C_{18}H_{12}N_6$	>98%	Fluka
2,2’-bipyridine	$C_{10}H_8N_2$	>99%	Sigma Aldrich
4,4’-bipyridine	$C_{10}H_8N_2$	>99%	Sigma Aldrich
Acetonitrile	CH_3CN	>99%	Merck, Darmstadt

Acetone	C_3H_6O	>99%	Merck, Darmstadt
Ethanol	CH_3CH_2OH	98%	Merck, Darmstadt
Methanol	CH_3OH	98%	Merck, Darmstadt

6.2 Index of used equipment

Equipment	Type	Manufacturer
Powder diffractometer	θ/2θ STADI P	Stoe & Cie, Darmstadt /D
Imaging-Plate-Diffraction-System	IPDS I S/N 48029	Stoe & Cie, Darmstadt /D
Imaging-Plate-Diffraction-System II	IPDS II	Stoe& Cie, Darmstadt /D
UV-VIS-NIR Spectrophotometer	U-2900	Hitachi

6.3 Index of software used for compound identification

Programs	**Application**
SHELXL-97 [57]	Structure refinement program through Difference-Fourier-Synthesis, the “least-squares”-refinement.
SHELXS-86/ -97 [58]	Crystal structure determination program from single-crystal diffraction data by Patterson or Direct Methods.
Stoe Win XPOW [59]	The STOE Powder Diffraction Software Package is for operating powder diffractometers and for evaluation and representation of powder diffractograms.

X-RED [37] und X-SHAPE [60]	Software for crystal optimisation and for numerical absorption correction.
Platon [61,62]	Software Package for checking space groups or symmetry analysis.
WinGX [63]	System of programs for solving, refining and analyzing single crystal X-ray diffraction data for small molecules.
SIR 92 [64]	The SIR (Semi-Invariants Representation) program is solving crystal structures by Direct Methods (Often integrated into WinGX).
Find it/ ICSD [65]	Database for single crystal data of inorganic compounds.
Conquest/ CSD [66]	Online-database for single crystal data of organic and organo-metallic compounds.
Diamond 3 [67]	Visualization software, that integrates a multitude of functions, which overcome the work with crystal structure data.

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8. Appendix

8.1 The crystal structure of catena(*μ*-pyridine-2,6-dicarboxylato O,N,O,O´,O´´)*bis*(*μ*-pyridine-2,6-dicarboxylato O,N,O,O´) neodymiate(III) octaaquabis(pyridine-2,6-dicarboxylato-O,N,O´)dineodymium(III) heptahydrate, $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$ (15)

$[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$ (**15**) crystallizes in the triclinic space group P-1 (2) with a = 12.877(1) Å, b = 13.291(1) Å, c = 17.915(2) Å, α = 68.81(1)°, β = 68.80(1)°, γ = 63.61(1)°, V = 2485.8(1) Å ^{3} and Z = 2. Crystallographic and refinement details are listed below in Table 1.1. The structure of (**15**) represents a coordination polymer. Its asymmetric unit contains three independent Nd(III) environments, which are coordinated to aqua and 2,6-pda ligands.

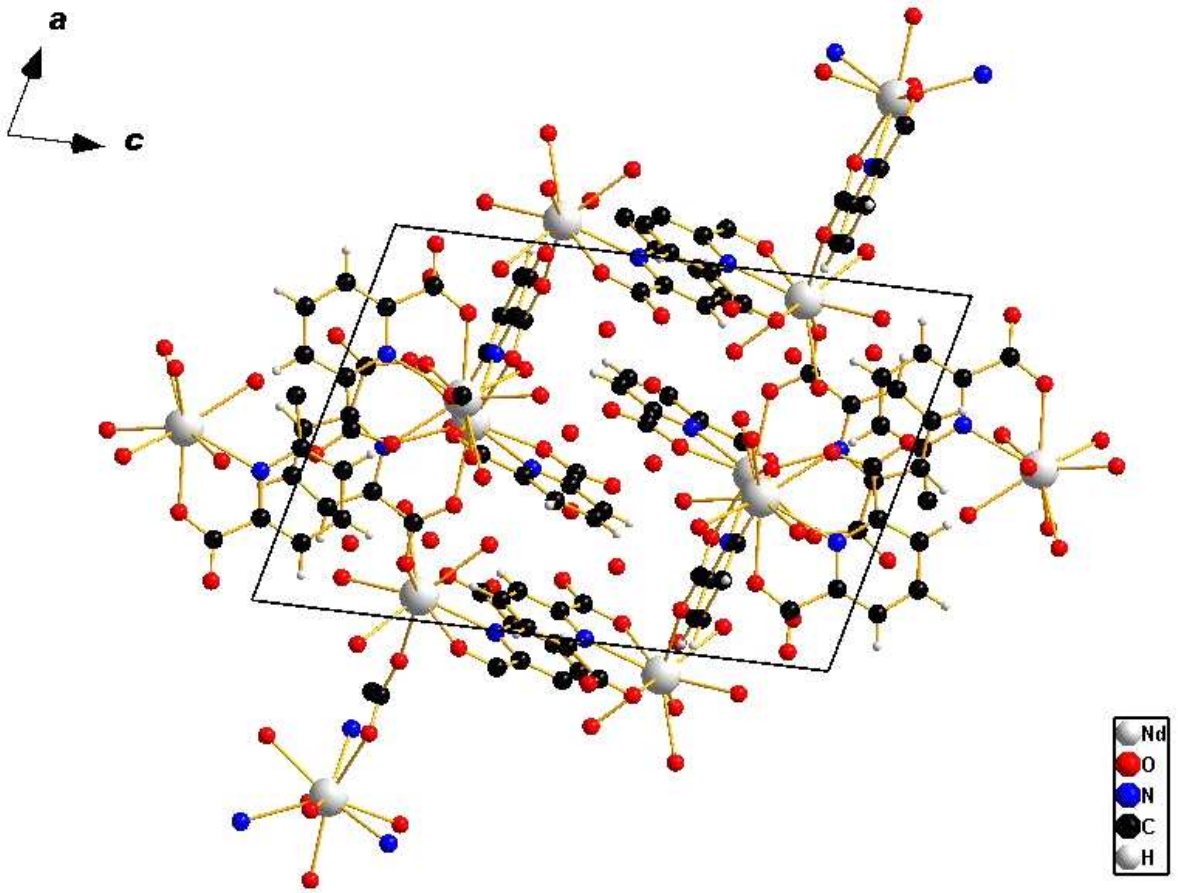

Fig. 1.: Projection of the unit cell of $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$ along the crystallographic b-axis.

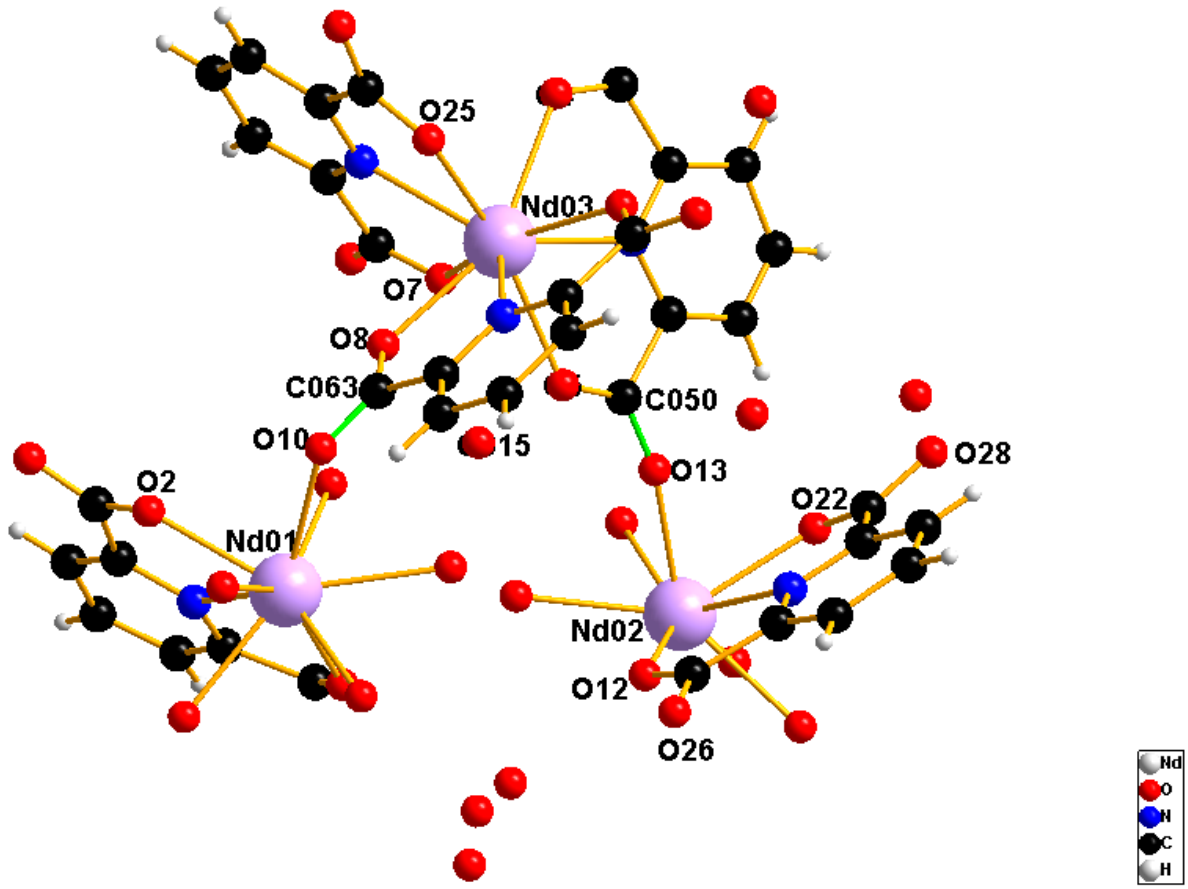

Fig.2: The asymmetric unit of $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$.

In (**15**) the Nd(III) cations are linked to chains, where the carboxylate groups of the 2,6-pda ligands exhibit a bridging role. Two different types of Nd(III) environments can be distinguished. The Nd01 and Nd02 ions are coordinated each by one 2,6-pda ligand in a k^3 *N,O,O'* mode, four aqua ligands and two oxygen atoms of the bridging carboxylate groups. The Nd03 ion is coordinated to three 2,6-pda ligands in a k^3 *N,O,O'* mode. The coordination number of all three Nd(III) ion is 9 and the geometry of the coordination polyhedra can be assigned to a tricapped trigonal prism. Nd-O distances as well as the O-Nd-O and N-Nd-N angles indicate distortion of the geometry around all three metal centers, whereas the geometry around the Nd(III) metal center is less distorted. This is due to the same coordination strength of the 2,6-pda ligands, since the other two Nd(III) centers are coordinated to aqua and 2,6-pda ligands, the distortion of the geometry is greater because of the difference in the coordinating strength of these ligands.

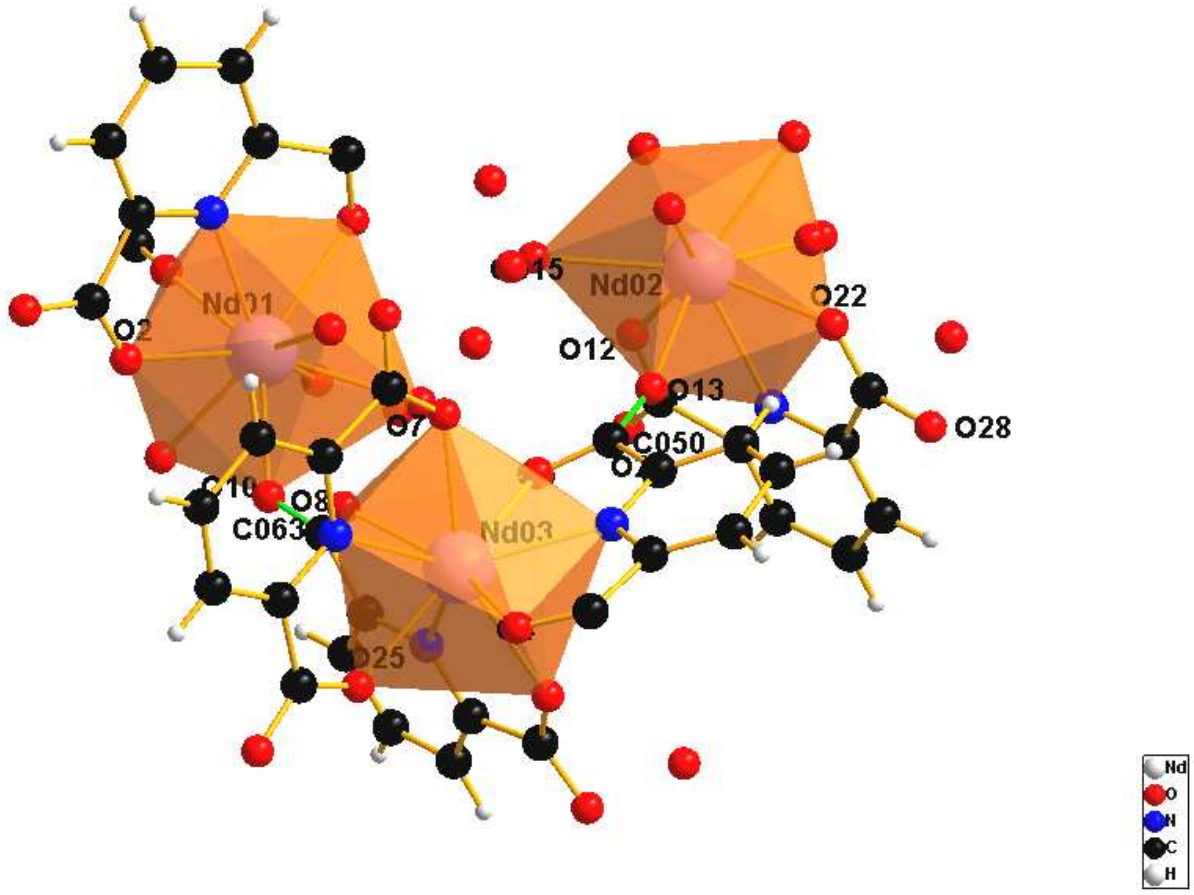

Fig.3: The geometry of the coordination polyhedra in $[Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$.

There are H-bonds formed by the lattice water molecules and O atoms of the carboxylic groups (shown as dashed blue bonds in Fig. 4). The C-O distances range from 1.247(13) to 1.283(15) Å, all carboxylic groups are deprotonated and are therefore counterbalancing the positive charge of the metal centers. The Nd-O distances exhibit bigger differences. The coordination of the three 2,6-pda ligands on the Nd03 center generates a -3 charge, the coordination around the Nd02 center results in the neutral $[Nd(2,6\text{-pda})(H_2O)_4O,O']$-complex. The charge resulting around the Nd01 is +1, $[Nd(2,6\text{-pda})(H_2O)_4O,O']^+$. In order to compensate the negative charge of the $[Ni(2,6\text{-pda})_3]^{3-}$ complex two more cations are needed. In the absence of any other positively charged chemical species, these could only be two H_3O^+ ions. This is feasible, since there are enough protons from the deprotonated 2,6-pda ligands.

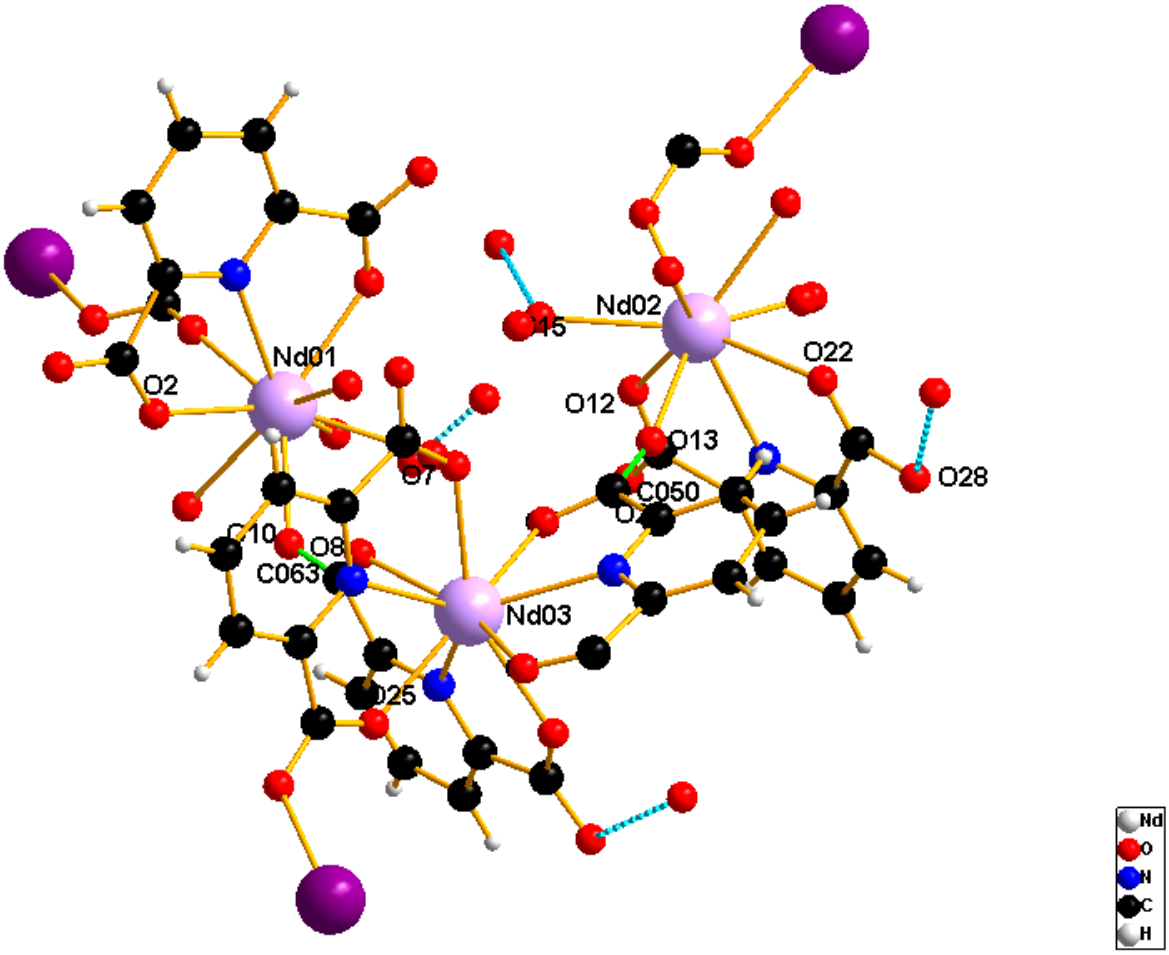

Fig.4: H-bonding and connection pattern of the monomers into a coordination polymer in [Nd(2,6-pda)$_3$][Nd(2,6-pda)(H$_2$O)$_6$]$_2$(H$_2$O)$_7$.

Table 1.1: Crystallographic and refinement details of $Nd(2,6\text{-pda})_3][Nd(2,6\text{-pda})(H_2O)_6]_2(H_2O)_7$.

Empirical formula	$C_{35}\,H_{46}\,N_5\,Nd_3\,O_{35}$
Formula weight	1510.49 $g \cdot mol^{-1}$
Crystal system	triclinic
Space group	P-1 (2)
Crystal color	violet
Unit cell dimensions	a = 12.877(1) Å b = 13.291(1) Å c = 17.915(2) Å α = 68.81(1)° β = 68.80(1)° γ = 63.61(1)°
Cell volume	2485.8(1) $Å^3$
Z	2
Density (calculated)	2.668 $g \cdot cm^{-3}$
Absorption coefficient	7.270 mm^{-1}
F (000)	1848.0
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem II
Radiation type, wavelength	Mo-K_α, λ = 71.07pm
Measurement temperature	170(2) K
2θ range	3.52°- 54.8°
$h_{min/max}$, $k_{min/max}$, $l_{min/max}$	-16 / 16, -16 / 16, -21 / 22
Reflections collected	34889
Independent reflections	10870
R_{int}	0.0941
Structure solving	SIR92
Refinement	SHELXL97 [57]
Parameters	704
GooF(S)	1.002[c]
Final R indices [$F_o > 2\sigma(F_o)$]	R_1[a] = 0.0688, wR_2[b] = 0.2096
R indices (all data)	R_1 = 0.0781, wR_2 = 0.2039

F_o and F_c represent the observed and calculated structure factors, n and p the number of reflections and refined parameters. [a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, [b] $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, [c] $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.
$w^{-1} = \sigma^2(|F_o|^2) + (0{,}0100 \cdot P)^2$, where $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 1.2: Selected distances/Å and angles/° in [[N d(2,6-pda)$_3$][Nd(2,6-pda)(H_2O)$_6$]$_2$(H_2O)$_7$.

Distances/Å

Atom 1	Atom 2	d[1,2]
Nd(01)	O(2)	2.428(9)
Nd(01)	O(16)	2.439(13)
Nd(01)	O(23)	2.478(9)
Nd(01)	O(10)	2.486(11)
Nd(02)	O(12)	2.408(9)
Nd(02)	O(13)	2.412(10)
Nd(02)	O(6)	2.430(10)
Nd(03)	O(8)	2.454(9)
Nd(03)	O(25)	2.461(9)
Nd(03)	O(5)	2.463(1)
Nd(03)	O(1)	2.486(7)
O(1)	C(067)	1.283(15)
O(2)	C(056)	1.247(13)
O(4)	C(062)	1.263(12)
O(5)	C(050)	1.265(12)
O(6)	C(053)	1.267(16)
O(7)	C(070)	1.271(16)
O(8)	C(063)	1.279(17)
O(10)	C(063)	1.254(17)
O(11)	C(062)	1.254(19)
O(12)	C(068)	1.264(13)
O(13)	C(050)	1.252(19)

Angles/°

Atom 1	Atom 2	Atom 3	Angle [1,2,3]
O(2)	Nd(01)	O(16)	139.9(3)
O(2)	Nd(01)	O(23)	125.3(4)
O(2)	Nd(01)	O(10)	76.5(4)
O(16)	Nd(01)	O(23)	81.7(4)
O(16)	Nd(01)	O(10)	103.3(4)
O(23)	Nd(01)	O(10)	138.7(4)
O(12)	Nd(02)	O(13)	90.0(4)
O(12)	Nd(02)	O(6)	74.6(3)
O(13)	Nd(02)	O(6)	141.9(3)
O(8)	Nd(03)	O(25)	86.9(3)
O(8)	Nd(03)	O(5)	76.2(3)
O(8)	Nd(03)	O(1)	123.8(3)
O(25)	Nd(03)	O(5)	152.1(3)
O(25)	Nd(03)	O(1)	78.8(3)
O(5)	Nd(03)	O(1)	92.4(3)

8.2 Atomic parameters and equivalent temperature coefficients

Table 1.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of (2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) tetrafluoroborate monohydrate, $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	1/4	0	0.05184(2)	0.02398(1)
C2	0.30538(10)	0.23574(18)	0.00600(12)	0.0278(4)
C4	0.38663(11)	0.3328(2)	0.06908(12)	0.0319(5)
C6	0.35881(9)	0.14253(18)	0.10972(12)	0.0258(4)
C21	0.2494(1)	0.22617(18)	0.04868(12)	0.0292(4)
C23	0.15846(10)	0.1131(2)	0.07990(13)	0.0337(5)
H23	0.13280	0.04350	-0.07280	0.040
C24	0.13894(11)	0.2022(2)	0.13468(14)	0.0400(5)
H24	0.10010	0.19340	-0.16200	0.048
C25	0.17744(11)	0.3036(2)	0.14813(14)	0.0398(5)
H25	0.16580	0.36260	-0.18590	0.048
C26	0.23421(1)	0.3161(2)	0.10421(14)	0.0372(5)
H26	0.26130	0.38350	-0.11200	0.045
C41	0.42599(12)	0.4467(2)	0.07989(14)	0.0379(5)
C43	0.50951(15)	0.5418(3)	0.14490(16)	0.0509(7)
H43	0.54250	0.53920	0.18260	0.061
C44	0.50063(16)	0.6496(3)	0.10223(16)	0.0552(7)
H44	0.52720	0.71740	0.11110	0.066
C45	0.45192(17)	0.6552(3)	0.04642(18)	0.0586(8)
H45	0.44470	0.72690	0.01710	0.070
C46	0.41354(15)	0.5511(2)	0.03474(17)	0.0497(7)
H46	0.38020	0.55180	-0.00260	0.060
C61	0.36343(9)	0.02974(19)	0.15869(12)	0.0269(4)
C63	0.31908(11)	-0.1621(2)	0.18314(14)	0.0338(5)
H63	0.28850	-0.22240	0.17180	0.041
C64	0.36495(11)	-0.1851(2)	0.24232(15)	0.0412(5)

H64	0.36460	-0.25930	0.27020	0.049
C65	0.41083(11)	-0.0964(2)	0.25890(15)	0.0399(5)
H65	0.44160	-0.10990	0.29850	0.048
C66	0.41074(10)	0.0130(2)	0.21602(13)	0.0326(5)
H66	0.44170	0.07340	0.22560	0.039
B1	1/2	0	0	0.078(3)
B2	1/4	1/2	0.1962(3)	0.0485(10)
F1	0.51282(12)	0.0947(3)	0.0694(2)	0.0513(12)
F2	0.44812(13)	0.0867(3)	-0.0238(2)	0.0496(12)
F3	0.5055(3)	-0.0379(5)	0.0606(3)	0.0678(19)
F4	0.44526(13)	-0.0621(3)	0.04127(18)	0.0454(11)
F5	0.20038(11)	0.45757(15)	0.24572(13)	0.0790(6)
F6	0.27098(10)	0.40214(16)	0.15216(13)	0.0741(6)
N1	0.31190(8)	0.13856(15)	0.05436(10)	0.0254(3)
N3	0.34356(10)	0.33390(16)	0.00859(11)	0.0337(4)
N5	0.39652(8)	0.24000(17)	0.12069(11)	0.0306(4)
N6	0.21275(8)	0.12386(17)	0.03715(10)	0.0281(4)
N2	0.47317(11)	0.44087(19)	0.13497(12)	0.0443(5)
N4	0.31750(8)	0.05624(16)	0.14216(10)	0.0268(4)

Table 1.2: Anisotropic displacement parameters of (2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel (II) tetrafluoroborate monohydrate, $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.02096(16)	0.02368(18)	0.02729(19)	0.00180(14)	0.00000	0.00000
C2	0.0358(10)	0.0217(9)	0.0259(10)	-0.0021(8)	-0.0023(8)	0.0020(8)
C4	0.0411(11)	0.0288(10)	0.0257(10)	-0.0088(9)	-0.0045(9)	0.0025(8)
C6	0.0220(8)	0.0279(10)	0.0274(10)	-0.0041(7)	-0.0012(7)	0.0026(8)
C21	0.0359(9)	0.0246(9)	0.0273(9)	0.0018(9)	-0.0050(9)	0.0001(8)
C23	0.0244(9)	0.0453(13)	0.0314(10)	0.0010(9)	-0.0045(8)	-0.0026(10)
C24	0.0330(11)	0.0554(15)	0.0316(11)	0.0106(10)	-0.0074(9)	-0.0031(11)
C25	0.0480(13)	0.0392(12)	0.0320(11)	0.0120(11)	-0.0107(10)	0.0004(10)
C26	0.0485(13)	0.0294(11)	0.0335(11)	0.0044(9)	-0.0113(9)	0.0013(9)
C41	0.0531(13)	0.0322(12)	0.0283(11)	-0.0152(10)	-0.0071(10)	0.0009(10)
C43	0.0679(17)	0.0520(15)	0.0328(12)	-0.0308(13)	-0.0083(12)	-0.0021(11)
C44	0.0834(19)	0.0402(14)	0.0418(14)	-0.0311(14)	-0.0037(14)	-0.0065(12)
C45	0.092(2)	0.0303(13)	0.0538(16)	-0.0204(14)	-0.0140(16)	0.0030(12)
C46	0.0734(18)	0.0316(12)	0.0442(14)	-0.0152(13)	-0.0162(13)	0.0035(11)
C61	0.0216(9)	0.0295(10)	0.0295(10)	-0.0029(7)	-0.0019(8)	0.0070(8)
C63	0.0336(10)	0.0291(11)	0.0386(12)	-0.0054(9)	-0.0016(9)	0.0077(9)
C64	0.0449(12)	0.0336(12)	0.0451(13)	-0.0021(10)	-0.0060(11)	0.0163(11)
C65	0.0365(11)	0.0425(13)	0.0407(13)	-0.0007(10)	-0.0097(10)	0.0139(11)
C66	0.0265(9)	0.0366(12)	0.0346(11)	-0.0054(9)	-0.0044(8)	0.0081(9)
B1	0.0256(18)	0.029(2)	0.178(9)	-0.0056(19)	0.019(3)	-0.017(4)
B2	0.073(3)	0.0229(16)	0.049(2)	-0.009(2)	0.00000	0.00000
F1	0.0329(16)	0.0393(18)	0.082(2)	-0.0033(11)	0.0067(14)	-0.0241(16)
F2	0.0341(16)	0.0399(17)	0.075(2)	0.0028(12)	0.0000(14)	-0.0170(15)
F3	0.079(4)	0.065(3)	0.059(3)	-0.005(2)	0.008(2)	0.020(2)
F4	0.0390(17)	0.0408(18)	0.057(2)	-0.0108(12)	0.0112(13)	-0.0115(13)
F5	0.1182(16)	0.0412(9)	0.0776(13)	-0.0257(10)	0.0347(12)	-0.0100(9)
F6	0.0912(13)	0.0400(9)	0.0912(14)	-0.0161(9)	0.0293(11)	-0.0253(9)

N1	0.0249(7)	0.0254(8)	0.0260(8)	-0.0008(6)	-0.0027(7)	0.0040(7)
N3	0.0459(10)	0.0261(9)	0.0289(9)	-0.0078(8)	-0.0084(8)	0.0031(8)
N5	0.0320(8)	0.0308(9)	0.0290(9)	-0.0073(7)	-0.0041(7)	0.0055(7)
N6	0.0273(8)	0.0296(9)	0.0274(9)	0.0031(7)	-0.0029(7)	-0.0008(7)
N2	0.0587(13)	0.0443(12)	0.0299(10)	-0.0257(10)	-0.0096(9)	0.0060(9)
N4	0.0229(8)	0.0278(9)	0.0299(9)	-0.0020(7)	-0.0004(7)	0.0062(7)
O1	0.0388(12)	0.0396(13)	0.0397(13)	0.00000	-0.0146(10)	0.00000

Table 2.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) Iodide monohydrate, $[Ni(tptz)_2](I)_2(H_2O)$ (2)

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.4190(1)	0.2437(1)	0.7150(1)	0.0341(3)
I1	-0.0006(1)	0.2644(1)	0.48930	0.0623(2)
I3	0.1447(2)	-0.0457(1)	0.9364(1)	0.0613(4)
I2	1/2	1/2	1.00000	0.174(1)
N1	0.5222(8)	0.3935(5)	0.7044(4)	0.0350(15)
N2	0.6198(8)	0.3841(5)	0.4749(4)	0.0363(16)
N3	0.3461(8)	0.1131(5)	0.6615(4)	0.0375(16)
N4	0.4829(8)	0.2776(4)	0.5889(4)	0.0344(15)
C1	0.5403(10)	0.4490(6)	0.7679(5)	0.0393(19)
H1	0.49370	0.42700	0.82390	0.047
N5	0.1901(8)	0.2952(5)	0.7517(4)	0.0372(16)
N6	0.6203(10)	0.2738(6)	0.2783(4)	0.058(2)
N7	0.6181(7)	0.1693(5)	0.7408(4)	0.0379(15)
N8	0.2113(8)	0.2361(5)	0.9739(4)	0.0380(16)
N9	0.5107(8)	0.2279(5)	0.4493(4)	0.0386(16)
C2	0.5922(9)	0.4272(5)	0.6230(4)	0.0331(17)
C3	0.5959(10)	0.3137(6)	0.4233(5)	0.0367(19)
N10	0.3730(8)	0.2166(4)	0.8416(4)	0.0342(15)
C4	0.7425(10)	0.1454(6)	0.6849(5)	0.045(2)
H2	0.74590	0.16130	0.62670	0.053
C5	0.6993(10)	0.5702(6)	0.6691(5)	0.044(2)
H3	0.75860	0.62910	0.65750	0.053
C6	0.2191(11)	-0.0444(7)	0.6622(7)	0.062(3)
H4	0.17140	-0.10250	0.69330	0.075
C7	0.3194(10)	0.0501(6)	0.5277(6)	0.049(2)
H5	0.33830	0.05790	0.46810	0.058
N11	0.4581(8)	0.1647(5)	0.9668(4)	0.0402(16)

C8	0.2976(11)	0.1848(6)	1.1054(5)	0.043(2)
N12	0.1654(11)	0.2218(6)	1.1491(5)	0.064(2)
C9	0.2717(10)	0.0317(6)	0.7041(6)	0.049(2)
H6	0.25410	0.02530	0.76370	0.059
C10	0.5662(9)	0.3622(6)	0.5569(4)	0.0339(18)
C11	-0.0127(10)	0.3105(6)	0.8754(6)	0.046(2)
H7	-0.04800	0.30180	0.93450	0.056
C12	0.4570(9)	0.2137(6)	0.5337(5)	0.0352(18)
C13	0.6661(10)	0.3328(6)	0.3315(5)	0.041(2)
C14	0.134(1)	0.2862(6)	0.8391(5)	0.0388(19)
C15	0.4779(9)	0.1762(6)	0.8831(5)	0.0372(18)
C16	0.0937(11)	0.3284(6)	0.7029(6)	0.048(2)
H8	0.12670	0.33350	0.64350	0.057
C17	0.6819(10)	0.5131(5)	0.6045(5)	0.039(2)
H9	0.73060	0.53230	0.54820	0.047
C18	0.7366(10)	0.0988(6)	0.8538(6)	0.046(2)
H10	0.73180	0.08320	0.91220	0.055
C19	0.4022(10)	0.1378(6)	1.1447(5)	0.0391(19)
H11	0.48950	0.11140	1.11260	0.047
C20	-0.1036(12)	0.3475(7)	0.8229(6)	0.056(2)
H12	-0.20130	0.36760	0.84570	0.067
C21	0.371(1)	0.1212(6)	0.5740(5)	0.0392(19)
C22	0.3248(10)	0.1959(6)	1.0107(5)	0.0375(19)
C23	0.6188(10)	0.1466(5)	0.8256(5)	0.0370(19)
C24	0.7933(13)	0.3641(7)	0.1619(6)	0.060(3)
H13	0.83290	0.37510	0.10330	0.072
C25	0.861(1)	0.0747(6)	0.7952(6)	0.046(2)
H14	0.94210	0.04220	0.81320	0.056
C26	0.1421(12)	0.2138(7)	1.2375(6)	0.058(3)
H15	0.05380	0.23910	1.26950	0.069
C27	0.8405(14)	0.4202(8)	0.2188(6)	0.071(3)
H16	0.91570	0.46930	0.19940	0.085

C28	0.7779(12)	0.4049(7)	0.3051(5)	0.056(3)
H17	0.81050	0.44250	0.34440	0.068
C29	0.2428(9)	0.2436(5)	0.8895(4)	0.0338(18)
C30	0.2387(11)	-0.0326(7)	0.5734(7)	0.060(3)
H18	0.19770	-0.08030	0.54490	0.071
C31	0.2484(13)	0.1687(7)	1.2788(6)	0.061(3)
H19	0.23320	0.16440	1.33830	0.073
C32	-0.0508(12)	0.3551(7)	0.7361(6)	0.057(3)
H20	-0.11370	0.37850	0.69960	0.068
C33	0.8658(11)	0.0986(6)	0.7091(6)	0.048(2)
H21	0.95040	0.08360	0.66820	0.057
C34	0.3769(12)	0.1303(7)	1.2310(5)	0.055(3)
H22	0.44790	0.09840	1.25860	0.066
C35	0.6263(11)	0.5383(6)	0.7531(5)	0.046(2)
H23	0.63520	0.57620	0.79840	0.056
C36	0.6836(14)	0.2898(8)	0.1944(6)	0.069(3)
H24	0.65260	0.24930	0.15630	0.082
O1	0.125(3)	0.4570(13)	1.0437(12)	0.276(11)

Table 2.2: Anisotropic displacement parameters of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) niickel(II) tetrafluoroborate monohydrate, $[Ni(tptz)_2](BF_4)_2(H_2O)$ (1), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0361(7)	0.0363(6)	0.0289(5)	0.0007(4)	-0.0066(4)	0.0026(4)
I1	0.0623(5)	0.0821(5)	0.0376(3)	-0.0166(4)	-0.0004(3)	0.0001(3)
I3	0.0734(11)	0.0691(8)	0.0446(7)	-0.0008(7)	-0.0245(6)	0.0070(6)
I2	0.207(2)	0.277(2)	0.0384(6)	-0.0895(18)	-0.0218(9)	-0.0083(10)
N1	0.041(5)	0.042(4)	0.024(3)	0.002(3)	-0.010(3)	-0.002(3)
N2	0.045(5)	0.039(4)	0.026(3)	0.006(3)	-0.009(3)	-0.004(3)
N3	0.031(4)	0.036(4)	0.047(4)	0.000(3)	-0.012(3)	0.001(3)
N4	0.044(5)	0.030(3)	0.031(3)	-0.001(3)	-0.013(3)	-0.002(3)
C1	0.047(6)	0.044(5)	0.027(4)	0.004(4)	-0.009(3)	-0.003(3)
N5	0.042(5)	0.041(4)	0.031(3)	0.005(3)	-0.013(3)	-0.005(3)
N6	0.080(7)	0.062(5)	0.032(4)	-0.008(4)	-0.013(4)	-0.009(3)
N7	0.028(4)	0.044(4)	0.038(3)	0.002(3)	-0.002(3)	0.007(3)
N8	0.038(5)	0.050(4)	0.026(3)	-0.002(3)	-0.006(3)	-0.004(3)
N9	0.043(5)	0.042(4)	0.031(3)	0.002(3)	-0.009(3)	-0.006(3)
C2	0.035(5)	0.035(4)	0.029(4)	0.008(3)	-0.010(3)	0.002(3)
C3	0.044(6)	0.035(4)	0.031(4)	0.010(4)	-0.008(3)	-0.007(3)
N10	0.034(4)	0.034(3)	0.033(3)	0.004(3)	-0.005(3)	0.004(3)
C4	0.035(6)	0.049(5)	0.045(5)	0.004(4)	0.000(4)	0.004(4)
C5	0.053(6)	0.035(4)	0.045(5)	-0.009(4)	-0.011(4)	-0.006(4)
C6	0.044(7)	0.038(5)	0.098(8)	-0.001(4)	0.001(5)	-0.004(5)
C7	0.043(6)	0.042(5)	0.064(6)	-0.004(4)	-0.014(4)	-0.010(4)
N11	0.031(5)	0.053(4)	0.036(3)	0.000(3)	-0.010(3)	0.008(3)
C8	0.052(6)	0.045(5)	0.033(4)	-0.015(4)	-0.010(4)	-0.002(3)
N12	0.072(7)	0.070(5)	0.049(5)	-0.005(5)	-0.011(4)	-0.006(4)
C9	0.044(6)	0.044(5)	0.054(5)	-0.001(4)	0.002(4)	0.002(4)
C10	0.035(5)	0.042(4)	0.025(4)	0.008(3)	-0.007(3)	-0.002(3)
C11	0.038(6)	0.051(5)	0.048(5)	0.008(4)	-0.003(4)	-0.008(4)
C12	0.033(5)	0.038(4)	0.037(4)	0.007(3)	-0.013(3)	-0.007(3)
C13	0.047(6)	0.046(5)	0.031(4)	0.007(4)	-0.012(4)	-0.005(3)

C14	0.040(6)	0.035(4)	0.045(4)	0.004(4)	-0.015(4)	-0.002(3)
C15	0.031(5)	0.040(4)	0.037(4)	-0.004(3)	-0.003(3)	0.005(3)
C16	0.051(7)	0.050(5)	0.047(5)	0.006(4)	-0.022(4)	-0.009(4)
C17	0.046(6)	0.032(4)	0.038(4)	0.001(4)	-0.006(4)	-0.006(3)
C18	0.036(6)	0.051(5)	0.056(5)	0.009(4)	-0.023(4)	-0.002(4)
C19	0.040(6)	0.048(5)	0.030(4)	0.001(4)	-0.011(3)	0.000(3)
C20	0.044(7)	0.060(6)	0.070(6)	0.006(5)	-0.022(5)	-0.011(5)
C21	0.035(6)	0.032(4)	0.048(5)	0.003(3)	-0.007(4)	0.000(3)
C22	0.045(6)	0.035(4)	0.031(4)	-0.004(4)	-0.006(4)	0.000(3)
C23	0.040(6)	0.033(4)	0.035(4)	-0.003(3)	-0.006(3)	0.008(3)
C24	0.078(8)	0.067(6)	0.032(4)	-0.004(5)	-0.003(4)	-0.001(4)
C25	0.025(6)	0.053(5)	0.060(5)	0.013(4)	-0.009(4)	0.001(4)
C26	0.064(8)	0.060(6)	0.049(5)	0.003(5)	-0.007(5)	-0.017(5)
C27	0.084(9)	0.067(7)	0.054(6)	-0.020(6)	0.002(5)	0.004(5)
C28	0.075(8)	0.061(6)	0.033(4)	-0.007(5)	-0.008(4)	-0.012(4)
C29	0.033(5)	0.036(4)	0.032(4)	0.003(3)	-0.006(3)	-0.002(3)
C30	0.050(7)	0.041(5)	0.088(8)	-0.006(4)	-0.008(5)	-0.025(5)
C31	0.091(9)	0.057(6)	0.034(5)	-0.008(5)	-0.016(5)	0.001(4)
C32	0.066(8)	0.044(5)	0.069(6)	0.008(5)	-0.034(6)	-0.004(4)
C33	0.038(6)	0.049(5)	0.051(5)	0.005(4)	0.001(4)	-0.001(4)
C34	0.074(8)	0.067(6)	0.026(4)	0.009(5)	-0.014(4)	0.000(4)
C35	0.060(7)	0.044(5)	0.038(4)	-0.003(4)	-0.013(4)	-0.010(4)
C36	0.099(9)	0.073(7)	0.036(5)	-0.011(6)	-0.015(5)	-0.018(5)
O1	0.41(3)	0.182(16)	0.219(19)	0.046(18)	-0.040(19)	-0.010(13)

Table 3.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II Iodide dihydrate, $[Ni(tptz)_2](I)_2(H_2O)_2$ (3).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.12200(3)	-0.73117(10)	0.36613(5)	0.0391(3)
I1	0	-0.00387(14)	1/4	0.0985(5)
I2	0.12215(3)	-0.48518(12)	0.61147(4)	0.1053(4)
I3	0.19452(4)	-0.18286(17)	0.51800(7)	0.0694(5)
C1	0.1055(2)	-0.9462(8)	0.2543(4)	0.041(2)
C2	0.0828(2)	-0.8213(8)	0.2292(4)	0.039(2)
C3	0.0668(2)	-0.6048(9)	0.2573(4)	0.043(2)
C4	0.0745(2)	-0.4942(9)	0.3116(4)	0.043(2)
C5	0.0575(3)	-0.365(1)	0.3029(5)	0.060(3)
H5	0.04040	-0.34480	0.26280	0.072
C6	0.0667(3)	-0.2672(11)	0.3553(6)	0.084(4)
H6	0.05610	-0.17870	0.35110	0.1
C7	0.2766(3)	-0.6817(10)	0.7185(5)	0.067(3)
H7	0.29710	-0.63570	0.72580	0.08
C8	0.0917(3)	-0.3027(10)	0.4137(6)	0.071(3)
H8	0.09780	-0.23910	0.45010	0.085
C9	0.1078(3)	-0.4321(10)	0.4187(5)	0.058(3)
H9	0.12530	-0.45330	0.45800	0.07
C10	0.2706(4)	-0.7534(11)	0.7735(4)	0.072(4)
H10	0.28640	-0.75060	0.81660	0.086
C11	0.0408(2)	-0.7012(9)	0.1554(4)	0.042(2)
C12	0.1488(3)	-1.0321(9)	0.3426(5)	0.059(3)
H12	0.16390	-1.02110	0.38600	0.071
C13	0.1493(3)	-1.1581(11)	0.3079(6)	0.074(4)
H13	0.16450	-1.23020	0.32750	0.089
C14	0.1270(3)	-1.1748(11)	0.2442(6)	0.072(3)
H14	0.12730	-1.25820	0.21990	0.087

C15	0.1041(3)	-1.0686(9)	0.2159(5)	0.049(3)
H15	0.08840	-1.07880	0.17290	0.059
C16	0.1912(2)	-0.6128(8)	0.4096(4)	0.038(2)
C17	0.1665(3)	-0.5642(9)	0.2960(4)	0.044(2)
H17	0.14850	-0.57200	0.25630	0.053
C18	0.0143(3)	-0.6899(9)	0.0887(5)	0.046(2)
C19	0.1947(3)	-0.4875(10)	0.2944(4)	0.051(3)
H19	0.19560	-0.44730	0.25390	0.061
C20	0.2212(3)	-0.4712(9)	0.3533(5)	0.049(2)
H20	0.24000	-0.41740	0.35360	0.058
C21	0.2193(3)	-0.5364(9)	0.4114(4)	0.045(2)
H21	0.23700	-0.52880	0.45170	0.055
C22	0.1861(3)	-0.6824(8)	0.4691(4)	0.038(2)
C23	0.2009(3)	-0.7488(9)	0.5793(4)	0.043(2)
C24	0.1497(3)	-0.8033(8)	0.5093(4)	0.041(2)
C25	0.1155(3)	-0.8632(9)	0.4918(5)	0.044(2)
C26	0.1047(3)	-0.9453(10)	0.5367(5)	0.060(3)
H26	0.11900	-0.96430	0.58030	0.072
C27	0.0721(3)	-0.9990(12)	0.5152(6)	0.072(3)
H27	0.06410	-1.05600	0.54370	0.087
C28	0.0518(3)	-0.9649(10)	0.4502(6)	0.069(3)
H28	0.02950	-0.99390	0.43530	0.083
C29	0.0651(3)	-0.8866(9)	0.4072(5)	0.053(3)
H29	0.05150	-0.86780	0.36300	0.064
C30	0.2256(3)	-0.7499(9)	0.6484(4)	0.044(2)
C31	0.2190(3)	-0.8237(10)	0.7005(5)	0.057(3)
H31	0.19880	-0.87240	0.69270	0.069
C32	-0.0069(3)	-0.7573(11)	-0.0218(5)	0.066(3)
H32	-0.00550	-0.81460	-0.05770	0.079
C33	-0.0333(3)	-0.6625(11)	-0.0336(5)	0.065(3)
H33	-0.04900	-0.65430	-0.07660	0.078
C34	-0.0358(3)	-0.5818(10)	0.0190(5)	0.060(3)

H34	-0.05370	-0.51900	0.01290	0.072
C35	-0.0116(3)	-0.5936(9)	0.0815(5)	0.054(3)
H35	-0.01270	-0.53800	0.11800	0.065
C36	0.2422(4)	-0.8250(12)	0.7629(5)	0.072(4)
H36	0.23820	-0.87580	0.79830	0.087
N1	0.0992(2)	-0.5272(7)	0.3688(4)	0.0448(19)
N2	0.08739(19)	-0.7169(7)	0.2759(3)	0.0422(18)
N3	0.1278(2)	-0.9270(7)	0.3168(3)	0.0429(18)
N4	0.16466(19)	-0.6262(7)	0.3518(3)	0.0379(18)
N5	0.0964(2)	-0.8380(7)	0.4265(4)	0.0427(19)
N7	0.1560(2)	-0.7427(7)	0.4571(3)	0.0385(17)
N8	0.0606(2)	-0.8185(7)	0.1673(3)	0.0428(19)
N9	0.04314(19)	-0.5933(7)	0.1991(3)	0.0426(19)
N10	0.0169(2)	-0.7715(8)	0.0381(4)	0.060(2)
N11	0.2099(2)	-0.6821(7)	0.5294(3)	0.0439(19)
N12	0.1708(2)	-0.8097(7)	0.5715(4)	0.044(2)
N13	0.2541(2)	-0.6764(8)	0.6562(3)	0.052(2)
O1	0.2593(3)	-0.4158(9)	0.5824(4)	0.103(3)
O2	0.1525(4)	-1.1457(15)	0.6483(8)	0.198(6)

Table 3.2: Anisotropic displacement parameters of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) Iodide dihydrate, $[Ni(tptz)_2](I)_2(H_2O)_2$ (3), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0415(8)	0.0340(6)	0.0384(6)	0.0048(5)	0.0077(5)	0.0008(5)
I1	0.0699(10)	0.0909(9)	0.0988(9)	0.00000	-0.0255(7)	0.00000
I2	0.1013(8)	0.1546(9)	0.0447(4)	-0.0082(6)	0.0004(4)	-0.0089(5)
I3	0.0613(12)	0.0921(11)	0.0511(8)	0.0038(8)	0.0122(7)	0.0127(7)
C1	0.041(7)	0.038(5)	0.044(5)	0.009(4)	0.015(4)	0.001(4)
C2	0.041(7)	0.034(5)	0.044(5)	0.002(4)	0.015(5)	0.005(4)
C3	0.043(7)	0.036(5)	0.050(5)	0.014(4)	0.014(5)	0.005(4)
C4	0.050(7)	0.036(5)	0.043(5)	0.007(4)	0.013(4)	-0.005(4)
C5	0.059(8)	0.049(6)	0.059(6)	0.021(5)	0.000(5)	-0.007(5)
C6	0.109(11)	0.050(6)	0.071(7)	0.036(7)	-0.002(7)	-0.012(6)
C7	0.074(9)	0.058(6)	0.054(6)	0.018(6)	-0.001(6)	-0.020(5)
C8	0.085(10)	0.039(6)	0.080(8)	0.012(5)	0.015(7)	-0.019(5)
C9	0.076(9)	0.050(6)	0.046(5)	0.011(5)	0.015(5)	-0.003(5)
C10	0.127(13)	0.056(7)	0.021(5)	0.027(7)	0.007(6)	0.001(5)
C11	0.039(7)	0.039(5)	0.045(5)	0.008(4)	0.008(4)	0.007(4)
C12	0.074(9)	0.047(6)	0.048(5)	0.022(5)	0.007(5)	0.003(5)
C13	0.082(10)	0.062(7)	0.066(7)	0.036(6)	0.004(7)	0.006(6)
C14	0.082(10)	0.048(6)	0.084(8)	0.025(6)	0.022(7)	-0.014(5)
C15	0.059(8)	0.039(5)	0.049(5)	0.016(5)	0.015(5)	-0.009(4)
C16	0.050(7)	0.036(5)	0.030(4)	0.002(4)	0.012(4)	0.004(3)
C17	0.054(7)	0.047(5)	0.032(5)	0.006(5)	0.014(5)	0.004(4)
C18	0.046(7)	0.043(5)	0.046(5)	0.007(4)	0.010(5)	0.007(4)
C19	0.066(8)	0.050(6)	0.040(5)	0.016(5)	0.023(5)	0.012(4)
C20	0.059(8)	0.040(5)	0.056(6)	-0.006(5)	0.029(5)	0.007(4)
C21	0.045(7)	0.049(6)	0.042(5)	-0.003(5)	0.013(5)	0.002(4)
C22	0.051(7)	0.033(5)	0.033(5)	0.005(4)	0.017(4)	0.002(4)
C23	0.060(8)	0.038(5)	0.032(5)	0.012(5)	0.015(5)	0.006(4)
C24	0.061(7)	0.032(5)	0.031(5)	0.004(4)	0.016(5)	0.001(4)

C25	0.046(7)	0.045(5)	0.049(5)	-0.008(4)	0.026(5)	-0.007(4)
C26	0.068(9)	0.065(7)	0.056(6)	-0.008(6)	0.031(6)	0.003(5)
C27	0.088(11)	0.066(7)	0.077(8)	-0.006(7)	0.047(7)	0.009(6)
C28	0.069(9)	0.058(7)	0.091(9)	-0.029(6)	0.042(7)	-0.021(6)
C29	0.056(8)	0.048(6)	0.055(6)	-0.013(5)	0.016(6)	-0.012(5)
C30	0.055(8)	0.039(5)	0.035(5)	0.015(5)	0.012(4)	0.000(4)
C31	0.074(9)	0.063(6)	0.040(5)	0.013(5)	0.026(6)	0.015(5)
C32	0.077(10)	0.067(7)	0.047(6)	0.012(6)	0.008(6)	-0.013(5)
C33	0.068(9)	0.057(7)	0.060(7)	0.006(6)	0.007(6)	0.002(5)
C34	0.047(8)	0.054(6)	0.068(7)	0.005(5)	0.005(6)	0.016(5)
C35	0.055(8)	0.045(6)	0.056(6)	0.012(5)	0.008(5)	-0.003(4)
C36	0.115(12)	0.055(7)	0.039(6)	0.006(7)	0.013(7)	0.006(5)
N1	0.045(6)	0.037(4)	0.049(4)	-0.001(3)	0.011(4)	-0.003(3)
N2	0.038(5)	0.036(4)	0.050(4)	0.004(3)	0.009(4)	-0.005(3)
N3	0.040(5)	0.046(4)	0.039(4)	0.007(4)	0.007(4)	0.005(3)
N4	0.053(6)	0.034(4)	0.026(4)	0.003(3)	0.010(4)	0.003(3)
N5	0.043(6)	0.039(4)	0.048(4)	-0.002(4)	0.017(4)	-0.003(3)
N7	0.045(5)	0.036(4)	0.035(4)	-0.002(4)	0.014(3)	0.002(3)
N8	0.041(6)	0.042(4)	0.040(4)	0.001(4)	0.006(4)	0.001(3)
N9	0.039(6)	0.040(4)	0.044(4)	0.012(3)	0.006(4)	0.011(3)
N10	0.055(6)	0.063(5)	0.054(5)	0.019(4)	0.006(4)	-0.005(4)
N11	0.053(6)	0.044(4)	0.031(4)	0.006(4)	0.009(4)	0.003(3)
N12	0.064(7)	0.030(4)	0.045(4)	0.003(4)	0.024(4)	0.005(3)
N13	0.060(7)	0.054(5)	0.033(4)	0.010(4)	0.000(4)	0.002(3)
O1	0.153(10)	0.083(6)	0.063(5)	-0.029(6)	0.018(5)	0.003(4)
O2	0.199(17)	0.184(13)	0.187(14)	0.053(12)	0.025(12)	0.008(10)

Table 4.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) nitrate heptahydrate, $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ (4).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.08686(9)	0.22490(8)	0.19088(5)	0.0475(4)
C1	0.2641(6)	0.1689(6)	0.2742(4)	0.046(2)
C2	0.2960(7)	0.2024(6)	0.3822(4)	0.051(2)
C3	0.1513(7)	0.2552(6)	0.3304(4)	0.046(2)
C4	0.0071(7)	0.2917(6)	0.0628(4)	0.051(2)
C5	-0.1414(7)	0.2528(6)	0.0099(4)	0.051(2)
C6	-0.0946(7)	0.1865(6)	0.1053(4)	0.049(2)
C7	0.2802(7)	0.1242(6)	0.2099(4)	0.048(2)
C8	0.2152(7)	0.0968(7)	0.1022(4)	0.054(2)
H1	0.16570	0.10610	0.06810	0.065
C9	0.2948(8)	0.0402(7)	0.0913(4)	0.057(2)
H2	0.29800	0.01190	0.05040	0.068
C10	0.3684(8)	0.0259(7)	0.1403(4)	0.059(2)
H3	0.42250	-0.01180	0.13280	0.07
C11	0.3624(7)	0.0674(7)	0.2005(4)	0.057(2)
H4	0.41190	0.05810	0.23470	0.068
C12	0.3656(8)	0.1961(7)	0.4443(4)	0.054(2)
C13	0.4196(10)	0.2473(8)	0.5516(5)	0.070(3)
H5	0.41570	0.28490	0.58730	0.084
C14	0.4949(10)	0.1856(8)	0.5531(5)	0.073(3)
H6	0.54110	0.18090	0.58970	0.088
C15	0.5008(10)	0.1303(8)	0.4987(5)	0.070(3)
H7	0.55060	0.08790	0.50010	0.084
C16	0.4371(7)	0.1364(6)	0.4447(4)	0.048(2)
H8	0.44280	0.09970	0.40850	0.057
C17	0.0537(7)	0.3046(6)	0.3257(4)	0.0443(19)

C18	-0.0873(8)	0.3388(6)	0.2554(4)	0.054(2)
H9	-0.12150	0.33450	0.21370	0.064
C19	-0.1352(8)	0.3842(7)	0.3065(4)	0.057(2)
H10	-0.19840	0.41200	0.29890	0.068
C20	-0.0839(7)	0.3864(7)	0.3705(4)	0.057(2)
H11	-0.11460	0.41480	0.40620	0.069
C21	0.0097(7)	0.3473(6)	0.3801(4)	0.052(2)
H12	0.04380	0.34890	0.42190	0.063
C22	0.1024(7)	0.3442(6)	0.0740(4)	0.051(2)
C23	0.2425(8)	0.3680(7)	0.1463(4)	0.061(3)
H13	0.27900	0.35710	0.18640	0.073
C24	0.2821(10)	0.4299(7)	0.1031(5)	0.067(3)
H14	0.34370	0.45830	0.11390	0.081
C25	0.2259(10)	0.4473(8)	0.0435(5)	0.072(3)
H15	0.24950	0.48820	0.01400	0.086
C26	0.1346(9)	0.4030(7)	0.0287(5)	0.064(3)
H16	0.09630	0.41310	-0.01080	0.077
C27	-0.2170(7)	0.2660(6)	-0.0484(4)	0.050(2)
C28	-0.3682(8)	0.2226(7)	-0.1040(4)	0.060(3)
H17	-0.42490	0.18630	-0.10720	0.072
C29	-0.3567(8)	0.2833(8)	-0.1525(5)	0.065(3)
H18	-0.40660	0.28900	-0.18690	0.078
C30	-0.2697(8)	0.3363(7)	-0.1498(4)	0.061(3)
H19	-0.25960	0.37690	-0.18270	0.073
C31	-0.1993(8)	0.3263(7)	-0.0968(5)	0.061(3)
H20	-0.14010	0.36010	-0.09360	0.073
C32	-0.0999(7)	0.1220(6)	0.1579(4)	0.047(2)
C33	-0.0214(8)	0.0695(6)	0.2547(4)	0.054(2)
H21	0.03180	0.07220	0.28730	0.065
C34	-0.0938(8)	0.0060(7)	0.2583(5)	0.057(2)
H22	-0.09000	-0.03320	0.29280	0.068
C35	-0.1718(8)	0.0020(7)	0.2096(4)	0.055(2)

H23	-0.22210	-0.03990	0.21140	0.066
C36	-0.1754(8)	0.0600(7)	0.1582(4)	0.056(2)
H24	-0.22710	0.05750	0.12460	0.067
N1	0.4479(17)	0.3377(15)	0.2676(7)	0.153(7)
N2	0.1741(14)	-0.0301(14)	0.3759(6)	0.122(6)
N3	0.1776(6)	0.2158(5)	0.2735(3)	0.0477(17)
N4	0.3271(6)	0.1614(5)	0.3276(3)	0.0486(17)
N5	0.2079(6)	0.2497(5)	0.3876(3)	0.0461(17)
N6	-0.0096(6)	0.2357(5)	0.1111(3)	0.0498(18)
N7	-0.0552(6)	0.3011(5)	0.0095(3)	0.0523(19)
N8	-0.1657(6)	0.1950(5)	0.0560(3)	0.0483(17)
N9	0.2071(6)	0.1390(6)	0.1609(3)	0.055(2)
N10	0.3500(9)	0.2540(7)	0.4978(4)	0.079(3)
N11	0.0049(6)	0.3013(5)	0.2633(3)	0.0468(17)
N12	0.1558(6)	0.3240(5)	0.1330(3)	0.0527(19)
N13	-0.2994(6)	0.2144(5)	-0.0518(3)	0.0533(19)
N14	-0.0244(6)	0.1269(5)	0.2068(3)	0.0505(18)
O1	-0.0107(8)	0.049(1)	0.0178(4)	0.141(6)
O2	0.4474(10)	-0.0076(8)	0.3613(4)	0.125(5)
O3	0.6005(6)	0.4029(5)	0.5366(3)	0.0647(18)
O4	0.4282(6)	0.4272(5)	0.4395(3)	0.0661(19)
O5	0.5948(7)	0.1670(8)	0.1718(4)	0.100(3)
O6	0.6961(13)	0.2973(11)	0.1799(8)	0.167(6)
O7	0.3955(13)	0.5302(10)	0.2470(7)	0.151(5)
O8	0.4387(14)	0.2788(12)	0.2264(7)	0.180(8)
O9	0.3701(6)	0.3618(6)	0.3066(4)	0.075(2)
O10	0.5439(11)	0.3649(11)	0.2494(13)	0.214(10)
O11	0.074(2)	-0.0366(15)	0.3847(6)	0.212(10)
O12	0.2132(10)	-0.0943(8)	0.4012(5)	0.115(4)
O13	0.200(2)	0.0135(16)	0.3445(16)	0.40(3)

Table 4.2: Anisotropic displacement parameters of bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine) nickel(II) nitrate heptahydrate, $[Ni(tptz)_2](NO_3)_2(H_2O)_7$ (4), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0510(7)	0.0641(8)	0.0272(5)	0.0041(6)	-0.0034(4)	-0.0028(5)
C1	0.040(4)	0.068(6)	0.032(3)	-0.002(4)	-0.001(3)	0.001(4)
C2	0.060(5)	0.062(6)	0.030(4)	-0.010(5)	-0.006(3)	-0.002(4)
C3	0.050(5)	0.058(5)	0.029(3)	0.000(4)	-0.001(3)	-0.001(3)
C4	0.060(5)	0.056(6)	0.037(4)	0.008(4)	-0.010(4)	-0.006(4)
C5	0.057(5)	0.066(6)	0.031(4)	0.006(5)	-0.006(3)	0.003(4)
C6	0.045(5)	0.070(6)	0.032(4)	0.002(4)	-0.005(3)	-0.008(4)
C7	0.042(4)	0.073(6)	0.029(3)	0.002(4)	0.005(3)	0.003(4)
C8	0.051(5)	0.080(7)	0.032(4)	0.001(5)	0.003(3)	-0.017(4)
C9	0.064(6)	0.069(6)	0.038(4)	-0.007(5)	0.006(4)	-0.013(4)
C10	0.064(6)	0.071(7)	0.042(4)	-0.002(5)	0.013(4)	-0.003(4)
C11	0.050(5)	0.079(7)	0.041(4)	0.000(5)	-0.002(4)	-0.001(4)
C12	0.060(6)	0.066(6)	0.034(4)	-0.009(5)	-0.007(4)	0.000(4)
C13	0.103(9)	0.070(7)	0.037(4)	0.001(6)	-0.015(5)	-0.004(4)
C14	0.091(8)	0.084(8)	0.043(5)	-0.008(7)	-0.026(5)	0.005(5)
C15	0.082(7)	0.080(8)	0.049(5)	0.008(6)	-0.022(5)	0.006(5)
C16	0.060(5)	0.052(5)	0.031(4)	0.002(4)	-0.013(3)	0.000(3)
C17	0.052(5)	0.055(5)	0.027(3)	0.004(4)	0.005(3)	-0.003(3)
C18	0.058(5)	0.061(6)	0.042(4)	0.008(5)	-0.006(4)	-0.002(4)
C19	0.058(5)	0.064(6)	0.048(5)	0.016(5)	0.004(4)	-0.003(4)
C20	0.051(5)	0.078(7)	0.043(4)	0.013(5)	0.002(4)	-0.012(4)
C21	0.060(5)	0.061(6)	0.036(4)	-0.001(5)	-0.004(4)	-0.004(4)
C22	0.058(5)	0.063(6)	0.033(4)	0.011(5)	-0.005(3)	-0.003(4)
C23	0.071(6)	0.074(7)	0.038(4)	0.006(6)	-0.009(4)	-0.009(4)
C24	0.080(7)	0.072(7)	0.049(5)	-0.005(6)	-0.017(5)	-0.006(5)
C25	0.099(9)	0.068(7)	0.047(5)	-0.013(6)	-0.009(5)	0.008(5)
C26	0.097(8)	0.056(6)	0.039(4)	0.009(6)	-0.015(5)	-0.002(4)
C27	0.052(5)	0.064(6)	0.032(4)	-0.002(5)	-0.010(3)	0.000(4)
C28	0.061(6)	0.084(8)	0.035(4)	-0.006(5)	-0.010(4)	-0.003(4)

C29	0.065(6)	0.091(8)	0.040(4)	-0.009(6)	-0.012(4)	0.008(5)
C30	0.071(6)	0.074(7)	0.039(4)	-0.006(5)	-0.011(4)	0.015(4)
C31	0.067(6)	0.071(7)	0.045(5)	-0.006(5)	-0.016(4)	-0.001(4)
C32	0.047(5)	0.059(6)	0.037(4)	-0.004(4)	-0.003(3)	-0.004(4)
C33	0.068(6)	0.063(6)	0.032(4)	0.001(5)	-0.007(4)	0.006(4)
C34	0.061(6)	0.058(6)	0.052(5)	-0.007(5)	-0.002(4)	0.015(4)
C35	0.056(5)	0.064(6)	0.046(4)	-0.004(5)	0.005(4)	0.005(4)
C36	0.058(5)	0.067(6)	0.043(4)	-0.004(5)	0.001(4)	0.001(4)
N1	0.175(18)	0.22(2)	0.067(8)	0.027(16)	-0.002(9)	-0.005(10)
N2	0.118(11)	0.206(19)	0.041(5)	0.033(13)	-0.030(6)	-0.012(8)
N3	0.052(4)	0.052(5)	0.039(3)	0.008(4)	-0.004(3)	-0.001(3)
N4	0.051(4)	0.064(5)	0.030(3)	0.003(4)	-0.002(3)	-0.002(3)
N5	0.051(4)	0.058(5)	0.030(3)	0.001(3)	-0.004(3)	0.003(3)
N6	0.064(5)	0.054(5)	0.032(3)	-0.004(4)	-0.009(3)	-0.002(3)
N7	0.058(4)	0.066(5)	0.033(3)	-0.002(4)	-0.010(3)	-0.001(3)
N8	0.055(4)	0.055(5)	0.035(3)	0.006(4)	-0.008(3)	-0.006(3)
N9	0.050(4)	0.086(6)	0.030(3)	-0.002(4)	0.002(3)	-0.007(3)
N10	0.122(8)	0.077(7)	0.039(4)	-0.012(6)	-0.016(5)	0.001(4)
N11	0.051(4)	0.058(5)	0.032(3)	0.004(3)	-0.003(3)	-0.001(3)
N12	0.060(5)	0.063(5)	0.035(3)	0.011(4)	-0.006(3)	-0.011(3)
N13	0.055(4)	0.071(5)	0.034(3)	0.008(4)	-0.006(3)	-0.002(3)
N14	0.054(4)	0.067(5)	0.031(3)	0.002(4)	-0.002(3)	0.004(3)
O1	0.103(7)	0.279(17)	0.042(4)	0.099(9)	0.022(4)	0.063(6)
O2	0.183(11)	0.14(1)	0.051(4)	0.085(9)	-0.011(6)	0.000(5)
O3	0.074(5)	0.069(5)	0.051(4)	0.000(4)	-0.004(3)	0.001(3)
O4	0.074(5)	0.078(5)	0.047(3)	0.001(4)	0.007(3)	0.001(3)
O5	0.087(6)	0.156(10)	0.057(4)	0.025(6)	-0.011(4)	-0.002(5)
O6	0.187(15)	0.171(14)	0.143(12)	-0.029(12)	-0.025(10)	-0.027(11)
O7	0.181(13)	0.148(12)	0.122(10)	0.029(10)	0.000(9)	-0.006(9)
O8	0.198(15)	0.247(19)	0.093(8)	0.075(14)	-0.027(9)	-0.079(11)
O9	0.072(5)	0.099(6)	0.053(4)	0.000(4)	-0.007(3)	-0.001(4)
O10	0.083(8)	0.176(16)	0.38(3)	-0.013(9)	-0.009(13)	0.126(18)

O11	0.26(2)	0.32(3)	0.064(7)	0.12(2)	0.013(10)	0.035(10)
O12	0.122(9)	0.135(10)	0.088(7)	0.017(7)	0.000(6)	0.040(7)
O13	0.37(3)	0.33(3)	0.49(4)	-0.27(3)	-0.35(3)	0.34(3

Table 5.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of Aquadithiocyanato(2,4,6-tris(2-pyridyl)-1,3,5-triazine) Ni(II), $[Ni(SCN)_2(tptz)(H_2O]$ (5).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.46764(5)	0.45770(3)	0.33146(4)	0.02878(13)
S1	0.92657(15)	0.57346(7)	0.34575(12)	0.0579(4)
S2	0.24402(19)	0.43146(7)	0.61569(9)	0.0604(4)
O1	0.5915(3)	0.41927(15)	0.2176(2)	0.0422(9)
N1	0.3749(4)	0.56380(18)	0.2601(2)	0.0321(10)
N2	0.4716(4)	0.32696(16)	0.3733(2)	0.0280(8)
N3	0.6510(5)	0.5091(2)	0.3755(3)	0.0425(12)
N4	0.3574(5)	0.4823(2)	0.4475(3)	0.0460(12)
N5	-0.0048(4)	0.20975(18)	0.0965(2)	0.0327(10)
N6	0.3023(4)	0.40589(18)	0.2669(2)	0.0282(9)
N7	0.1829(4)	0.28194(18)	0.2164(3)	0.0294(9)
N8	0.1200(4)	0.41891(19)	0.1574(2)	0.0317(10)
C1	0.2203(5)	0.4524(2)	0.2096(3)	0.0265(10)
C2	-0.0936(6)	0.1747(3)	0.0365(3)	0.0405(13)
H2	-0.09560	0.11560	0.03210	0.049
C3	0.1048(5)	0.3343(2)	0.1626(3)	0.0271(11)
C4	0.1790(6)	0.6039(3)	0.1617(3)	0.0454(14)
H3	0.09920	0.58790	0.12780	0.054
C5	0.7679(5)	0.5364(2)	0.3625(3)	0.0346(12)
C6	0.5562(5)	0.2919(2)	0.4359(3)	0.0358(12)
H4	0.61880	0.32690	0.46800	0.043
C7	0.4645(6)	0.1537(3)	0.4083(3)	0.0451(13)
H5	0.46420	0.09530	0.41930	0.054
C8	0.2581(5)	0.5447(2)	0.2087(3)	0.0282(10)
C9	-0.0032(5)	0.2953(2)	0.1008(3)	0.0295(12)
C10	0.3107(5)	0.4617(3)	0.5175(3)	0.0373(11)

C11	0.5549(6)	0.2059(3)	0.4553(3)	0.0452(14)
H8	0.61490	0.18380	0.50000	0.054
C12	0.2794(5)	0.3207(2)	0.2665(3)	0.0251(10)
C13	0.4135(5)	0.6459(2)	0.2617(3)	0.0444(14)
H9	0.49510	0.66100	0.29440	0.053
C14	0.3383(6)	0.7092(2)	0.2175(4)	0.0462(15)
H10	0.36670	0.76580	0.22250	0.055
C15	-0.0885(5)	0.3462(3)	0.0482(3)	0.0377(12)
H11	-0.08310	0.40520	0.05270	0.045
C16	0.2220(7)	0.6877(3)	0.1664(4)	0.0523(18)
H551	0.17180	0.72950	0.13480	0.063
C17	0.3787(4)	0.27475(18)	0.3296(4)	0.0259(8)
C18	0.3721(4)	0.1886(2)	0.3432(4)	0.0380(12)
H788	0.30880	0.15460	0.31050	0.046
C19	-0.1829(7)	0.3082(3)	-0.0118(4)	0.0452(16)
H998	-0.24540	0.34100	-0.04650	0.054
C20	-0.1826(6)	0.2208(3)	-0.0192(4)	0.0441(14)
H999	-0.24160	0.19350	-0.06110	0.053

Table 5.2: Anisotropic displacement parameters of Aquadithiocyanato(2,4,6-tris(2-pyridyl)-1,3,5-triazine) Ni(II), $[Ni(SCN)_2(tptz)(H_2O]$ (5), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0305(3)	0.0232(2)	0.0326(3)	-0.0039(2)	-0.0009(4)	-0.0005(3)
S1	0.0415(10)	0.0521(6)	0.0802(12)	-0.0082(5)	-0.0005(10)	-0.0053(9)
S2	0.0927(13)	0.0505(8)	0.0379(8)	-0.0349(7)	0.0022(8)	-0.0060(6)
O1	0.054(3)	0.0320(15)	0.040(2)	-0.0124(13)	0.0159(17)	-0.0052(14)
N1	0.035(3)	0.0220(19)	0.039(2)	-0.0057(15)	0.0008(19)	-0.0019(16)
N2	0.027(3)	0.0241(16)	0.0325(19)	0.0010(15)	0.0035(19)	0.0040(13)
N3	0.039(4)	0.037(2)	0.051(3)	-0.0092(18)	-0.007(2)	-0.0166(17)
N4	0.054(4)	0.047(2)	0.037(3)	-0.001(2)	0.011(2)	-0.010(2)
N5	0.036(3)	0.0270(17)	0.035(2)	-0.0029(16)	0.0019(18)	-0.0002(15)
N6	0.030(3)	0.0207(17)	0.034(2)	-0.0033(15)	-0.0014(18)	0.0036(15)
N7	0.029(3)	0.0256(18)	0.033(2)	-0.0091(16)	0.0016(19)	0.0007(16)
N8	0.028(3)	0.0262(18)	0.041(2)	-0.0024(15)	-0.0045(19)	0.0040(17)
C1	0.030(3)	0.0250(19)	0.024(2)	-0.001(2)	-0.003(2)	0.001(2)
C2	0.047(4)	0.033(2)	0.041(3)	-0.007(2)	-0.004(3)	-0.008(2)
C3	0.025(3)	0.023(2)	0.033(3)	0.0000(18)	0.002(2)	0.0059(19)
C4	0.053(4)	0.026(2)	0.056(4)	-0.001(2)	-0.013(3)	0.007(2)
C5	0.035(3)	0.0245(19)	0.045(3)	0.000(2)	-0.008(2)	-0.007(2)
C6	0.034(4)	0.036(2)	0.037(3)	0.003(2)	-0.010(2)	0.0070(19)
C7	0.051(4)	0.033(2)	0.051(3)	0.001(3)	-0.007(3)	0.018(2)
C8	0.028(3)	0.0226(18)	0.034(3)	-0.002(2)	-0.004(2)	0.002(2)
C9	0.029(4)	0.026(2)	0.033(2)	-0.0028(18)	0.006(2)	0.0030(18)
C10	0.044(3)	0.027(2)	0.041(3)	-0.003(2)	-0.001(2)	-0.012(2)
C11	0.043(4)	0.045(3)	0.048(3)	0.006(2)	-0.013(3)	0.012(2)
C12	0.021(3)	0.025(2)	0.030(3)	-0.0056(17)	0.004(2)	-0.0042(19)
C13	0.051(4)	0.024(2)	0.058(3)	-0.007(2)	-0.011(3)	-0.001(2)
C14	0.055(4)	0.020(2)	0.064(4)	-0.006(2)	-0.004(3)	-0.004(2)
C15	0.039(4)	0.032(2)	0.042(3)	-0.003(2)	-0.007(3)	0.003(2)
C16	0.061(5)	0.025(3)	0.071(4)	0.007(3)	0.002(4)	0.014(2)

C17	0.025(2)	0.0198(16)	0.033(2)	-0.0050(14)	0.003(3)	0.004(3)
C18	0.037(3)	0.0277(18)	0.049(3)	-0.0029(17)	-0.007(3)	0.007(3)
C19	0.039(5)	0.045(3)	0.051(4)	0.001(3)	-0.015(3)	-0.001(3)
C20	0.043(4)	0.046(3)	0.044(3)	-0.001(2)	-0.004(3)	-0.007(2

Table 6.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of (pyridine-2,6-dicarboxylato k^3N,O,O')(tptz k^3N,N,N')nickel(II) pentahydrate, [Ni(2,6 pda)(tptz)]$(H_2O)_5$ (6).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.21514(8)	0.27925(7)	0.72435(4)	0.0459(2)
O1	0.4012(4)	0.0679(4)	0.7364(2)	0.0550(9)
C1	0.1004(7)	0.5312(6)	0.5829(3)	0.0660(16)
O2	0.0683(4)	0.4948(4)	0.6603(2)	0.0598(10)
C2	0.4762(7)	0.0474(6)	0.6702(3)	0.0540(13)
N1	-0.0513(5)	0.2155(4)	0.9351(2)	0.0465(10)
O3	0.5867(5)	-0.0674(4)	0.6626(3)	0.0812(13)
N2	0.3018(5)	0.2917(4)	0.6114(2)	0.0476(10)
N3	0.0420(5)	0.1950(5)	0.7225(2)	0.0498(10)
N4	-0.0117(5)	0.3029(5)	1.1249(2)	0.0530(11)
N5	0.1186(5)	0.3125(4)	0.9705(2)	0.0460(10)
O4	0.0318(7)	0.6477(5)	0.5332(3)	0.1067(19)
N6	0.1281(5)	0.2696(4)	0.8380(2)	0.0450(10)
C3	0.4226(6)	0.1769(6)	0.5951(3)	0.0493(13)
C4	0.2387(7)	0.4169(6)	0.5527(3)	0.0543(14)
N7	0.3471(5)	0.3563(4)	0.7840(2)	0.0483(10)
C5	0.0055(6)	0.2626(5)	0.9871(3)	0.0449(12)
C6	-0.0348(6)	0.1761(5)	0.7955(3)	0.0462(12)
C7	0.3086(6)	0.3573(5)	0.8649(3)	0.0437(11)
C8	-0.1472(6)	0.1183(6)	0.8080(3)	0.0543(13)
H1	-0.19710	0.10680	0.85900	0.065
C9	-0.0656(6)	0.2558(5)	1.0718(3)	0.0471(12)
C10	0.1781(6)	0.3117(5)	0.8945(3)	0.0417(11)
C11	0.2977(8)	0.4322(7)	0.4733(3)	0.0768(19)
H2	0.25420	0.51970	0.43270	0.092
C12	0.3845(6)	0.3980(6)	0.9145(3)	0.0532(13)

H3	0.35490	0.39840	0.96950	0.064
C13	0.0142(6)	0.2215(5)	0.8610(3)	0.0433(11)
C14	-0.1098(8)	0.0994(7)	0.6680(4)	0.0686(17)
H4	-0.13450	0.07460	0.62310	0.082
C15	-0.2371(7)	0.1877(6)	1.1740(3)	0.0652(16)
H5	-0.31240	0.14910	1.19050	0.078
C16	0.5440(7)	0.4396(6)	0.7982(4)	0.0634(16)
H5	0.62340	0.46830	0.77370	0.076
C17	-0.1792(6)	0.1976(6)	1.0937(3)	0.0546(13)
H6	-0.21480	0.16640	1.05540	0.066
C18	-0.1824(7)	0.2352(6)	1.2290(3)	0.0639(16)
H7	-0.21950	0.22950	1.28330	0.077
C19	0.0021(7)	0.1579(6)	0.6594(3)	0.0610(15)
H8	0.05100	0.17180	0.60820	0.073
C20	0.5053(7)	0.4379(6)	0.8800(4)	0.0631(15)
H9	0.56010	0.46340	0.91220	0.076
C21	-0.1831(7)	0.0783(7)	0.7421(4)	0.0657(16)
H10	-0.25670	0.03740	0.74850	0.079
C22	0.4858(8)	0.1856(7)	0.5160(3)	0.0727(18)
H11	0.56940	0.10550	0.50410	0.087
C23	0.4235(9)	0.3144(8)	0.4551(4)	0.085(2)
H12	0.46580	0.32220	0.40190	0.102
C24	-0.0713(7)	0.2914(6)	1.2016(3)	0.0613(15)
H13	-0.03490	0.32380	1.23910	0.074
C25	0.4627(6)	0.3979(6)	0.7528(3)	0.0565(14)
H14	0.49000	0.39870	0.69740	0.068
O5	-0.2320(5)	0.6227(5)	0.7209(3)	0.0669(11)
O6	0.2447(6)	0.3982(5)	1.1076(3)	0.0730(12)
O7	0.5530(7)	-0.0986(6)	0.8887(3)	0.0884(15)
O8	0.3224(6)	-0.0240(6)	1.0116(4)	0.0932(15)
O9	-0.1765(9)	0.9074(7)	0.5421(5)	0.139(2)
H15	0.245(7)	0.393(6)	1.1625(10)	0.073(18)

H16	0.384(7)	-0.043(8)	0.967(3)	0.10(3)
H18	0.553(12)	-0.053(10)	0.8345(18)	0.16(4)
H19	0.154(5)	0.392(9)	1.103(5)	0.12(3)
H20	0.593(10)	-0.189(4)	0.879(5)	0.13(3)
H21	-0.137(4)	0.614(8)	0.700(4)	0.11(3)
H22	-0.263(10)	0.721(2)	0.715(5)	0.13(3)
H23	-0.123(6)	0.963(5)	0.513(3)	0.054(16)
H17	0.361(8)	0.004(8)	1.048(3)	0.10(3)

Table 6.2: Anisotropic displacement parameters of (pyridine-2,6-dicarboxylato k^3N,O,O')(tptz k^3N,N,N')nickel(II) pentahydrate, [Ni(2,6 pda)(tptz)]$(H_2O)_5$ (6), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0489(4)	0.0471(4)	0.0391(3)	-0.0176(3)	0.0037(3)	-0.0097(3)
O1	0.061(2)	0.051(2)	0.0447(18)	-0.0167(18)	0.0017(18)	-0.0077(16)
C1	0.068(4)	0.050(3)	0.056(3)	-0.008(3)	0.002(3)	0.000(3)
O2	0.061(3)	0.054(2)	0.052(2)	-0.0117(19)	0.0089(19)	-0.0124(17)
C2	0.060(4)	0.048(3)	0.053(3)	-0.018(3)	-0.001(3)	-0.015(2)
N1	0.050(3)	0.056(2)	0.041(2)	-0.027(2)	0.006(2)	-0.0154(19)
O3	0.081(3)	0.054(2)	0.083(3)	0.001(2)	0.006(3)	-0.022(2)
N2	0.048(3)	0.046(2)	0.044(2)	-0.014(2)	0.001(2)	-0.0108(19)
N3	0.058(3)	0.055(2)	0.036(2)	-0.022(2)	-0.002(2)	-0.0102(18)
N4	0.063(3)	0.059(3)	0.043(2)	-0.030(2)	0.007(2)	-0.016(2)
N5	0.050(3)	0.049(2)	0.044(2)	-0.025(2)	0.004(2)	-0.0120(18)
O4	0.114(4)	0.064(3)	0.073(3)	0.015(3)	0.009(3)	0.013(2)
N6	0.045(3)	0.049(2)	0.044(2)	-0.022(2)	0.000(2)	-0.0106(19)
C3	0.051(3)	0.050(3)	0.045(3)	-0.016(3)	0.005(2)	-0.015(2)
C4	0.062(4)	0.049(3)	0.043(3)	-0.017(3)	0.001(3)	-0.006(2)
N7	0.048(3)	0.045(2)	0.049(2)	-0.018(2)	0.007(2)	-0.0115(19)
C5	0.046(3)	0.046(3)	0.043(2)	-0.019(2)	0.001(2)	-0.010(2)
C6	0.049(3)	0.047(3)	0.043(2)	-0.019(3)	0.001(2)	-0.012(2)
C7	0.040(3)	0.042(3)	0.045(3)	-0.015(2)	0.000(2)	-0.009(2)
C8	0.049(3)	0.061(3)	0.057(3)	-0.025(3)	0.000(3)	-0.016(3)
C9	0.054(3)	0.046(3)	0.039(2)	-0.019(3)	0.004(2)	-0.008(2)
C10	0.044(3)	0.044(3)	0.038(2)	-0.019(2)	0.004(2)	-0.010(2)
C11	0.094(5)	0.071(4)	0.045(3)	-0.022(4)	0.012(3)	-0.003(3)
C12	0.057(4)	0.058(3)	0.053(3)	-0.031(3)	0.002(3)	-0.014(2)
C13	0.043(3)	0.045(3)	0.042(2)	-0.018(2)	0.002(2)	-0.011(2)
C14	0.076(5)	0.082(4)	0.060(3)	-0.033(4)	-0.012(3)	-0.029(3)
C15	0.069(4)	0.067(4)	0.062(3)	-0.034(3)	0.017(3)	-0.015(3)
C16	0.057(4)	0.068(4)	0.076(4)	-0.038(3)	0.018(3)	-0.021(3)

C17	0.060(4)	0.061(3)	0.051(3)	-0.033(3)	0.007(3)	-0.015(2)
C18	0.073(4)	0.061(3)	0.050(3)	-0.022(3)	0.013(3)	-0.011(3)
C19	0.073(4)	0.067(4)	0.046(3)	-0.029(3)	-0.005(3)	-0.015(3)
C20	0.060(4)	0.066(4)	0.076(4)	-0.037(3)	-0.002(3)	-0.017(3)
C21	0.062(4)	0.081(4)	0.069(4)	-0.036(4)	-0.004(3)	-0.027(3)
C22	0.080(5)	0.068(4)	0.052(3)	-0.010(3)	0.010(3)	-0.019(3)
C23	0.099(6)	0.085(5)	0.046(3)	-0.018(4)	0.020(4)	-0.013(3)
C24	0.080(4)	0.062(3)	0.044(3)	-0.029(3)	0.006(3)	-0.017(3)
C25	0.054(4)	0.063(3)	0.056(3)	-0.031(3)	0.016(3)	-0.015(3)
O5	0.067(3)	0.071(3)	0.061(2)	-0.031(2)	0.009(2)	-0.012(2)
O6	0.081(3)	0.098(3)	0.060(3)	-0.055(3)	0.006(2)	-0.023(2)
O7	0.100(4)	0.088(3)	0.058(3)	-0.014(3)	-0.011(3)	-0.020(3)
O8	0.084(4)	0.098(4)	0.115(4)	-0.048(3)	0.019(3)	-0.041(3)
O9	0.140(6)	0.093(4)	0.164(6)	-0.034(4)	0.037(5)	-0.035(4)

Table 7.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ (7).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.16092(8)	-0.04196(8)	0.17171()	0.0335(4)
C12	0.0986(6)	-0.0143(6)	0.2721(4)	0.031(2)
C14	0.0763(6)	0.1229(6)	0.3098(4)	0.034(2)
C16	0.1304(6)	0.1215(6)	0.2341(4)	0.034(2)
C22	0.1722(7)	-0.0950(7)	0.0498(4)	0.041(3)
H22	0.13970	-0.04490	0.03780	0.049
C23	0.1940(7)	-0.1426(8)	0.0066(5)	0.048(3)
H23	0.17960	-0.12230	-0.03310	0.057
C24	0.2386(6)	-0.2228(6)	0.0233(4)	0.030(2)
C25	0.2589(7)	-0.2473(7)	0.0825(5)	0.046(3)
H25	0.28700	-0.30070	0.09520	0.055
C26	0.2376(7)	-0.1925(6)	0.1240(5)	0.044(3)
H26	0.25370	-0.20960	0.16440	0.052
C121	0.1012(6)	-0.1149(6)	0.2686(4)	0.030(2)
C123	0.1253(7)	-0.2400(7)	0.2161(5)	0.047(3)
H123	0.13800	-0.26470	0.18350	0.056
C124	0.1075(8)	-0.3003(7)	0.2573(6)	0.055(3)
H124	0.10980	-0.36380	0.25200	0.067
C125	0.0872(7)	-0.2672(7)	0.3039(5)	0.049(3)
H125	0.07620	-0.30720	0.33150	0.059
C126	0.0825(7)	-0.1696(7)	0.3110(5)	0.044(3)
H126	0.06770	-0.14410	0.34250	0.053
C141	0.0481(6)	0.1780(6)	0.3525(4)	0.035(2)
C143	-0.0033(7)	0.1772(8)	0.4312(5)	0.053(3)
H143	-0.02420	0.14520	0.45710	0.063
C144	0.0026(9)	0.2708(8)	0.4373(6)	0.066(4)
H144	-0.01140	0.30100	0.46770	0.079
C145	0.0301(10)	0.3194(8)	0.3970(7)	0.081(5)

H145	0.03370	0.38340	0.39910	0.097
C146	0.0520(8)	0.2717(7)	0.3536(6)	0.056(4)
H146	0.06930	0.30340	0.32540	0.067
C161	0.1644(6)	0.1629(6)	0.1894(4)	0.035(2)
C163	0.2122(7)	0.1350(8)	0.1115(5)	0.048(3)
H163	0.22530	0.09410	0.08540	0.057
C164	0.2239(8)	0.2290(8)	0.1048(5)	0.060(4)
H164	0.24510	0.25020	0.07570	0.072
C165	0.2030(8)	0.2891(7)	0.1424(6)	0.054(3)
H165	0.20980	0.35220	0.13900	0.065
C166	0.1715(8)	0.2555(7)	0.1862(5)	0.050(3)
H166	0.15620	0.29500	0.21180	0.06
N1	0.1265(5)	0.0281(5)	0.2321(3)	0.0334(19)
N2	0.0715(5)	0.0294(5)	0.3116(4)	0.0350(18)
N3	0.1055(5)	0.1712(5)	0.2730(4)	0.035(2)
N4	0.1956(5)	-0.1173(5)	0.1089(4)	0.035(2)
N5	0.287(4)	0.042(2)	0.3828(1)	0.45(5)
N6	-0.0861(15)	-0.2056(15)	0.0483(1)	0.67(9)
N7	0.1248(5)	-0.1485(5)	0.2224(4)	0.038(2)
N8	0.0189(5)	0.1286(6)	0.3908(4)	0.038(2)
N9	0.1831(5)	0.1002(5)	0.1538(4)	0.036(2)
O1	0.2704(4)	-0.0512(5)	0.2304(3)	0.0484(18)
O2	0.0530(4)	-0.0361(5)	0.1098(3)	0.0492(18)
O3	0.3954(14)	-0.0197(8)	0.1871(1)	0.265(17)
O4	0.2354(15)	-0.003(5)	0.394(4)	1.18(15)
O5	0.325(5)	0.030(6)	0.437(2)	1.9(2)
O6	0.3024(10)	0.0649(9)	0.3366(9)	0.149(7)
O7	-0.1207(19)	-0.280(2)	0.0381(1)	0.38(3)
O8	-0.0982(10)	-0.1224(15)	0.0383(7)	0.174(9)
O9	-0.0167(14)	-0.2091(12)	0.0727(1)	0.172(9)

Table 7.2: Anisotropic displacement parameters of $[Ni_2(4,4'\text{-bipy})(tptz)_2(H_2O)_4](NO_3)_4(H_2O)_2$ (7), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0464(8)	0.0277(6)	0.0336(6)	0.0027(7)	0.0228(5)	-0.0048(6)
C12	0.038(6)	0.032(5)	0.030(4)	-0.006(4)	0.022(4)	-0.004(3)
C14	0.043(6)	0.032(5)	0.032(5)	-0.010(4)	0.019(5)	-0.008(4)
C16	0.050(7)	0.025(4)	0.033(5)	0.000(4)	0.020(5)	-0.006(4)
C22	0.052(7)	0.042(5)	0.031(5)	0.017(5)	0.016(5)	-0.010(4)
C23	0.053(8)	0.054(6)	0.039(6)	0.025(6)	0.019(5)	0.008(5)
C24	0.033(6)	0.035(5)	0.025(4)	0.007(4)	0.013(4)	-0.011(4)
C25	0.057(8)	0.046(6)	0.041(6)	0.021(5)	0.023(6)	0.007(5)
C26	0.068(8)	0.036(5)	0.038(5)	0.020(5)	0.034(6)	-0.001(4)
C121	0.040(6)	0.027(4)	0.028(4)	0.005(4)	0.017(4)	0.001(4)
C123	0.066(8)	0.031(5)	0.054(7)	0.006(5)	0.035(6)	-0.006(5)
C124	0.078(10)	0.029(5)	0.071(8)	0.001(5)	0.041(8)	0.002(5)
C125	0.061(8)	0.035(5)	0.056(7)	-0.001(5)	0.024(6)	0.015(5)
C126	0.051(8)	0.039(5)	0.046(6)	-0.002(5)	0.020(6)	0.003(5)
C141	0.035(6)	0.036(5)	0.036(5)	-0.002(4)	0.015(5)	-0.013(4)
C143	0.064(9)	0.056(7)	0.051(7)	-0.005(6)	0.036(7)	-0.016(5)
C144	0.092(12)	0.054(7)	0.068(9)	-0.005(7)	0.050(9)	-0.030(6)
C145	0.128(15)	0.037(6)	0.106(12)	0.000(7)	0.081(12)	-0.017(7)
C146	0.083(10)	0.039(6)	0.065(8)	-0.004(6)	0.053(8)	-0.016(5)
C161	0.046(7)	0.025(4)	0.034(5)	-0.007(4)	0.012(5)	0.000(3)
C163	0.068(9)	0.049(6)	0.037(6)	0.004(6)	0.032(6)	0.015(5)
C164	0.092(11)	0.053(7)	0.048(7)	-0.016(7)	0.040(7)	-0.001(5)
C165	0.076(10)	0.030(5)	0.066(8)	-0.016(6)	0.034(7)	0.001(5)
C166	0.077(9)	0.038(5)	0.045(6)	-0.018(6)	0.033(7)	-0.015(4)
N1	0.047(5)	0.033(4)	0.027(4)	0.000(4)	0.021(4)	-0.001(3)
N2	0.042(5)	0.030(4)	0.038(4)	0.000(4)	0.020(4)	-0.002(3)
N3	0.042(6)	0.027(4)	0.041(5)	-0.002(4)	0.019(4)	-0.004(3)
N4	0.038(5)	0.037(4)	0.038(4)	0.009(4)	0.021(4)	-0.006(3)
N5	0.95(14)	0.22(3)	0.35(5)	0.36(6)	0.46(8)	0.22(4)

N6	1.5(2)	0.39(6)	0.17(4)	0.64(11)	0.42(8)	0.16(4)
N7	0.055(6)	0.026(4)	0.038(4)	0.000(4)	0.021(4)	0.001(3)
N8	0.045(6)	0.044(5)	0.031(4)	0.000(4)	0.018(4)	-0.005(3)
N9	0.044(5)	0.035(4)	0.036(4)	0.001(4)	0.023(4)	-0.002(3)
O1	0.053(5)	0.048(4)	0.045(4)	0.005(4)	0.014(4)	0.003(3)
O2	0.049(5)	0.049(4)	0.054(4)	-0.002(4)	0.022(4)	-0.007(4)
O3	0.38(3)	0.057(7)	0.53(4)	-0.052(11)	0.41(3)	-0.093(13)
O4	0.036(16)	1.3(2)	2.0(3)	0.01(5)	-0.04(6)	-1.0(2)
O5	2.0(2)	2.0(2)	0.65(9)	2.0(2)	-1.00(13)	-1.00(13)
O6	0.127(13)	0.078(9)	0.207(19)	-0.005(8)	-0.002(13)	-0.061(11)
O7	0.32(4)	0.68(8)	0.14(2)	-0.36(5)	0.08(2)	-0.12(3)
O8	0.126(14)	0.32(3)	0.078(10)	-0.063(16)	0.031(10)	-0.065(14)
O9	0.31(3)	0.119(13)	0.121(16)	-0.067(15)	0.122(18)	-0.023(11)

Table 8.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of tris(1,10-Phenanthroline-*N,N'*) nickel(II) bis(tetrafluoroborate) monohydrate, $[Ni(Phen)_3](BF_4)_2(H_2O)$ (8).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.96948(6)	0.23192(5)	0.27406(4)	0.04361(19)
C1	0.9685(6)	0.0390(4)	0.1542(3)	0.0620(13)
C2	0.7485(7)	0.1109(5)	0.1345(4)	0.0784(17)
H1	0.68930	0.16620	0.14650	0.094
C3	0.6951(10)	0.0254(7)	0.0763(5)	0.103(2)
H2	0.60110	0.02360	0.05100	0.123
C4	0.7779(11)	-0.0557(7)	0.0557(5)	0.104(3)
H3	0.74160	-0.11400	0.01710	0.125
C5	0.9229(9)	-0.0499(5)	0.0946(4)	0.087(2)
C6	1.0208(14)	-0.1298(6)	0.0785(6)	0.119(3)
H4	0.99130	-0.18930	0.03960	0.143
C7	1.1549(13)	-0.1218(6)	0.1180(7)	0.118(3)
H5	1.21670	-0.17530	0.10490	0.141
C8	1.2048(8)	-0.0328(5)	0.1798(5)	0.087(2)
C9	1.3407(9)	-0.0194(7)	0.2257(7)	0.113(3)
H6	1.40660	-0.07100	0.21690	0.136
C10	1.3768(6)	0.0686(7)	0.2831(6)	0.099(2)
H7	1.46800	0.07820	0.31270	0.119
C11	1.2740(5)	0.1456(5)	0.2974(4)	0.0752(16)
H8	1.29800	0.20450	0.33820	0.09
C12	1.1096(6)	0.0487(4)	0.1973(4)	0.0627(13)
C13	0.9473(6)	0.4172(4)	0.1806(3)	0.0550(11)
C14	1.1742(6)	0.3553(5)	0.1492(3)	0.0687(14)
H9	1.23950	0.30370	0.15230	0.082
C15	1.2165(8)	0.4428(7)	0.1038(4)	0.093(2)
H10	1.31030	0.45120	0.07970	0.112
C16	1.1178(9)	0.5162(6)	0.0952(4)	0.092(2)

H11	1.14330	0.57340	0.06310	0.111
C17	0.9781(7)	0.5058(5)	0.1344(3)	0.0740(15)
C18	0.8679(10)	0.5768(5)	0.1280(4)	0.093(2)
H12	0.88760	0.63530	0.09640	0.112
C19	0.7349(9)	0.5616(5)	0.1668(4)	0.0833(18)
H13	0.66350	0.60800	0.15910	0.1
C20	0.7025(6)	0.4767(4)	0.2187(4)	0.0672(14)
C21	0.5728(6)	0.4612(5)	0.2675(5)	0.0810(18)
H14	0.49840	0.50610	0.26380	0.097
C22	0.5562(6)	0.3818(6)	0.3193(5)	0.0816(18)
H15	0.47160	0.37290	0.35290	0.098
C23	0.6652(5)	0.3131(4)	0.3228(4)	0.0656(14)
H16	0.65180	0.25850	0.35910	0.079
C24	0.8097(5)	0.4041(4)	0.2252(3)	0.0532(11)
C25	0.9409(5)	0.1877(4)	0.4579(3)	0.0551(12)
C26	0.8109(5)	0.0511(4)	0.3704(4)	0.0669(14)
H17	0.77980	0.01940	0.31440	0.08
C27	0.7686(7)	-0.0005(6)	0.4449(6)	0.095(2)
H18	0.71080	-0.06490	0.43850	0.113
C28	0.8136(8)	0.0455(6)	0.5264(5)	0.097(2)
H19	0.78410	0.01360	0.57680	0.116
C29	0.9039(7)	0.1403(6)	0.5353(4)	0.0776(17)
C30	0.9585(10)	0.1944(8)	0.6189(4)	0.105(2)
H20	0.93510	0.16460	0.67120	0.126
C31	1.0403(9)	0.2845(9)	0.6231(4)	0.110(3)
H21	1.07430	0.31640	0.67850	0.131
C32	1.0797(6)	0.3361(5)	0.5457(4)	0.0741(16)
C33	1.1663(7)	0.4317(6)	0.5461(5)	0.092(2)
H22	1.20280	0.46680	0.59990	0.111
C34	1.1985(6)	0.4748(5)	0.4693(5)	0.0838(19)
H23	1.25470	0.53950	0.46990	0.101
C35	1.1449(5)	0.4191(4)	0.3890(4)	0.0645(13)

H24	1.16750	0.44770	0.33600	0.077
C36	1.0298(5)	0.2854(4)	0.4631(3)	0.0533(11)
N1	0.8805(5)	0.1180(3)	0.1741(3)	0.0599(10)
N2	1.1464(4)	0.1366(3)	0.2549(3)	0.0571(10)
N3	1.0433(4)	0.3428(3)	0.1883(2)	0.0551(9)
N4	0.7894(4)	0.3225(3)	0.2756(3)	0.0514(9)
N5	0.8922(4)	0.1418(3)	0.3758(3)	0.0506(9)
N6	1.0627(4)	0.3267(3)	0.3856(2)	0.0492(9)
B2	0.5454(11)	0.2848(10)	0.0022(6)	0.107(3)
B1	1.5058(12)	0.295(3)	0.5508(10)	0.31(2)
F1	1.4221(14)	0.2923(11)	0.6200(7)	0.293(6)
F2	1.6343(9)	0.2877(9)	0.5458(9)	0.287(6)
F3	1.5345(13)	0.1807(10)	0.6114(7)	0.260(5)
F4	1.4286(13)	0.2222(9)	0.4896(5)	0.260(5)
F5	0.5292(7)	0.2104(10)	-0.0616(7)	0.302(7)
F6	0.4759(6)	0.2518(6)	0.0763(4)	0.172(3)
F7	0.6947(6)	0.3008(4)	0.0187(3)	0.1263(15)
F8	0.4859(17)	0.3591(13)	-0.0175(7)	0.393(11)
O1	1.3370(9)	0.1564(7)	0.7678(5)	0.165(3)

Table 8.2: Anisotropic displacement parameters of tris(1,10-Phenanthroline-*N,N'*) nickel(II) bis(tetrafluoroborate) monohydrate, $[Ni(Phen)_3](BF_4)_2(H_2O)$ (8), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0461(2)	0.0510(2)	0.0472(2)	0.0002(2)	0.03001(17)	0.0004(2)
C1	0.0490(17)	0.0474(18)	0.0417(16)	0.0065(14)	0.0280(14)	0.0039(14)
C2	0.0530(19)	0.062(2)	0.065(2)	-0.0012(17)	0.0408(18)	-0.0020(18)
C3	0.0508(19)	0.069(2)	0.063(2)	-0.0050(18)	0.0346(18)	-0.0005(19)
C4	0.0546(19)	0.061(2)	0.055(2)	-0.0059(17)	0.0307(17)	-0.0037(17)
C5	0.0547(18)	0.053(2)	0.0459(18)	0.0036(16)	0.0293(16)	0.0036(15)
C6	0.069(2)	0.064(2)	0.0476(19)	0.0026(19)	0.0339(18)	-0.0049(17)
C7	0.079(3)	0.066(2)	0.055(2)	0.010(2)	0.046(2)	-0.0018(18)
C8	0.065(2)	0.063(2)	0.0509(19)	0.0102(18)	0.0404(18)	0.0072(17)
C9	0.0531(18)	0.051(2)	0.057(2)	0.0021(15)	0.0385(17)	-0.0007(16)
C10	0.0531(19)	0.067(2)	0.054(2)	-0.0044(17)	0.0304(17)	-0.0015(17)
C11	0.058(2)	0.077(3)	0.063(2)	-0.011(2)	0.0335(19)	-0.013(2)
C12	0.061(2)	0.064(2)	0.085(3)	-0.0150(19)	0.046(2)	-0.014(2)
C13	0.062(2)	0.056(2)	0.078(3)	-0.0016(17)	0.051(2)	-0.0005(19)
C14	0.091(3)	0.063(3)	0.100(3)	-0.004(2)	0.073(3)	0.007(2)
C15	0.089(3)	0.071(3)	0.077(3)	0.004(2)	0.061(3)	0.016(2)
C16	0.073(2)	0.065(2)	0.063(2)	0.0093(19)	0.051(2)	0.0105(18)
C17	0.0493(17)	0.0490(19)	0.0570(19)	-0.0166(15)	0.0354(16)	-0.0136(16)
C18	0.057(2)	0.057(2)	0.070(2)	0.0060(17)	0.0397(19)	0.0028(18)
C19	0.063(2)	0.066(3)	0.092(3)	0.0042(19)	0.051(2)	-0.004(2)
C20	0.066(2)	0.061(2)	0.099(3)	-0.011(2)	0.061(2)	-0.022(2)
C21	0.060(2)	0.061(2)	0.067(2)	-0.0231(18)	0.0466(19)	-0.0216(18)
C22	0.087(3)	0.086(3)	0.071(3)	-0.028(3)	0.060(2)	-0.024(2)
C23	0.080(3)	0.086(3)	0.052(2)	-0.027(2)	0.044(2)	-0.012(2)
C24	0.0563(19)	0.067(2)	0.0483(19)	-0.0203(18)	0.0297(17)	-0.0048(18)
C25	0.0477(17)	0.0484(19)	0.0472(17)	0.0037(15)	0.0304(15)	0.0025(15)
C26	0.0483(18)	0.064(2)	0.056(2)	0.0132(17)	0.0322(16)	0.0092(17)
C27	0.0392(16)	0.076(3)	0.055(2)	0.0035(17)	0.0234(15)	0.0029(18)

C28	0.0470(18)	0.062(2)	0.0560(19)	-0.0099(16)	0.0310(16)	-0.0074(17)
C29	0.0496(17)	0.0491(19)	0.0481(17)	-0.0023(15)	0.0314(15)	-0.0029(15)
C30	0.067(2)	0.084(3)	0.067(2)	0.018(2)	0.051(2)	0.010(2)
C31	0.058(2)	0.097(3)	0.076(3)	0.010(2)	0.048(2)	0.004(2)
C32	0.0519(19)	0.079(3)	0.068(2)	-0.0006(18)	0.0405(19)	-0.002(2)
C33	0.0519(18)	0.056(2)	0.0445(17)	0.0072(16)	0.0323(15)	0.0072(16)
C34	0.081(3)	0.091(3)	0.052(2)	0.013(2)	0.042(2)	0.018(2)
C35	0.065(2)	0.095(3)	0.049(2)	0.005(2)	0.0319(19)	0.008(2)
C36	0.0543(19)	0.081(3)	0.0456(19)	-0.0004(18)	0.0282(17)	0.0011(18)
C37	0.0553(19)	0.056(2)	0.053(2)	0.0041(16)	0.0381(17)	0.0014(16)
C38	0.067(2)	0.084(3)	0.050(2)	-0.018(2)	0.0288(19)	0.007(2)
C39	0.055(2)	0.074(3)	0.070(3)	0.000(2)	0.028(2)	0.022(2)
C40	0.0538(19)	0.061(2)	0.065(2)	0.0088(17)	0.0331(18)	0.0118(19)
C41	0.0456(16)	0.051(2)	0.0442(17)	-0.0128(14)	0.0264(14)	-0.0053(14)
C42	0.063(2)	0.048(2)	0.062(2)	0.0029(17)	0.0385(19)	0.0016(17)
C43	0.057(2)	0.050(2)	0.055(2)	0.0016(17)	0.0339(18)	0.0003(16)
N1	0.0465(14)	0.0532(16)	0.0481(15)	0.0033(12)	0.0310(12)	0.0026(12)
N2	0.0494(14)	0.0557(17)	0.0474(15)	0.0020(13)	0.0304(13)	0.0007(13)
N3	0.0497(14)	0.0478(16)	0.0544(16)	-0.0002(12)	0.0334(13)	0.0011(13)
N4	0.0455(14)	0.0461(16)	0.0490(15)	0.0024(12)	0.0272(12)	0.0011(12)
N5	0.0504(14)	0.0594(18)	0.0531(16)	0.0013(13)	0.0343(13)	0.0013(14)
N6	0.0521(15)	0.0604(18)	0.0492(16)	-0.0001(14)	0.0316(13)	0.0017(13)
N7	0.0480(14)	0.0524(17)	0.0505(15)	0.0004(13)	0.0295(13)	0.0030(13)
O1	0.0863(18)	0.0747(18)	0.089(2)	-0.0028(15)	0.0579(17)	-0.0079(16)
O2	0.0635(15)	0.0759(18)	0.0587(15)	0.0065(14)	0.0249(13)	-0.0007(13)
O3	0.141(3)	0.094(2)	0.087(2)	-0.003(2)	0.066(2)	0.0002(19)
O4	0.0791(17)	0.0645(16)	0.0668(16)	0.0028(14)	0.0461(14)	-0.0059(13)
O5	0.119(4)	0.126(4)	0.133(4)	0.00000	0.096(4)	0.00000
O6	0.098(2)	0.181(4)	0.120(3)	-0.029(3)	0.068(2)	-0.015(3)
O7	0.169(4)	0.296(8)	0.193(5)	0.004(5)	0.141(4)	0.033(5)
O8	0.0796(18)	0.093(2)	0.0684(17)	0.0048(16)	0.0425(15)	0.0130(15)
O9	0.111(2)	0.116(3)	0.115(3)	0.006(2)	0.077(2)	0.016(2)

O10	0.141(3)	0.117(3)	0.278(6)	-0.037(3)	0.156(4)	-0.065(4)
O11	0.134(4)	0.328(8)	0.155(4)	0.084(4)	0.110(3)	0.062(5)
O12	0.0797(17)	0.0476(15)	0.0759(18)	0.0085(13)	0.0406(15)	0.0089(13)
O13	0.0629(15)	0.0553(16)	0.0674(16)	-0.0032(12)	0.0217(13)	-0.0019(13)
O14	0.0569(14)	0.0512(15)	0.0804(18)	0.0054(12)	0.0269(13)	0.0013(13)
O15	0.0706(16)	0.0462(14)	0.0851(18)	-0.0076(13)	0.0432(15)	-0.0099(13)

Table 9.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of $[Ni(Cl)(Phen)_2(H_2O)](Cl)(H_2O)_2$ (9).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.74802(2)	-0.00201(2)	0.07209(2)	0.02682(16)
C1	0.69945(13)	-0.12726(17)	-0.02880(18)	0.0307(7)
C2	0.63065(15)	-0.08873(19)	-0.0141(2)	0.0377(8)
H1	0.61990	-0.05790	0.00880	0.045
C3	0.59026(16)	-0.1408(2)	-0.0665(2)	0.0437(9)
H2	0.55330	-0.14440	-0.07780	0.052
C4	0.60446(15)	-0.1866(2)	-0.1014(2)	0.0413(9)
H3	0.57730	-0.22140	-0.13690	0.05
C5	0.66072(15)	-0.18050(18)	-0.08286(19)	0.0354(8)
C6	0.68098(17)	-0.2269(2)	-0.1151(2)	0.0427(9)
H4	0.65540	-0.26220	-0.15150	0.051
C7	0.73609(18)	-0.2199(2)	-0.0935(2)	0.0462(10)
H5	0.74790	-0.25050	-0.11540	0.055
C8	0.77677(16)	-0.16635(19)	-0.0377(2)	0.0399(8)
C9	0.79939(14)	0.12370(18)	0.0597(2)	0.0327(7)
C10	0.86145(15)	0.0885(2)	0.1957(2)	0.0417(9)
H6	0.87040	0.05760	0.23630	0.05
C11	0.90106(17)	0.1447(2)	0.2178(2)	0.0533(12)
H7	0.93500	0.15130	0.27250	0.064
C12	0.88954(17)	0.1893(2)	0.1587(3)	0.0555(12)
H8	0.91630	0.22550	0.17260	0.067
C13	0.83727(16)	0.18018(19)	0.0773(2)	0.0439(10)
C14	0.8193(2)	0.2254(2)	0.0099(3)	0.0544(12)
H9	0.84440	0.26230	0.01980	0.065
C15	0.7678(2)	0.2155(2)	-0.0657(3)	0.0558(13)
H10	0.75750	0.24600	-0.10730	0.067
C16	0.72800(17)	0.1600(2)	-0.0851(2)	0.0430(9)

C17	0.71924(14)	0.03569(18)	0.1777(2)	0.0532(11)
C18	0.66111(16)	0.10363(19)	0.0610(2)	0.064
H11	0.64810	0.11500	0.00900	0.0543(12)
C19	0.63687(17)	0.1406(2)	0.0911(3)	0.065
H12	0.60920	0.17660	0.06040	0.0449(10)
C20	0.65407(17)	0.1235(2)	0.1654(3)	0.054
H13	0.63800	0.14750	0.18600	0.0319(7)
C21	0.69609(15)	0.06959(19)	0.2117(2)	0.0535(12)
C22	0.7171(2)	0.0464(2)	0.2908(3)	0.064
H14	0.70140	0.06730	0.31350	0.0521(12)
C23	0.75818(18)	-0.0038(2)	0.3327(2)	0.062
H15	0.77110	-0.01650	0.38430	0.0413(9)
C24	0.78311(15)	-0.0387(2)	0.3000(2)	0.05
C25	0.61373(13)	-0.31421(17)	0.12703(19)	0.0320(7)
C26	0.67616(14)	-0.3174(2)	0.1866(2)	0.0296(6)
H16	0.69560	-0.36030	0.20840	0.0314(6)
C27	0.70883(14)	-0.2561(2)	0.2128(2)	0.0325(6)
H17	0.75080	-0.25710	0.25130	0.0305(6)
C28	0.67864(14)	-0.1931(2)	0.1813(2)	0.0367(6)
H18	0.69990	-0.15110	0.19770	0.260(7)
C29	0.61622(14)	-0.19355(17)	0.12472(19)	0.367(13)
C30	0.83583(17)	-0.1575(2)	-0.0106(2)	0.0394(2)
H19	0.85070	-0.18820	-0.02840	0.0475(3)
C31	0.87085(18)	-0.1041(2)	0.0414(3)	0.02682(16)
H20	0.90950	-0.09740	0.05860	0.0307(7)
C32	0.84846(15)	-0.0592(2)	0.0688(2)	0.0377(8)
H21	0.87300	-0.02310	0.10480	0.045
C33	0.75813(14)	-0.11898(18)	-0.00651(19)	0.0437(9)
C34	0.67231(19)	0.1477(2)	-0.1636(2)	0.052
H22	0.65900	0.17810	-0.20670	0.0413(9)
C35	0.63808(18)	0.0918(2)	-0.1768(2)	0.05
H23	0.60150	0.08360	-0.22890	0.0354(8)

C36	0.65785(15)	0.0472(2)	-0.1123(2)	0.0427(9)
H24	0.63410	0.00870	-0.12230	0.051
C37	0.74456(15)	0.11282(18)	-0.0227(2)	0.0462(10)
C38	0.82575(18)	-0.0925(2)	0.3397(2)	0.055
H25	0.83990	-0.10780	0.39120	0.0399(8)
C39	0.84679(17)	-0.1228(2)	0.3036(3)	0.0327(7)
H26	0.87450	-0.15940	0.32970	0.0417(9)
C40	0.82611(15)	-0.09828(19)	0.2268(2)	0.05
H27	0.84150	-0.11820	0.20320	0.0533(12)
C41	0.76368(13)	-0.01829(16)	0.22252(19)	0.064
C42	0.57622(16)	-0.38045(19)	0.0902(2)	0.0555(12)
C43	0.58007(15)	-0.12557(18)	0.0904(2)	0.067
N1	0.68456(11)	-0.08122(14)	0.00474(16)	0.0439(10)
N2	0.81175(11)	0.07838(14)	0.11850(16)	0.0544(12)
N3	0.70172(11)	0.05319(14)	0.10265(16)	0.065
N4	0.58427(11)	-0.25316(14)	0.09707(16)	0.0558(13)
N5	0.79335(12)	-0.06597(15)	0.04537(17)	0.067
N6	0.70984(12)	0.05711(15)	-0.03597(17)	0.0430(9)
N7	0.78531(11)	-0.04757(14)	0.18649(16)	0.0532(11)
O1	0.47752(12)	-0.46333(15)	-0.10860(18)	0.064
O2	0.46431(11)	-0.25091(14)	-0.06490(16)	0.0543(12)
O3	0.45569(18)	-0.23896(18)	-0.1999(2)	0.065
O4	0.46870(11)	-0.03349(14)	-0.09366(15)	0.0449(10)
O5	1/2	-0.0159(3)	-1/4	0.054
O6	0.53416(16)	0.0636(3)	-0.1175(2)	0.0319(7)
O7	0.5184(3)	0.2178(4)	-0.1140(4)	0.0535(12)
O8	0.57554(12)	-0.09630(16)	-0.25933(17)	0.064
O9	0.95633(16)	-0.1223(2)	0.2623(2)	0.0521(12)
O10	0.9680(2)	0.0415(2)	0.1624(4)	0.062
O11	0.9402(2)	0.1502(4)	0.0544(3)	0.0413(9)
O12	0.60010(12)	-0.43589(13)	0.12938(17)	0.05
O13	0.52331(11)	-0.37465(14)	0.02254(16)	0.0320(7)

O14	0.52384(11)	-0.13082(13)	0.03301(17)	0.0296(6)
O15	0.60868(11)	-0.06998(13)	0.12087(17)	0.0314(6)

Table 9.2: Anisotropic displacement parameters of $[Ni(Cl)(Phen)_2(H_2O)](Cl)(H_2O)_2$ (9), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0461(2)	0.0510(2)	0.0472(2)	0.0002(2)	0.03001(17)	0.0004(2)
C1	0.0490(17)	0.0474(18)	0.0417(16)	0.0065(14)	0.0280(14)	0.0039(14)
C2	0.0530(19)	0.062(2)	0.065(2)	-0.0012(17)	0.0408(18)	-0.0020(18)
C3	0.0508(19)	0.069(2)	0.063(2)	-0.0050(18)	0.0346(18)	-0.0005(19)
C4	0.0546(19)	0.061(2)	0.055(2)	-0.0059(17)	0.0307(17)	-0.0037(17)
C5	0.0547(18)	0.053(2)	0.0459(18)	0.0036(16)	0.0293(16)	0.0036(15)
C6	0.069(2)	0.064(2)	0.0476(19)	0.0026(19)	0.0339(18)	-0.0049(17)
C7	0.079(3)	0.066(2)	0.055(2)	0.010(2)	0.046(2)	-0.0018(18)
C8	0.065(2)	0.063(2)	0.0509(19)	0.0102(18)	0.0404(18)	0.0072(17)
C9	0.0531(18)	0.051(2)	0.057(2)	0.0021(15)	0.0385(17)	-0.0007(16)
C10	0.0531(19)	0.067(2)	0.054(2)	-0.0044(17)	0.0304(17)	-0.0015(17)
C11	0.058(2)	0.077(3)	0.063(2)	-0.011(2)	0.0335(19)	-0.013(2)
C12	0.061(2)	0.064(2)	0.085(3)	-0.0150(19)	0.046(2)	-0.014(2)
C13	0.062(2)	0.056(2)	0.078(3)	-0.0016(17)	0.051(2)	-0.0005(19)
C14	0.091(3)	0.063(3)	0.100(3)	-0.004(2)	0.073(3)	0.007(2)
C15	0.089(3)	0.071(3)	0.077(3)	0.004(2)	0.061(3)	0.016(2)
C16	0.073(2)	0.065(2)	0.063(2)	0.0093(19)	0.051(2)	0.0105(18)
C17	0.0493(17)	0.0490(19)	0.0570(19)	-0.0166(15)	0.0354(16)	-0.0136(16)
C18	0.057(2)	0.057(2)	0.070(2)	0.0060(17)	0.0397(19)	0.0028(18)
C19	0.063(2)	0.066(3)	0.092(3)	0.0042(19)	0.051(2)	-0.004(2)
C20	0.066(2)	0.061(2)	0.099(3)	-0.011(2)	0.061(2)	-0.022(2)
C21	0.060(2)	0.061(2)	0.067(2)	-0.0231(18)	0.0466(19)	-0.0216(18)
C22	0.087(3)	0.086(3)	0.071(3)	-0.028(3)	0.060(2)	-0.024(2)
C23	0.080(3)	0.086(3)	0.052(2)	-0.027(2)	0.044(2)	-0.012(2)
C24	0.0563(19)	0.067(2)	0.0483(19)	-0.0203(18)	0.0297(17)	-0.0048(18)
C25	0.0477(17)	0.0484(19)	0.0472(17)	0.0037(15)	0.0304(15)	0.0025(15)
C26	0.0483(18)	0.064(2)	0.056(2)	0.0132(17)	0.0322(16)	0.0092(17)
C27	0.0392(16)	0.076(3)	0.055(2)	0.0035(17)	0.0234(15)	0.0029(18)

C28	0.0470(18)	0.062(2)	0.0560(19)	-0.0099(16)	0.0310(16)	-0.0074(17)
C29	0.0496(17)	0.0491(19)	0.0481(17)	-0.0023(15)	0.0314(15)	-0.0029(15)
C30	0.067(2)	0.084(3)	0.067(2)	0.018(2)	0.051(2)	0.010(2)
C31	0.058(2)	0.097(3)	0.076(3)	0.010(2)	0.048(2)	0.004(2)
C32	0.0519(19)	0.079(3)	0.068(2)	-0.0006(18)	0.0405(19)	-0.002(2)
C33	0.0519(18)	0.056(2)	0.0445(17)	0.0072(16)	0.0323(15)	0.0072(16)
C34	0.081(3)	0.091(3)	0.052(2)	0.013(2)	0.042(2)	0.018(2)
C35	0.065(2)	0.095(3)	0.049(2)	0.005(2)	0.0319(19)	0.008(2)
C36	0.0543(19)	0.081(3)	0.0456(19)	-0.0004(18)	0.0282(17)	0.0011(18)
C37	0.0553(19)	0.056(2)	0.053(2)	0.0041(16)	0.0381(17)	0.0014(16)
C38	0.067(2)	0.084(3)	0.050(2)	-0.018(2)	0.0288(19)	0.007(2)
C39	0.055(2)	0.074(3)	0.070(3)	0.000(2)	0.028(2)	0.022(2)
C40	0.0538(19)	0.061(2)	0.065(2)	0.0088(17)	0.0331(18)	0.0118(19)
C41	0.0456(16)	0.051(2)	0.0442(17)	-0.0128(14)	0.0264(14)	-0.0053(14)
C42	0.063(2)	0.048(2)	0.062(2)	0.0029(17)	0.0385(19)	0.0016(17)
C43	0.057(2)	0.050(2)	0.055(2)	0.0016(17)	0.0339(18)	0.0003(16)
N1	0.0465(14)	0.0532(16)	0.0481(15)	0.0033(12)	0.0310(12)	0.0026(12)
N2	0.0494(14)	0.0557(17)	0.0474(15)	0.0020(13)	0.0304(13)	0.0007(13)
N3	0.0497(14)	0.0478(16)	0.0544(16)	-0.0002(12)	0.0334(13)	0.0011(13)
N4	0.0455(14)	0.0461(16)	0.0490(15)	0.0024(12)	0.0272(12)	0.0011(12)
N5	0.0504(14)	0.0594(18)	0.0531(16)	0.0013(13)	0.0343(13)	0.0013(14)
N6	0.0521(15)	0.0604(18)	0.0492(16)	-0.0001(14)	0.0316(13)	0.0017(13)
N7	0.0480(14)	0.0524(17)	0.0505(15)	0.0004(13)	0.0295(13)	0.0030(13)
O1	0.0863(18)	0.0747(18)	0.089(2)	-0.0028(15)	0.0579(17)	-0.0079(16)
O2	0.0635(15)	0.0759(18)	0.0587(15)	0.0065(14)	0.0249(13)	-0.0007(13)
O3	0.141(3)	0.094(2)	0.087(2)	-0.003(2)	0.066(2)	0.0002(19)
O4	0.0791(17)	0.0645(16)	0.0668(16)	0.0028(14)	0.0461(14)	-0.0059(13)
O5	0.119(4)	0.126(4)	0.133(4)	0.00000	0.096(4)	0.00000
O6	0.098(2)	0.181(4)	0.120(3)	-0.029(3)	0.068(2)	-0.015(3)
O7	0.169(4)	0.296(8)	0.193(5)	0.004(5)	0.141(4)	0.033(5)
O8	0.0796(18)	0.093(2)	0.0684(17)	0.0048(16)	0.0425(15)	0.0130(15)
O9	0.111(2)	0.116(3)	0.115(3)	0.006(2)	0.077(2)	0.016(2)

O10	0.141(3)	0.117(3)	0.278(6)	-0.037(3)	0.156(4)	-0.065(4)
O11	0.134(4)	0.328(8)	0.155(4)	0.084(4)	0.110(3)	0.062(5)
O12	0.0797(17)	0.0476(15)	0.0759(18)	0.0085(13)	0.0406(15)	0.0089(13)
O13	0.0629(15)	0.0553(16)	0.0674(16)	-0.0032(12)	0.0217(13)	-0.0019(13)
O14	0.0569(14)	0.0512(15)	0.0804(18)	0.0054(12)	0.0269(13)	0.0013(13)
O15	0.0706(16)	0.0462(14)	0.0851(18)	-0.0076(13)	0.0432(15)	-0.0099(13)

Table 10.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of tris(1,10-Phenanthroline-*N,N'*)-nickel(II) bis(triiodide) monohydrate, $[Ni(Phen)_3](I_3)_2(H_2O)$ (10).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	1.04399(10)	0.16955(9)	0.24347(6)	0.0643(3)
I11	1.11576(6)	-0.17779(6)	0.03629(4)	0.0579(3)
I12	1.38499(6)	-0.26200(6)	0.12053(4)	0.0628(3)
I13	1.65063(7)	-0.33924(7)	0.21215(4)	0.0716(3)
I21	1.45541(7)	0.26971(8)	0.30473(5)	0.0833(4)
I22	1.29632(7)	0.32411(7)	0.44216(4)	0.1243(6)
I23	1.15666(11)	0.36544(10)	0.58378(6)	0.0396(4)
C102	0.7661(9)	0.3524(8)	0.1575(5)	0.040(3)
H102	0.80190	0.40800	0.16350	0.048(3)
C103	0.6353(8)	0.3887(9)	0.1194(6)	0.058
H103	0.58530	0.46690	0.10060	0.058(4)
C104	0.5811(9)	0.3099(10)	0.1099(6)	0.069
H104	0.49380	0.33250	0.08430	0.040(2)
C105	0.6582(8)	0.1950(9)	0.1391(5)	0.066(4)
C106	0.6087(10)	0.1040(9)	0.1331(6)	0.08
H106	0.52240	0.12340	0.10730	0.042(2)
C107	0.6822(9)	-0.0074(10)	0.1633(6)	0.044(3)
H107	0.64600	-0.06340	0.15920	0.038(2)
C108	0.8184(9)	-0.0394(8)	0.2023(5)	0.047(3)
C109	0.9016(10)	-0.1561(9)	0.2337(6)	0.037(3)
H109	0.86890	-0.21460	0.23100	0.042(2)
C110	1.0326(9)	-0.1811(8)	0.2684(5)	0.046(3)
H110	1.09090	-0.25690	0.28880	0.056
C111	1.0748(9)	-0.0897(8)	0.2720(5)	0.041(3)
H111	1.16250	-0.10680	0.29570	0.042(2)
C113	0.8693(8)	0.0447(7)	0.2081(5)	0.038(3)

C114	0.7882(7)	0.1645(7)	0.1774(5)	0.056(4)
C202	0.8276(9)	0.2554(9)	0.3701(6)	0.067
H202	0.75660	0.29540	0.33290	0.045(3)
C203	0.7930(12)	0.2625(11)	0.4461(8)	0.062(4)
H203	0.70010	0.30860	0.45850	0.041(3)
C204	0.8932(13)	0.2034(12)	0.5009(6)	0.045(3)
H204	0.86940	0.20790	0.55090	0.060(4)
C205	1.0319(10)	0.1356(9)	0.4822(6)	0.071
C206	1.1423(14)	0.0659(11)	0.5374(7)	0.053(3)
H206	1.12330	0.06540	0.58830	0.063
C207	1.2755(13)	0.0003(11)	0.5146(7)	0.079(5)
H207	1.34650	-0.04560	0.55060	0.095
C208	1.3085(10)	0.0001(8)	0.4381(6)	0.049(3)
C209	1.4485(10)	-0.0688(9)	0.4124(8)	0.069(5)
H209	1.52190	-0.11740	0.44660	0.082
C210	1.4711(9)	-0.0612(9)	0.3378(8)	0.052(3)
H210	1.56180	-0.10360	0.32070	0.063
C211	1.3609(8)	0.0090(8)	0.2857(6)	0.056(4)
H211	1.37870	0.01220	0.23460	0.067
C213	1.2038(8)	0.0661(8)	0.3834(6)	0.056(4)
C214	1.0608(8)	0.1335(7)	0.4063(5)	0.067
C302	1.0466(8)	0.4069(8)	0.2684(5)	0.055(4)
H302	1.01220	0.39220	0.31630	0.066
C303	1.0641(9)	0.5104(8)	0.2479(6)	0.048(3)
H303	1.04640	0.56190	0.28130	0.058
C304	1.1088(9)	0.5349(8)	0.1760(6)	0.049(3)
H304	1.11880	0.60510	0.15970	0.059
C305	1.1390(8)	0.4554(7)	0.1275(5)	0.057(4)
C306	1.1870(8)	0.4741(8)	0.0525(6)	0.069
H306	1.19280	0.54480	0.03250	0.059(4)
C307	1.2242(8)	0.3889(8)	0.0103(5)	0.071
H307	1.25680	0.40220	-0.03820	0.054(3)

C308	1.2149(8)	0.2807(8)	0.0379(5)	0.064
C309	1.2585(9)	0.1892(9)	-0.0020(5)	0.060(4)
H309	1.29670	0.19750	-0.04960	0.084(5)
C310	1.2457(9)	0.0882(8)	0.0281(5)	0.1
H310	1.27410	0.02740	0.00110	0.045(3)
C311	1.1896(8)	0.0757(7)	0.1002(5)	0.074(5)
H311	1.18150	0.00600	0.12080	0.089
C313	1.1619(7)	0.2636(7)	0.1095(5)	0.060(4)
C314	1.1236(7)	0.3517(7)	0.1548(5)	0.072
N101	0.8423(6)	0.2433(6)	0.1857(4)	0.065(4)
N112	0.9980(6)	0.0202(6)	0.2437(4)	0.078
N201	0.9620(7)	0.1915(6)	0.3507(4)	0.077(5)
N212	1.2288(6)	0.0722(6)	0.3092(4)	0.093
N301	1.0752(6)	0.3260(6)	0.2252(4)	0.078(5)
N312	1.1478(6)	0.1610(6)	0.1397(4)	0.093
O1	0.6243(12)	0.3372(18)	0.6285(7)	0.0643(3)

Table 10.2: Anisotropic displacement parameters of tris(1,10-Phenanthroline-*N,N'*)-nickel(II) bis(triiodide) monohydrate, $[Ni(Phen)_3](I_3)_2(H_2O)$ (10), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0346(5)	0.0322(7)	0.0355(8)	-0.0146(5)	0.0012(5)	-0.0053(5)
I11	0.0567(4)	0.0469(5)	0.0616(5)	-0.0154(3)	-0.0049(3)	-0.0042(4)
I12	0.0523(3)	0.0398(4)	0.0608(5)	-0.0136(3)	0.0062(3)	-0.0113(3)
I13	0.0612(4)	0.0654(5)	0.0742(6)	-0.0266(4)	-0.0083(4)	-0.0139(4)
I21	0.0560(4)	0.1112(7)	0.0704(6)	-0.0355(4)	0.0145(4)	-0.0278(5)
I22	0.0610(4)	0.0603(5)	0.0501(5)	-0.0192(3)	-0.0043(3)	-0.0040(4)
I23	0.1412(8)	0.1250(9)	0.0545(7)	-0.0145(7)	0.0223(6)	-0.0187(6)
C102	0.056(5)	0.041(6)	0.053(8)	-0.020(5)	-0.002(5)	0.000(5)
C103	0.038(5)	0.053(7)	0.058(8)	0.004(5)	-0.010(4)	-0.003(5)
C104	0.036(5)	0.075(9)	0.067(8)	-0.025(6)	-0.009(5)	-0.010(6)
C105	0.037(5)	0.052(7)	0.039(6)	-0.015(5)	0.006(4)	-0.025(5)
C106	0.054(5)	0.047(7)	0.065(8)	-0.028(5)	-0.006(5)	-0.017(6)
C107	0.047(5)	0.066(8)	0.071(8)	-0.034(5)	0.012(5)	-0.036(6)
C108	0.051(5)	0.045(6)	0.037(6)	-0.028(5)	0.015(4)	-0.015(5)
C109	0.074(6)	0.038(6)	0.066(8)	-0.031(5)	0.020(5)	-0.019(6)
C110	0.058(6)	0.034(6)	0.055(7)	-0.020(5)	0.000(5)	-0.004(5)
C111	0.050(5)	0.034(6)	0.045(7)	-0.007(4)	-0.009(4)	0.002(5)
C113	0.036(4)	0.028(5)	0.039(6)	-0.018(4)	0.014(4)	-0.011(4)
C114	0.035(4)	0.037(5)	0.031(6)	-0.018(4)	0.002(3)	-0.008(4)
C202	0.040(5)	0.064(7)	0.061(8)	-0.015(5)	0.008(4)	-0.019(6)
C203	0.075(7)	0.072(9)	0.094(12)	-0.033(7)	0.052(8)	-0.040(8)
C204	0.089(8)	0.117(11)	0.028(8)	-0.046(8)	0.001(6)	-0.019(7)
C205	0.067(6)	0.065(8)	0.036(8)	-0.031(6)	-0.002(5)	-0.007(6)
C206	0.120(9)	0.072(9)	0.036(8)	-0.049(8)	-0.016(7)	0.000(6)
C207	0.087(8)	0.075(9)	0.068(10)	-0.044(7)	-0.029(7)	0.012(7)
C208	0.062(6)	0.047(7)	0.047(8)	-0.032(5)	-0.018(5)	0.010(5)
C209	0.056(6)	0.040(7)	0.086(10)	-0.008(5)	-0.025(6)	0.004(6)
C210	0.039(5)	0.047(7)	0.09(1)	-0.003(5)	-0.013(5)	0.003(7)

C211	0.047(5)	0.043(6)	0.065(8)	-0.005(5)	-0.003(5)	-0.012(6)
C213	0.048(5)	0.038(6)	0.044(7)	-0.025(4)	-0.014(4)	0.001(5)
C214	0.049(5)	0.035(5)	0.030(6)	-0.013(4)	-0.009(4)	-0.001(4)
C302	0.043(4)	0.040(6)	0.039(6)	-0.020(4)	0.007(4)	-0.011(5)
C303	0.068(6)	0.031(6)	0.058(7)	-0.027(5)	0.008(5)	-0.025(5)
C304	0.055(5)	0.027(5)	0.074(8)	-0.018(4)	0.009(5)	-0.018(5)
C305	0.037(4)	0.028(5)	0.055(7)	-0.007(4)	0.005(4)	-0.009(5)
C306	0.054(5)	0.034(6)	0.052(7)	-0.012(4)	-0.001(5)	0.003(5)
C307	0.048(5)	0.043(6)	0.041(6)	-0.025(5)	0.009(4)	0.000(5)
C308	0.041(4)	0.040(6)	0.036(6)	-0.022(4)	0.005(4)	-0.009(5)
C309	0.060(5)	0.071(8)	0.037(7)	-0.035(6)	0.016(5)	-0.014(6)
C310	0.060(5)	0.035(6)	0.042(7)	-0.016(4)	0.014(4)	-0.023(5)
C311	0.046(5)	0.027(5)	0.053(7)	-0.016(4)	0.003(4)	-0.008(5)
C313	0.027(4)	0.029(5)	0.045(6)	-0.014(4)	-0.001(3)	-0.003(4)
C314	0.032(4)	0.025(5)	0.032(6)	-0.013(4)	-0.004(3)	-0.002(4)
N101	0.035(3)	0.031(4)	0.035(5)	-0.013(3)	0.001(3)	-0.006(4)
N112	0.040(4)	0.039(5)	0.030(5)	-0.023(3)	0.001(3)	-0.001(4)
N201	0.042(4)	0.028(4)	0.048(6)	-0.017(3)	0.003(3)	-0.003(4)
N212	0.037(4)	0.039(5)	0.043(6)	-0.016(3)	-0.004(3)	-0.009(4)
N301	0.032(3)	0.040(5)	0.040(5)	-0.019(3)	0.002(3)	-0.014(4)
N312	0.043(4)	0.029(4)	0.030(5)	-0.012(3)	-0.002(3)	-0.013(4)
O1	0.128(8)	0.51(3)	0.131(12)	-0.119(14)	0.070(8)	-0.103(15

Table 11.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of $[Ni(Phen)_3](pda)(H_2O)_{11}$ (11).

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.74802(2)	-0.00201(2)	0.07209(2)	0.04785(13)
C1	0.69945(13)	-0.12726(17)	-0.02880(18)	0.0467(7)
C2	0.63065(15)	-0.08873(19)	-0.0141(2)	0.0577(9)
H1	0.61990	-0.05790	0.00880	0.069
C3	0.59026(16)	-0.1408(2)	-0.0665(2)	0.0621(9)
H2	0.55330	-0.14440	-0.07780	0.075
C4	0.60446(15)	-0.1866(2)	-0.1014(2)	0.0600(9)
H3	0.57730	-0.22140	-0.13690	0.072
C5	0.66072(15)	-0.18050(18)	-0.08286(19)	0.0531(8)
C6	0.68098(17)	-0.2269(2)	-0.1151(2)	0.0625(9)
H4	0.65540	-0.26220	-0.15150	0.075
C7	0.73609(18)	-0.2199(2)	-0.0935(2)	0.0645(10)
H5	0.74790	-0.25050	-0.11540	0.077
C8	0.77677(16)	-0.16635(19)	-0.0377(2)	0.0571(9)
C9	0.79939(14)	0.12370(18)	0.0597(2)	0.0512(8)
C10	0.86145(15)	0.0885(2)	0.1957(2)	0.0606(9)
H6	0.87040	0.05760	0.23630	0.073
C11	0.90106(17)	0.1447(2)	0.2178(2)	0.0698(10)
H7	0.93500	0.15130	0.27250	0.084
C12	0.88954(17)	0.1893(2)	0.1587(3)	0.0697(10)
H8	0.91630	0.22550	0.17260	0.084
C13	0.83727(16)	0.18018(19)	0.0773(2)	0.0610(9)
C14	0.8193(2)	0.2254(2)	0.0099(3)	0.0760(11)
H9	0.84440	0.26230	0.01980	0.091
C15	0.7678(2)	0.2155(2)	-0.0657(3)	0.0737(11)
H10	0.75750	0.24600	-0.10730	0.088
C16	0.72800(17)	0.1600(2)	-0.0851(2)	0.0612(9)

C17	0.71924(14)	0.03569(18)	0.1777(2)	0.0506(8)
C18	0.66111(16)	0.10363(19)	0.0610(2)	0.0616(9)
H11	0.64810	0.11500	0.00900	0.074
C19	0.63687(17)	0.1406(2)	0.0911(3)	0.0720(11)
H12	0.60920	0.17660	0.06040	0.086
C20	0.65407(17)	0.1235(2)	0.1654(3)	0.0691(11)
H13	0.63800	0.14750	0.18600	0.083
C21	0.69609(15)	0.06959(19)	0.2117(2)	0.0578(9)
C22	0.7171(2)	0.0464(2)	0.2908(3)	0.0743(11)
H14	0.70140	0.06730	0.31350	0.089
C23	0.75818(18)	-0.0038(2)	0.3327(2)	0.0712(10)
H15	0.77110	-0.01650	0.38430	0.085
C24	0.78311(15)	-0.0387(2)	0.3000(2)	0.0597(9)
C25	0.61373(13)	-0.31421(17)	0.12703(19)	0.0477(7)
C26	0.67616(14)	-0.3174(2)	0.1866(2)	0.0569(9)
H16	0.69560	-0.36030	0.20840	0.068
C27	0.70883(14)	-0.2561(2)	0.2128(2)	0.0610(9)
H17	0.75080	-0.25710	0.25130	0.073
C28	0.67864(14)	-0.1931(2)	0.1813(2)	0.0562(8)
H18	0.69990	-0.15110	0.19770	0.067
C29	0.61622(14)	-0.19355(17)	0.12472(19)	0.0488(7)
C30	0.83583(17)	-0.1575(2)	-0.0106(2)	0.0670(10)
H19	0.85070	-0.18820	-0.02840	0.08
C31	0.87085(18)	-0.1041(2)	0.0414(3)	0.0732(11)
H20	0.90950	-0.09740	0.05860	0.088
C32	0.84846(15)	-0.0592(2)	0.0688(2)	0.0643(10)
H21	0.87300	-0.02310	0.10480	0.077
C33	0.75813(14)	-0.11898(18)	-0.00651(19)	0.0495(8)
C34	0.67231(19)	0.1477(2)	-0.1636(2)	0.0749(11)
H22	0.65900	0.17810	-0.20670	0.09
C35	0.63808(18)	0.0918(2)	-0.1768(2)	0.0729(11)
H23	0.60150	0.08360	-0.22890	0.087

C36	0.65785(15)	0.0472(2)	-0.1123(2)	0.0627(9)
H24	0.63410	0.00870	-0.12230	0.075
C37	0.74456(15)	0.11282(18)	-0.0227(2)	0.0523(8)
C38	0.82575(18)	-0.0925(2)	0.3397(2)	0.0728(11)
H25	0.83990	-0.10780	0.39120	0.087
C39	0.84679(17)	-0.1228(2)	0.3036(3)	0.0752(12)
H26	0.87450	-0.15940	0.32970	0.09
C40	0.82611(15)	-0.09828(19)	0.2268(2)	0.0636(9)
H27	0.84150	-0.11820	0.20320	0.076
C41	0.76368(13)	-0.01829(16)	0.22252(19)	0.0483(8)
C42	0.57622(16)	-0.38045(19)	0.0902(2)	0.0579(8)
C43	0.58007(15)	-0.12557(18)	0.0904(2)	0.0552(8)
N1	0.68456(11)	-0.08122(14)	0.00474(16)	0.0486(6)
N2	0.81175(11)	0.07838(14)	0.11850(16)	0.0511(6)
N3	0.70172(11)	0.05319(14)	0.10265(16)	0.0505(6)
N4	0.58427(11)	-0.25316(14)	0.09707(16)	0.0489(6)
N5	0.79335(12)	-0.06597(15)	0.04537(17)	0.0533(7)
N6	0.70984(12)	0.05711(15)	-0.03597(17)	0.0543(7)
N7	0.78531(11)	-0.04757(14)	0.18649(16)	0.0516(7)
O1	0.47752(12)	-0.46333(15)	-0.10860(18)	0.0817(8)
O2	0.46431(11)	-0.25091(14)	-0.06490(16)	0.0760(7)
O3	0.45569(18)	-0.23896(18)	-0.1999(2)	0.1118(11)
O4	0.46870(11)	-0.03349(14)	-0.09366(15)	0.0703(7)
O5	1/2	-0.0159(3)	-1/4	0.1151(17)
O6	0.53416(16)	0.0636(3)	-0.1175(2)	0.1334(14)
O7	0.5184(3)	0.2178(4)	-0.1140(4)	0.201(3)
O8	0.57554(12)	-0.09630(16)	-0.25933(17)	0.0836(8)
O9	0.95633(16)	-0.1223(2)	0.2623(2)	0.1099(11)
O10	0.9680(2)	0.0415(2)	0.1624(4)	0.162(2)
O11	0.9402(2)	0.1502(4)	0.0544(3)	0.193(3)
O12	0.60010(12)	-0.43589(13)	0.12938(17)	0.0741(7)
O13	0.52331(11)	-0.37465(14)	0.02254(16)	0.0759(8)

O14	0.52384(11)	-0.13082(13)	0.03301(17)	0.0748(8)
O15	0.60868(11)	-0.06998(13)	0.12087(17)	0.0718(7)

Table 11.2: Anisotropic displacement parameters of $[Ni(Phen)_3](pda)(H_2O)_{11}$ (11), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0461(2)	0.0510(2)	0.0472(2)	0.0002(2)	0.03001(17)	0.0004(2)
C1	0.0490(17)	0.0474(18)	0.0417(16)	0.0065(14)	0.0280(14)	0.0039(14)
C2	0.0530(19)	0.062(2)	0.065(2)	-0.0012(17)	0.0408(18)	-0.0020(18)
C3	0.0508(19)	0.069(2)	0.063(2)	-0.0050(18)	0.0346(18)	-0.0005(19)
C4	0.0546(19)	0.061(2)	0.055(2)	-0.0059(17)	0.0307(17)	-0.0037(17)
C5	0.0547(18)	0.053(2)	0.0459(18)	0.0036(16)	0.0293(16)	0.0036(15)
C6	0.069(2)	0.064(2)	0.0476(19)	0.0026(19)	0.0339(18)	-0.0049(17)
C7	0.079(3)	0.066(2)	0.055(2)	0.010(2)	0.046(2)	-0.0018(18)
C8	0.065(2)	0.063(2)	0.0509(19)	0.0102(18)	0.0404(18)	0.0072(17)
C9	0.0531(18)	0.051(2)	0.057(2)	0.0021(15)	0.0385(17)	-0.0007(16)
C10	0.0531(19)	0.067(2)	0.054(2)	-0.0044(17)	0.0304(17)	-0.0015(17)
C11	0.058(2)	0.077(3)	0.063(2)	-0.011(2)	0.0335(19)	-0.013(2)
C12	0.061(2)	0.064(2)	0.085(3)	-0.0150(19)	0.046(2)	-0.014(2)
C13	0.062(2)	0.056(2)	0.078(3)	-0.0016(17)	0.051(2)	-0.0005(19)
C14	0.091(3)	0.063(3)	0.100(3)	-0.004(2)	0.073(3)	0.007(2)
C15	0.089(3)	0.071(3)	0.077(3)	0.004(2)	0.061(3)	0.016(2)
C16	0.073(2)	0.065(2)	0.063(2)	0.0093(19)	0.051(2)	0.0105(18)
C17	0.0493(17)	0.0490(19)	0.0570(19)	-0.0166(15)	0.0354(16)	-0.0136(16)
C18	0.057(2)	0.057(2)	0.070(2)	0.0060(17)	0.0397(19)	0.0028(18)
C19	0.063(2)	0.066(3)	0.092(3)	0.0042(19)	0.051(2)	-0.004(2)
C20	0.066(2)	0.061(2)	0.099(3)	-0.011(2)	0.061(2)	-0.022(2)
C21	0.060(2)	0.061(2)	0.067(2)	-0.0231(18)	0.0466(19)	-0.0216(18)
C22	0.087(3)	0.086(3)	0.071(3)	-0.028(3)	0.060(2)	-0.024(2)
C23	0.080(3)	0.086(3)	0.052(2)	-0.027(2)	0.044(2)	-0.012(2)
C24	0.0563(19)	0.067(2)	0.0483(19)	-0.0203(18)	0.0297(17)	-0.0048(18)
C25	0.0477(17)	0.0484(19)	0.0472(17)	0.0037(15)	0.0304(15)	0.0025(15)
C26	0.0483(18)	0.064(2)	0.056(2)	0.0132(17)	0.0322(16)	0.0092(17)
C27	0.0392(16)	0.076(3)	0.055(2)	0.0035(17)	0.0234(15)	0.0029(18)

C28	0.0470(18)	0.062(2)	0.0560(19)	-0.0099(16)	0.0310(16)	-0.0074(17)
C29	0.0496(17)	0.0491(19)	0.0481(17)	-0.0023(15)	0.0314(15)	-0.0029(15)
C30	0.067(2)	0.084(3)	0.067(2)	0.018(2)	0.051(2)	0.010(2)
C31	0.058(2)	0.097(3)	0.076(3)	0.010(2)	0.048(2)	0.004(2)
C32	0.0519(19)	0.079(3)	0.068(2)	-0.0006(18)	0.0405(19)	-0.002(2)
C33	0.0519(18)	0.056(2)	0.0445(17)	0.0072(16)	0.0323(15)	0.0072(16)
C34	0.081(3)	0.091(3)	0.052(2)	0.013(2)	0.042(2)	0.018(2)
C35	0.065(2)	0.095(3)	0.049(2)	0.005(2)	0.0319(19)	0.008(2)
C36	0.0543(19)	0.081(3)	0.0456(19)	-0.0004(18)	0.0282(17)	0.0011(18)
C37	0.0553(19)	0.056(2)	0.053(2)	0.0041(16)	0.0381(17)	0.0014(16)
C38	0.067(2)	0.084(3)	0.050(2)	-0.018(2)	0.0288(19)	0.007(2)
C39	0.055(2)	0.074(3)	0.070(3)	0.000(2)	0.028(2)	0.022(2)
C40	0.0538(19)	0.061(2)	0.065(2)	0.0088(17)	0.0331(18)	0.0118(19)
C41	0.0456(16)	0.051(2)	0.0442(17)	-0.0128(14)	0.0264(14)	-0.0053(14)
C42	0.063(2)	0.048(2)	0.062(2)	0.0029(17)	0.0385(19)	0.0016(17)
C43	0.057(2)	0.050(2)	0.055(2)	0.0016(17)	0.0339(18)	0.0003(16)
N1	0.0465(14)	0.0532(16)	0.0481(15)	0.0033(12)	0.0310(12)	0.0026(12)
N2	0.0494(14)	0.0557(17)	0.0474(15)	0.0020(13)	0.0304(13)	0.0007(13)
N3	0.0497(14)	0.0478(16)	0.0544(16)	-0.0002(12)	0.0334(13)	0.0011(13)
N4	0.0455(14)	0.0461(16)	0.0490(15)	0.0024(12)	0.0272(12)	0.0011(12)
N5	0.0504(14)	0.0594(18)	0.0531(16)	0.0013(13)	0.0343(13)	0.0013(14)
N6	0.0521(15)	0.0604(18)	0.0492(16)	-0.0001(14)	0.0316(13)	0.0017(13)
N7	0.0480(14)	0.0524(17)	0.0505(15)	0.0004(13)	0.0295(13)	0.0030(13)
O1	0.0863(18)	0.0747(18)	0.089(2)	-0.0028(15)	0.0579(17)	-0.0079(16)
O2	0.0635(15)	0.0759(18)	0.0587(15)	0.0065(14)	0.0249(13)	-0.0007(13)
O3	0.141(3)	0.094(2)	0.087(2)	-0.003(2)	0.066(2)	0.0002(19)
O4	0.0791(17)	0.0645(16)	0.0668(16)	0.0028(14)	0.0461(14)	-0.0059(13)
O5	0.119(4)	0.126(4)	0.133(4)	0.00000	0.096(4)	0.00000
O6	0.098(2)	0.181(4)	0.120(3)	-0.029(3)	0.068(2)	-0.015(3)
O7	0.169(4)	0.296(8)	0.193(5)	0.004(5)	0.141(4)	0.033(5)
O8	0.0796(18)	0.093(2)	0.0684(17)	0.0048(16)	0.0425(15)	0.0130(15)
O9	0.111(2)	0.116(3)	0.115(3)	0.006(2)	0.077(2)	0.016(2)

O10	0.141(3)	0.117(3)	0.278(6)	-0.037(3)	0.156(4)	-0.065(4)
O11	0.134(4)	0.328(8)	0.155(4)	0.084(4)	0.110(3)	0.062(5)
O12	0.0797(17)	0.0476(15)	0.0759(18)	0.0085(13)	0.0406(15)	0.0089(13)
O13	0.0629(15)	0.0553(16)	0.0674(16)	-0.0032(12)	0.0217(13)	-0.0019(13)
O14	0.0569(14)	0.0512(15)	0.0804(18)	0.0054(12)	0.0269(13)	0.0013(13)
O15	0.0706(16)	0.0462(14)	0.0851(18)	-0.0076(13)	0.0432(15)	-0.0099(13)

Table 12.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of $[Ni(2,6\text{-}pda)_2]_2[Ni(1,10'\text{-}phen)_2(H_2O)_2](H_2O)_9$ (12)

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.57190(4)	0.27873(4)	0.35880(4)	0.03364(15)
Ni2	0.68375(4)	0.20724(4)	0.82433(4)	0.03496(15)
Ni3	0.96817(5)	0.42744(5)	0.30285(4)	0.04812(19)
C1	0.5983(3)	0.1799(3)	0.2085(3)	0.0361(9)
C2	0.7627(4)	0.1888(4)	0.2160(3)	0.0446(11)
H1	0.80510	0.20770	0.24370	0.054
C3	0.8114(4)	0.1404(4)	0.1416(4)	0.0517(12)
H2	0.88420	0.12970	0.11940	0.062
C4	0.7505(4)	0.1094(4)	0.1023(3)	0.0487(12)
H3	0.78170	0.07580	0.05380	0.058
C5	0.6400(4)	0.1283(3)	0.1353(3)	0.0402(10)
C6	0.5699(4)	0.0981(3)	0.0993(3)	0.0449(11)
H4	0.59710	0.06230	0.05220	0.054
C7	0.4646(4)	0.1207(3)	0.1323(3)	0.0461(11)
H5	0.42070	0.10020	0.10750	0.055
C8	0.4190(4)	0.1754(3)	0.2048(3)	0.0407(10)
C9	0.5162(4)	0.1757(3)	0.5411(3)	0.0390(10)
C10	0.6206(4)	0.0684(3)	0.4468(4)	0.0466(11)
H6	0.65790	0.05530	0.38890	0.056
C11	0.6191(4)	-0.0054(4)	0.5199(4)	0.0549(13)
H7	0.65440	-0.06630	0.51090	0.066
C12	0.5643(4)	0.0136(4)	0.6059(4)	0.0559(14)
H8	0.56260	-0.03470	0.65540	0.067
C13	0.5113(4)	0.1054(4)	0.6186(3)	0.0471(12)
C14	0.4553(4)	0.1326(5)	0.7053(4)	0.0574(14)
H9	0.45150	0.08690	0.75710	0.069
C15	0.4078(4)	0.2232(4)	0.7136(3)	0.0537(13)
H10	0.37230	0.23860	0.77100	0.064

C16	0.4110(4)	0.2957(4)	0.6361(3)	0.0422(10)
C17	0.5286(3)	0.3026(3)	0.9634(3)	0.0341(9)
C18	0.4888(3)	0.3598(3)	1.0302(3)	0.0364(9)
H10	0.41730	0.37120	1.05890	0.044
C19	0.5591(4)	0.3994(3)	1.0531(3)	0.0392(10)
H11	0.53490	0.43750	1.09840	0.047
C20	0.6655(4)	0.3828(3)	1.0088(3)	0.0389(10)
H12	0.71300	0.40900	1.02390	0.047
C21	0.6991(3)	0.3259(3)	0.9413(3)	0.0335(9)
C22	0.7342(3)	0.1789(3)	0.6402(3)	0.0332(9)
C23	0.7766(3)	0.1306(3)	0.5664(3)	0.0380(9)
H13	0.77600	0.16120	0.50780	0.046
C24	0.8201(4)	0.0352(3)	0.5829(3)	0.0422(10)
H14	0.84920	0.00130	0.53460	0.051
C25	0.8208(4)	-0.0109(3)	0.6713(3)	0.0402(10)
H15	0.84970	-0.07490	0.68260	0.048
C26	0.7770(3)	0.0422(3)	0.7411(3)	0.0335(9)
C27	0.9456(3)	0.3312(4)	0.4861(3)	0.0446(11)
C28	0.9223(4)	0.3206(4)	0.5803(3)	0.0469(11)
H15	0.93800	0.26150	0.61450	0.056
C29	0.8755(4)	0.3994(4)	0.6218(3)	0.0461(11)
H16	0.85890	0.39370	0.68480	0.055
C30	0.8531(4)	0.4871(4)	0.5702(3)	0.0453(11)
H17	0.82080	0.54060	0.59770	0.054
C31	0.8802(3)	0.4931(4)	0.4762(3)	0.0412(10)
C32	1.1152(3)	0.4241(4)	0.1291(3)	0.0404(10)
C33	1.1556(4)	0.4031(4)	0.0419(3)	0.0438(11)
H18	1.22590	0.40340	0.01200	0.053
C34	1.0884(4)	0.3814(4)	0.0002(3)	0.0472(12)
H19	1.11430	0.36570	-0.05810	0.057
C35	0.9830(4)	0.3829(4)	0.0443(3)	0.0455(11)
H20	0.93790	0.36870	0.01640	0.055

C36	0.9469(3)	0.4062(4)	0.1310(3)	0.0429(11)
C37	0.3101(4)	0.2018(4)	0.2420(3)	0.0466(11)
H21	0.26240	0.18680	0.21720	0.056
C38	0.2749(4)	0.2495(4)	0.3149(4)	0.0498(12)
H21	0.20310	0.26600	0.34060	0.06
C39	0.3473(4)	0.2734(3)	0.3505(3)	0.0433(10)
H22	0.32230	0.30520	0.40040	0.052
C40	0.4867(3)	0.2035(3)	0.2438(3)	0.0340(9)
C41	0.3645(4)	0.3912(4)	0.6402(3)	0.0460(11)
H23	0.32830	0.41050	0.69590	0.055
C42	0.3724(4)	0.4554(4)	0.5626(3)	0.0460(11)
H24	0.34110	0.51860	0.56490	0.055
C43	0.4281(3)	0.4255(3)	0.4788(3)	0.0392(10)
H25	0.43310	0.46970	0.42590	0.047
C44	0.4650(3)	0.2709(3)	0.5498(3)	0.0361(9)
C45	0.4699(3)	0.2477(3)	0.9314(3)	0.0380(9)
C46	0.8095(3)	0.3003(3)	0.8851(3)	0.0381(10)
C47	0.6826(3)	0.2827(3)	0.6375(3)	0.0335(9)
C48	0.7694(3)	0.0083(3)	0.8413(3)	0.0363(9)
C49	0.9947(4)	0.2533(4)	0.4285(4)	0.0504(13)
C50	0.8663(3)	0.5831(4)	0.4106(3)	0.0451(11)
C51	1.1755(3)	0.4444(4)	0.1892(3)	0.0409(10)
C52	0.8370(4)	0.4120(4)	0.1909(3)	0.0446(11)
N1	0.6594(3)	0.2090(3)	0.2488(2)	0.0375(8)
N2	0.5713(3)	0.1564(3)	0.4560(3)	0.0384(8)
N3	0.6310(3)	0.2865(3)	0.9210(2)	0.0337(7)
N4	0.7360(3)	0.1340(3)	0.7238(2)	0.0332(7)
N5	0.9252(3)	0.4169(3)	0.4369(3)	0.0429(9)
N6	1.0139(3)	0.4252(3)	0.1709(3)	0.0441(9)
N7	0.4508(3)	0.2521(3)	0.3152(2)	0.0365(8)
N8	0.4738(3)	0.3356(3)	0.4733(2)	0.0352(8)
O1	0.9303(3)	0.6880(3)	0.1866(2)	0.0535(9)

O2	0.6029(3)	0.4930(2)	0.7629(3)	0.0527(9)
O3	1.0605(4)	0.0754(6)	0.6281(4)	0.126(3)
O4	1.0018(4)	0.1697(6)	0.2224(6)	0.177(4)
O5	0.9167(5)	0.0900(5)	0.3660(4)	0.119(2)
O6	1.1733(3)	0.1356(3)	0.8190(3)	0.0602(10)
O7	0.9915(3)	0.0860(3)	0.8169(3)	0.0760(12)
O8	0.7251(3)	-0.1382(3)	1.0471(2)	0.0582(9)
O9	0.2299(3)	0.1496(4)	0.6323(3)	0.0742(12)
O11	0.7057(2)	0.2956(2)	0.3915(2)	0.0386(7)
O12	0.5731(2)	0.4097(2)	0.2801(2)	0.0403(7)
O13	0.3688(2)	0.2588(2)	0.9684(2)	0.0444(7)
O14	0.5177(2)	0.1956(2)	0.8742(2)	0.0399(7)
O15	0.8802(2)	0.3324(3)	0.8998(2)	0.0489(8)
O16	0.8241(2)	0.2477(2)	0.8263(2)	0.0409(7)
O17	0.6706(2)	0.3313(2)	0.5648(2)	0.0410(7)
O18	0.6562(2)	0.3119(2)	0.71416(19)	0.0366(7)
O19	0.8002(3)	-0.0782(2)	0.8675(2)	0.0442(7)
O20	0.7288(2)	0.0707(2)	0.8932(2)	0.0419(7)
O21	1.0139(3)	0.1701(3)	0.4659(3)	0.0612(10)
O22	1.0106(3)	0.2799(3)	0.3429(2)	0.0548(9)
O23	0.8240(3)	0.6583(3)	0.4381(2)	0.0550(9)
O24	0.9017(2)	0.5713(3)	0.3254(2)	0.0482(8)
O25	1.2686(2)	0.4527(2)	0.1562(2)	0.0434(7)
O26	1.1230(2)	0.4488(3)	0.2712(2)	0.0471(8)
O27	0.7636(2)	0.4139(3)	0.1581(2)	0.0516(9)
O28	0.8271(2)	0.4144(3)	0.2755(2)	0.0490(8)
H26	0.687(5)	0.313(5)	0.445(5)	0.09(2)
H27	0.739(5)	0.351(5)	0.357(4)	0.066(18)

Table 12.2: Anisotropic displacement parameters of $[Ni(2,6\text{-}pda)_2]_2[Ni(1,10'\text{-}phen)_2(H_2O)_2](H_2O)_9$ (12), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0335(3)	0.0370(3)	0.0310(3)	-0.0032(2)	-0.0108(2)	-0.0067(2)
Ni2	0.0365(3)	0.0408(3)	0.0287(3)	-0.0041(2)	-0.0089(2)	-0.0106(2)
Ni3	0.0322(3)	0.0849(5)	0.0341(3)	-0.0128(3)	-0.0044(2)	-0.0273(3)
C1	0.039(2)	0.037(2)	0.033(2)	-0.0066(18)	-0.0132(18)	-0.0026(18)
C2	0.033(2)	0.055(3)	0.045(3)	0.001(2)	-0.010(2)	-0.019(2)
C3	0.040(3)	0.062(3)	0.051(3)	-0.001(2)	-0.008(2)	-0.019(3)
C4	0.051(3)	0.049(3)	0.044(3)	-0.001(2)	-0.009(2)	-0.017(2)
C5	0.049(3)	0.038(2)	0.035(2)	-0.007(2)	-0.0123(19)	-0.0063(19)
C6	0.059(3)	0.045(3)	0.036(2)	-0.014(2)	-0.016(2)	-0.007(2)
C7	0.067(3)	0.044(3)	0.037(2)	-0.020(2)	-0.025(2)	0.001(2)
C8	0.047(3)	0.044(3)	0.036(2)	-0.014(2)	-0.019(2)	0.0032(19)
C9	0.041(2)	0.042(2)	0.038(2)	-0.0122(19)	-0.0167(19)	0.0008(19)
C10	0.050(3)	0.038(3)	0.057(3)	-0.003(2)	-0.026(2)	-0.008(2)
C11	0.058(3)	0.036(3)	0.080(4)	-0.010(2)	-0.035(3)	-0.001(3)
C12	0.060(3)	0.049(3)	0.062(3)	-0.018(3)	-0.030(3)	0.012(3)
C13	0.049(3)	0.051(3)	0.049(3)	-0.020(2)	-0.027(2)	0.009(2)
C14	0.055(3)	0.079(4)	0.042(3)	-0.027(3)	-0.021(2)	0.013(3)
C15	0.050(3)	0.080(4)	0.032(2)	-0.023(3)	-0.011(2)	0.002(2)
C16	0.038(2)	0.059(3)	0.033(2)	-0.016(2)	-0.0108(19)	-0.005(2)
C17	0.030(2)	0.041(2)	0.0281(19)	-0.0046(17)	-0.0042(16)	-0.0046(17)
C18	0.036(2)	0.040(2)	0.029(2)	0.0001(18)	-0.0061(17)	-0.0082(17)
C19	0.047(3)	0.039(2)	0.031(2)	-0.0041(19)	-0.0114(19)	-0.0083(18)
C20	0.042(2)	0.043(2)	0.035(2)	-0.0052(19)	-0.0134(19)	-0.0100(19)
C21	0.035(2)	0.039(2)	0.0286(19)	-0.0047(17)	-0.0115(17)	-0.0085(17)
C22	0.032(2)	0.041(2)	0.0286(19)	-0.0076(17)	-0.0080(16)	-0.0088(17)
C23	0.038(2)	0.044(3)	0.032(2)	-0.0053(19)	-0.0082(18)	-0.0099(19)
C24	0.041(2)	0.046(3)	0.040(2)	-0.004(2)	-0.0054(19)	-0.021(2)
C25	0.042(2)	0.041(2)	0.039(2)	-0.0072(19)	-0.0109(19)	-0.0081(19)

C26	0.032(2)	0.035(2)	0.033(2)	-0.0038(17)	-0.0099(17)	-0.0065(17)
C27	0.032(2)	0.066(3)	0.042(2)	-0.011(2)	-0.0072(19)	-0.023(2)
C28	0.038(2)	0.066(3)	0.044(3)	-0.010(2)	-0.012(2)	-0.020(2)
C29	0.039(2)	0.071(3)	0.034(2)	-0.014(2)	-0.0056(19)	-0.021(2)
C30	0.038(2)	0.065(3)	0.039(2)	-0.008(2)	-0.012(2)	-0.020(2)
C31	0.031(2)	0.062(3)	0.035(2)	-0.010(2)	-0.0068(18)	-0.019(2)
C32	0.030(2)	0.061(3)	0.032(2)	-0.0080(19)	-0.0045(17)	-0.016(2)
C33	0.036(2)	0.061(3)	0.036(2)	-0.006(2)	-0.0084(19)	-0.017(2)
C34	0.040(3)	0.070(3)	0.034(2)	-0.008(2)	-0.0074(19)	-0.020(2)
C35	0.040(2)	0.068(3)	0.035(2)	-0.011(2)	-0.0123(19)	-0.018(2)
C36	0.033(2)	0.068(3)	0.037(2)	-0.013(2)	-0.0107(18)	-0.020(2)
C37	0.046(3)	0.049(3)	0.050(3)	-0.017(2)	-0.022(2)	0.004(2)
C38	0.035(2)	0.055(3)	0.060(3)	-0.014(2)	-0.015(2)	0.000(2)
C39	0.035(2)	0.046(3)	0.047(3)	-0.0065(19)	-0.011(2)	-0.006(2)
C40	0.037(2)	0.036(2)	0.029(2)	-0.0067(17)	-0.0116(17)	-0.0019(17)
C41	0.039(2)	0.066(3)	0.036(2)	-0.013(2)	-0.0025(19)	-0.020(2)
C42	0.046(3)	0.047(3)	0.046(3)	-0.005(2)	-0.008(2)	-0.018(2)
C43	0.037(2)	0.039(2)	0.040(2)	-0.0048(18)	-0.0074(19)	-0.0095(19)
C44	0.034(2)	0.044(2)	0.032(2)	-0.0097(18)	-0.0114(17)	-0.0024(18)
C45	0.038(2)	0.042(2)	0.032(2)	-0.0055(18)	-0.0083(18)	-0.0047(19)
C46	0.038(2)	0.050(3)	0.030(2)	-0.0100(19)	-0.0096(17)	-0.0086(19)
C47	0.033(2)	0.042(2)	0.029(2)	-0.0098(17)	-0.0081(17)	-0.0089(18)
C48	0.032(2)	0.042(2)	0.034(2)	-0.0067(18)	-0.0083(17)	-0.0053(19)
C49	0.034(2)	0.072(4)	0.054(3)	-0.015(2)	-0.005(2)	-0.030(3)
C50	0.033(2)	0.067(3)	0.039(2)	-0.006(2)	-0.0081(19)	-0.021(2)
C51	0.030(2)	0.057(3)	0.040(2)	-0.0066(19)	-0.0087(18)	-0.020(2)
C52	0.038(2)	0.067(3)	0.036(2)	-0.013(2)	-0.0100(19)	-0.019(2)
N1	0.0369(19)	0.038(2)	0.0392(19)	-0.0007(15)	-0.0135(16)	-0.0122(16)
N2	0.041(2)	0.037(2)	0.041(2)	-0.0069(16)	-0.0178(16)	-0.0062(16)
N3	0.0336(18)	0.0384(19)	0.0284(17)	-0.0061(15)	-0.0078(14)	-0.0046(15)
N4	0.0317(18)	0.039(2)	0.0316(17)	-0.0089(14)	-0.0097(14)	-0.0064(15)
N5	0.0311(19)	0.065(3)	0.038(2)	-0.0089(17)	-0.0073(16)	-0.0206(19)

N6	0.034(2)	0.069(3)	0.0351(19)	-0.0131(18)	-0.0072(16)	-0.0182(19)
N7	0.0325(18)	0.039(2)	0.0379(19)	-0.0062(15)	-0.0104(15)	-0.0055(16)
N8	0.0353(19)	0.039(2)	0.0323(18)	-0.0088(15)	-0.0094(15)	-0.0054(15)
O1	0.049(2)	0.071(2)	0.0436(19)	-0.0078(17)	-0.0130(16)	-0.0181(17)
O2	0.0458(19)	0.050(2)	0.070(2)	0.0054(15)	-0.0296(18)	-0.0210(18)
O3	0.065(3)	0.249(8)	0.088(4)	-0.012(4)	-0.020(3)	-0.096(5)
O4	0.086(4)	0.247(8)	0.266(9)	0.094(5)	-0.116(5)	-0.221(8)
O5	0.115(5)	0.131(5)	0.102(4)	-0.016(4)	-0.025(4)	-0.012(4)
O6	0.053(2)	0.074(3)	0.056(2)	-0.0099(19)	-0.0168(18)	-0.0132(19)
O7	0.056(2)	0.082(3)	0.093(3)	-0.006(2)	-0.017(2)	-0.032(3)
O8	0.062(2)	0.073(3)	0.048(2)	-0.0293(19)	-0.0173(18)	-0.0047(18)
O9	0.060(2)	0.094(3)	0.068(3)	-0.003(2)	-0.019(2)	-0.020(2)
O11	0.0387(17)	0.0452(19)	0.0351(16)	-0.0045(14)	-0.0141(14)	-0.0100(15)
O12	0.0382(16)	0.0460(18)	0.0358(16)	-0.0064(13)	-0.0110(13)	-0.0038(13)
O13	0.0327(16)	0.053(2)	0.0464(18)	-0.0043(14)	-0.0086(14)	-0.0115(15)
O14	0.0373(16)	0.0478(18)	0.0363(16)	-0.0059(13)	-0.0082(13)	-0.0143(14)
O15	0.0400(18)	0.070(2)	0.0443(18)	-0.0134(16)	-0.0108(14)	-0.0218(17)
O16	0.0351(16)	0.055(2)	0.0361(16)	-0.0076(14)	-0.0080(13)	-0.0182(14)
O17	0.0488(18)	0.0422(17)	0.0335(16)	-0.0051(14)	-0.0165(14)	-0.0047(13)
O18	0.0415(17)	0.0371(16)	0.0325(15)	-0.0031(13)	-0.0122(13)	-0.0093(12)
O19	0.054(2)	0.0351(17)	0.0420(17)	-0.0040(14)	-0.0165(15)	-0.0023(14)
O20	0.0463(18)	0.0441(18)	0.0318(15)	-0.0040(14)	-0.0083(13)	-0.0056(13)
O21	0.057(2)	0.068(3)	0.061(2)	-0.0136(19)	-0.0043(19)	-0.029(2)
O22	0.0403(18)	0.084(3)	0.046(2)	-0.0092(17)	-0.0053(15)	-0.0335(19)
O23	0.050(2)	0.069(2)	0.048(2)	-0.0068(18)	-0.0108(16)	-0.0206(18)
O24	0.0402(18)	0.071(2)	0.0348(16)	-0.0096(16)	-0.0059(14)	-0.0183(16)
O25	0.0305(16)	0.061(2)	0.0430(17)	-0.0113(14)	-0.0056(13)	-0.0182(15)
O26	0.0337(16)	0.079(2)	0.0356(16)	-0.0115(15)	-0.0054(13)	-0.0277(16)
O27	0.0338(17)	0.089(3)	0.0388(17)	-0.0174(17)	-0.0103(14)	-0.0162(17)
O28	0.0346(17)	0.085(3)	0.0348(16)	-0.0178(16)	-0.0065(13)	-0.0217(17)

Table 13.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ (13)

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.49076(7)	0.27068(4)	0.69450(4)	0.03833(18)
Ni2	0.04249(7)	0.25428(4)	0.99683(4)	0.04407(19)
Ni3	0.89019(6)	0.25742(4)	0.31160(3)	0.03079(16)
C1	0.5668(5)	0.0903(3)	0.6298(3)	0.0370(12)
C2	0.6904(5)	0.0637(3)	0.2572(2)	0.0282(11)
C3	-0.1727(5)	0.0748(3)	0.9377(3)	0.0350(12)
C4	0.4980(5)	0.4402(3)	0.8291(3)	0.0405(12)
C5	0.1463(5)	0.4426(3)	0.9854(3)	0.0349(12)
C6	1.0761(5)	0.0129(3)	0.2691(3)	0.0397(13)
H6	1.16370	0.00570	0.27470	0.048
C7	0.1141(5)	0.3688(3)	0.9055(3)	0.0413(12)
C8	0.8371(5)	-0.0552(3)	0.2342(3)	0.0358(12)
H8	0.76100	-0.11000	0.21410	0.043
C9	0.9662(5)	-0.0685(3)	0.2414(3)	0.0433(13)
H9	0.97770	-0.13220	0.22750	0.052
C10	-0.1508(6)	-0.0902(4)	0.8858(3)	0.0494(15)
H10	-0.18880	-0.15890	0.86370	0.059
C11	0.1911(5)	0.5448(3)	1.0114(3)	0.0417(13)
H11	0.21120	0.57520	0.97770	0.05
C12	0.8228(4)	0.0403(3)	0.2574(2)	0.0289(11)
C13	1.0554(5)	0.1051(3)	0.2885(3)	0.0401(13)
H13	1.13140	0.16000	0.30640	0.048
C14	0.5655(5)	-0.0087(3)	0.2299(3)	0.0399(12)
H14	0.56300	-0.07590	0.20820	0.048
C15	0.8559(5)	0.3690(4)	0.4660(3)	0.0461(13)
C16	0.1349(5)	0.4537(3)	1.1097(3)	0.0360(12)
C17	0.7762(5)	0.5278(4)	0.3371(5)	0.070(2)
H17	0.76160	0.56220	0.30740	0.083

C18	0.3092(6)	-0.0277(4)	0.5624(3)	0.0578(16)
H18	0.22170	-0.06650	0.53820	0.069
C19	0.9476(5)	0.2426(4)	0.4646(3)	0.0498(15)
H19	0.98530	0.19120	0.43820	0.06
C20	0.0438(5)	0.0497(4)	0.9325(3)	0.0426(13)
C21	0.3333(6)	0.0744(4)	0.6045(3)	0.0432(13)
C22	0.5784(5)	0.1877(4)	0.2939(3)	0.0418(13)
H22	0.58180	0.25500	0.31470	0.05
C23	0.5463(7)	-0.0114(4)	0.5896(3)	0.0559(16)
H23	0.61910	-0.03980	0.58470	0.067
C24	0.8394(6)	0.3919(5)	0.5421(4)	0.0696(18)
H24	0.80120	0.44310	0.56820	0.083
C25	0.4480(5)	0.0192(4)	0.2350(3)	0.0463(13)
H25	0.36450	-0.02860	0.21560	0.056
C26	0.8217(5)	0.4252(4)	0.4226(3)	0.0483(14)
C27	0.4527(5)	0.1183(4)	0.2689(3)	0.0481(14)
H27	0.37290	0.13840	0.27490	0.058
C28	0.8127(5)	0.4390(4)	0.3061(3)	0.0535(15)
H28	0.82320	0.41400	0.25520	0.064
C29	0.4143(7)	-0.0699(4)	0.5568(3)	0.0654(19)
H29	0.39790	-0.13850	0.53090	0.078
C30	0.2057(5)	0.6017(3)	1.0887(3)	0.0452(14)
H30	0.23460	0.67080	1.10690	0.054
C31	-0.2461(6)	0.1567(4)	0.9598(3)	0.0427(13)
C32	0.1779(5)	0.5569(3)	1.1385(3)	0.0436(13)
H32	0.18770	0.59480	1.19040	0.052
C33	0.2291(6)	0.1325(5)	0.6206(3)	0.0536(15)
C34	0.5102(6)	0.5389(4)	0.8747(3)	0.0611(16)
H34	0.49810	0.55880	0.92540	0.073
C35	-0.2354(5)	-0.0275(3)	0.9054(3)	0.0427(13)
H35	-0.32970	-0.05240	0.89740	0.051
C36	0.7010(5)	0.1682(4)	0.6708(3)	0.0428(13)

C37	0.8817(7)	0.3360(6)	0.5773(4)	0.081(2)
H37	0.87210	0.34930	0.62770	0.097
C38	0.5571(6)	0.5772(4)	0.7672(3)	0.0540(15)
H38	0.57780	0.62360	0.74560	0.065
C39	-0.0122(6)	-0.0525(4)	0.8984(3)	0.0491(15)
H39	0.04380	-0.09520	0.88430	0.059
C40	0.7843(5)	0.5124(4)	0.4553(4)	0.074(2)
H40	0.77420	0.53640	0.50630	0.089
C41	0.9369(6)	0.2622(5)	0.5383(3)	0.0663(18)
H41	0.96730	0.22510	0.56180	0.08
C42	0.5422(5)	0.4762(3)	0.7235(3)	0.0406(13)
C43	0.7621(6)	0.5634(4)	0.4122(5)	0.082(3)
H43	0.73740	0.62260	0.43400	0.099
C44	0.5503(5)	0.4276(4)	0.6403(3)	0.0421(13)
C45	0.1926(6)	0.1047(5)	0.9518(3)	0.0545(16)
C46	0.5413(6)	0.6069(4)	0.8415(4)	0.0700(18)
H46	0.55150	0.67410	0.87050	0.084
C47	0.0991(5)	0.3919(4)	1.1553(3)	0.0418(13)
C48	0.4706(5)	0.3550(4)	0.8542(3)	0.0423(13)
N1	0.9067(4)	0.2934(3)	0.4277(2)	0.0382(10)
N2	0.8333(4)	0.3885(3)	0.3488(3)	0.0410(11)
N3	0.6943(4)	0.1617(3)	0.2893(2)	0.0322(9)
N4	0.9335(4)	0.1211(2)	0.2834(2)	0.0302(9)
N5	0.4608(4)	0.1288(3)	0.6355(2)	0.0349(10)
N6	-0.0400(4)	0.1094(3)	0.9504(2)	0.0366(10)
N7	0.1205(4)	0.4005(3)	1.0359(2)	0.0383(10)
N8	0.5130(4)	0.4122(3)	0.7574(2)	0.0370(10)
O1	0.0544(3)	0.2979(2)	1.11665(18)	0.0491(9)
O2	0.0634(4)	0.2804(2)	0.89292(18)	0.0543(10)
O3	0.1353(3)	0.4035(2)	0.85490(19)	0.0515(9)
H3	0.11470	0.35760	0.81270	0.077
O4	0.1127(4)	0.4339(2)	1.2245(2)	0.0546(10)

O5	0.4646(3)	0.2706(2)	0.80605(19)	0.0472(9)
O6	0.4617(4)	0.3769(2)	0.9235(2)	0.0577(10)
H6A	0.44700	0.32610	0.93170	0.087
O7	0.5245(3)	0.3328(2)	0.61393(18)	0.0476(9)
O8	0.5763(4)	0.4789(3)	0.6036(2)	0.0607(11)
O9	-0.1684(4)	0.2441(2)	0.9867(2)	0.0532(10)
O10	0.6904(3)	0.2559(2)	0.70472(18)	0.0463(9)
O11	0.8059(4)	0.1402(3)	0.6691(2)	0.0621(11)
O12	0.2758(4)	0.2236(3)	0.6627(2)	0.0557(10)
O13	0.1084(4)	0.0896(3)	0.5927(2)	0.0780(13)
O14	0.8576(4)	0.2381(3)	0.1970(2)	0.0465(9)
O15	1.0871(4)	0.3369(2)	0.3172(2)	0.0490(10)
O16	0.2162(4)	0.1984(3)	0.9860(2)	0.0594(10)
O17	0.2782(4)	0.0580(3)	0.9356(2)	0.0761(13)
O18	-0.3721(4)	0.1317(3)	0.9500(2)	0.0606(11)
O19	0.0510(6)	0.2837(3)	0.7215(2)	0.0524(11)
O20	0.4831(4)	0.2583(3)	0.9791(2)	0.0559(10)
O21	0.6655(4)	0.6767(3)	0.6324(3)	0.0678(12)
O22	0.6178(5)	0.1117(3)	0.0993(3)	0.0791(13)
O23	0.3683(6)	0.2346(3)	0.4663(3)	0.0854(15)
O24	0.1446(6)	0.0688(4)	0.4423(3)	0.0993(17)
H192	-0.019(6)	0.242(5)	0.701(4)	0.09(3)
H191	0.118(7)	0.251(5)	0.696(4)	0.12(3)
H141	0.775(3)	0.199(3)	0.165(2)	0.055(16)
H142	0.927(3)	0.262(3)	0.172(2)	0.058(17)
H151	1.179(3)	0.337(4)	0.333(3)	0.065(17)
H152	1.097(6)	0.376(4)	0.287(3)	0.12(2)
H201	0.394(3)	0.217(3)	0.974(3)	0.08(2)
H211	0.647(5)	0.697(4)	0.591(2)	0.071(18)
H221	0.567(9)	0.096(7)	0.050(3)	0.23(5)
H231	0.427(9)	0.269(6)	0.515(3)	0.19(4)
H202	0.528(6)	0.209(4)	0.953(3)	0.11(2)

H241	0.084(4)	0.101(3)	0.474(3)	0.040(17)
H212	0.628(8)	0.608(2)	0.599(4)	0.18(4)
H242	0.149(9)	0.069(7)	0.493(2)	0.18(4)
H232	0.331(9)	0.272(6)	0.508(3)	0.16(4)
H222	0.643(9)	0.049(4)	0.083(5)	0.21(5)

Table 13.2: Anisotropic displacement parameters of $[Ni(2,6\text{-pda})(2,6\text{-pdaH})]_2[Ni(2,2'\text{-bipy})_2(H_2O)_2](H_2O)_6$ (13), in $Å^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0444(4)	0.0285(3)	0.0385(4)	0.0116(3)	0.0064(4)	0.0085(3)
Ni2	0.0611(5)	0.0274(4)	0.0377(4)	-0.0006(3)	0.0089(4)	0.0136(3)
Ni3	0.0360(4)	0.0231(3)	0.0320(4)	0.0078(3)	0.0068(3)	0.0096(3)
C1	0.055(3)	0.033(3)	0.024(3)	0.011(2)	0.010(3)	0.013(2)
C2	0.034(3)	0.025(2)	0.025(3)	0.006(2)	0.006(2)	0.010(2)
C3	0.046(3)	0.027(2)	0.031(3)	0.006(2)	0.006(3)	0.013(2)
C4	0.050(3)	0.037(3)	0.034(3)	0.017(2)	0.014(3)	0.009(2)
C5	0.040(3)	0.030(2)	0.030(3)	-0.002(2)	0.007(2)	0.013(2)
C6	0.040(3)	0.042(3)	0.047(3)	0.024(3)	0.012(3)	0.022(3)
C7	0.048(3)	0.035(3)	0.040(3)	0.001(2)	0.008(3)	0.020(2)
C8	0.045(3)	0.026(2)	0.035(3)	0.007(2)	0.004(3)	0.013(2)
C9	0.068(4)	0.032(3)	0.039(3)	0.026(3)	0.015(3)	0.016(2)
C10	0.084(4)	0.023(3)	0.036(3)	0.007(3)	0.009(3)	0.011(2)
C11	0.041(3)	0.034(3)	0.050(3)	0.001(2)	0.007(3)	0.021(3)
C12	0.033(3)	0.029(2)	0.024(3)	0.006(2)	0.006(2)	0.010(2)
C13	0.041(3)	0.034(3)	0.049(3)	0.012(2)	0.006(3)	0.019(2)
C14	0.043(3)	0.035(3)	0.034(3)	0.003(2)	0.000(3)	0.011(2)
C15	0.031(3)	0.046(3)	0.042(3)	-0.002(2)	0.006(3)	0.004(3)
C16	0.038(3)	0.035(3)	0.030(3)	0.001(2)	0.006(3)	0.013(2)
C17	0.041(4)	0.046(4)	0.129(7)	0.014(3)	0.008(4)	0.042(4)
C18	0.068(4)	0.035(3)	0.048(4)	-0.013(3)	0.001(3)	0.010(3)
C19	0.057(4)	0.046(3)	0.040(3)	-0.005(3)	-0.005(3)	0.022(3)
C20	0.053(3)	0.047(3)	0.031(3)	0.008(3)	0.010(3)	0.022(2)
C21	0.054(4)	0.039(3)	0.028(3)	0.001(3)	0.004(3)	0.011(2)
C22	0.033(3)	0.035(3)	0.050(3)	0.009(2)	0.004(3)	0.010(2)
C23	0.096(5)	0.041(3)	0.042(3)	0.032(3)	0.020(3)	0.019(3)
C24	0.057(4)	0.079(5)	0.046(4)	0.009(3)	0.021(4)	0.000(3)
C25	0.035(3)	0.047(3)	0.046(3)	0.001(2)	-0.003(3)	0.014(3)
C26	0.033(3)	0.038(3)	0.053(4)	0.007(2)	0.016(3)	-0.003(3)

C27	0.033(3)	0.061(4)	0.046(3)	0.016(3)	0.006(3)	0.016(3)
C28	0.044(3)	0.042(3)	0.082(4)	0.015(3)	0.012(3)	0.030(3)
C29	0.109(6)	0.029(3)	0.039(4)	-0.001(3)	0.006(4)	0.005(3)
C30	0.057(3)	0.020(2)	0.051(3)	0.003(2)	0.002(3)	0.010(2)
C31	0.062(4)	0.034(3)	0.031(3)	0.012(3)	0.002(3)	0.013(2)
C32	0.056(3)	0.029(3)	0.038(3)	0.006(2)	0.003(3)	0.011(2)
C33	0.053(4)	0.069(4)	0.040(4)	0.013(3)	0.017(3)	0.024(3)
C34	0.088(4)	0.037(3)	0.052(4)	0.022(3)	0.030(4)	0.006(3)
C35	0.050(3)	0.030(3)	0.038(3)	-0.006(2)	-0.006(3)	0.015(2)
C36	0.051(3)	0.044(3)	0.037(3)	0.023(3)	0.003(3)	0.014(2)
C37	0.081(5)	0.103(6)	0.039(4)	-0.007(4)	0.010(4)	0.027(4)
C38	0.067(4)	0.030(3)	0.065(4)	0.014(3)	0.022(4)	0.016(3)
C39	0.084(4)	0.037(3)	0.033(3)	0.022(3)	0.016(3)	0.017(3)
C40	0.052(4)	0.046(4)	0.096(5)	0.023(3)	0.019(4)	-0.010(3)
C41	0.075(5)	0.062(4)	0.041(4)	-0.017(3)	-0.005(4)	0.021(3)
C42	0.039(3)	0.033(3)	0.046(3)	0.009(2)	0.009(3)	0.012(3)
C43	0.050(4)	0.035(3)	0.136(7)	0.022(3)	0.006(5)	0.001(4)
C44	0.039(3)	0.045(3)	0.048(3)	0.022(2)	0.015(3)	0.017(3)
C45	0.054(4)	0.070(4)	0.048(4)	0.011(4)	0.011(3)	0.034(3)
C46	0.110(5)	0.025(3)	0.063(4)	0.013(3)	0.032(4)	0.005(3)
C47	0.048(3)	0.034(3)	0.041(3)	0.005(2)	0.007(3)	0.016(2)
C48	0.046(3)	0.040(3)	0.036(3)	0.010(3)	0.005(3)	0.010(3)
N1	0.038(2)	0.030(2)	0.035(2)	-0.0014(18)	0.003(2)	0.0063(19)
N2	0.035(2)	0.027(2)	0.057(3)	0.0093(18)	0.012(2)	0.012(2)
N3	0.030(2)	0.030(2)	0.034(2)	0.0090(17)	0.0028(19)	0.0109(18)
N4	0.029(2)	0.030(2)	0.033(2)	0.0081(17)	0.0046(19)	0.0141(18)
N5	0.044(3)	0.031(2)	0.029(2)	0.0106(19)	0.009(2)	0.0100(18)
N6	0.051(3)	0.029(2)	0.030(2)	0.006(2)	0.006(2)	0.0150(18)
N7	0.046(3)	0.032(2)	0.034(2)	0.0004(19)	0.009(2)	0.0159(19)
N8	0.039(2)	0.035(2)	0.036(3)	0.0150(19)	0.010(2)	0.0099(19)
O1	0.073(3)	0.0305(19)	0.039(2)	-0.0006(17)	0.013(2)	0.0159(16)
O2	0.083(3)	0.0302(19)	0.040(2)	-0.0026(18)	0.011(2)	0.0128(16)

O3	0.070(3)	0.047(2)	0.038(2)	0.0039(18)	0.012(2)	0.0233(17)
O4	0.079(3)	0.043(2)	0.033(2)	0.0008(19)	0.005(2)	0.0150(18)
O5	0.063(2)	0.0298(18)	0.041(2)	0.0109(17)	0.0111(19)	0.0061(16)
O6	0.087(3)	0.044(2)	0.042(2)	0.017(2)	0.019(2)	0.0153(18)
O7	0.067(2)	0.0327(19)	0.046(2)	0.0182(17)	0.0115(19)	0.0154(16)
O8	0.082(3)	0.047(2)	0.064(3)	0.018(2)	0.023(2)	0.033(2)
O9	0.073(3)	0.0283(19)	0.055(2)	0.0093(18)	0.008(2)	0.0151(17)
O10	0.049(2)	0.0312(18)	0.046(2)	0.0070(16)	-0.0021(18)	0.0054(16)
O11	0.054(2)	0.063(2)	0.078(3)	0.033(2)	0.009(2)	0.027(2)
O12	0.054(2)	0.054(2)	0.055(3)	0.021(2)	0.008(2)	0.014(2)
O13	0.041(2)	0.101(3)	0.065(3)	-0.006(2)	0.003(2)	0.020(3)
O14	0.050(3)	0.046(2)	0.037(2)	0.0024(19)	0.004(2)	0.0151(18)
O15	0.040(2)	0.051(2)	0.064(3)	0.0030(18)	0.003(2)	0.038(2)
O16	0.054(2)	0.055(2)	0.060(3)	-0.006(2)	0.009(2)	0.025(2)
O17	0.064(3)	0.108(4)	0.073(3)	0.036(3)	0.028(3)	0.045(3)
O18	0.046(2)	0.049(2)	0.076(3)	0.0085(19)	-0.003(2)	0.019(2)
O19	0.065(3)	0.047(2)	0.044(2)	0.015(2)	0.007(2)	0.018(2)
O20	0.056(3)	0.049(2)	0.057(3)	0.012(2)	0.015(2)	0.017(2)
O21	0.064(3)	0.053(3)	0.084(3)	0.004(2)	-0.008(3)	0.034(3)
O22	0.089(4)	0.073(3)	0.063(3)	-0.002(3)	0.007(3)	0.027(3)
O23	0.138(4)	0.057(3)	0.056(3)	0.031(3)	0.003(3)	0.017(2)
O24	0.111(5)	0.097(4)	0.072(4)	-0.015(3)	-0.015(4)	0.043(3

Table 14.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of Aqua(2,2'-bipyridine-k^2N,N')(pyridine 2,6-dicarboxylato-k^3N,O,O) nickel(II) dihydrate, $[Ni(H_2O)(2,2'\text{-bipy})(2,6\text{-pda})](H_2O)_2$ (14)

Atom	x/a	y/b	z/c	U_{eq}
Ni1	0.62159(9)	-0.15182(7)	0.66225(6)	0.0208(3)
Ni2	0.86575(9)	0.14779(7)	0.90670(6)	0.0210(3)
C1	0.5552(9)	-0.1338(6)	0.8210(6)	0.040(3)
H1	0.55350	-0.17890	0.82290	0.048
C2	0.5348(10)	-0.0992(8)	0.8861(6)	0.048(3)
H2	0.52200	-0.12030	0.93080	0.058
C3	0.5346(11)	-0.0301(8)	0.8811(7)	0.052(4)
H3	0.52160	-0.00500	0.92290	0.062
C4	0.5531(10)	-0.0021(7)	0.8159(7)	0.043(3)
H4	0.55100	0.04280	0.81140	0.052
C34	0.5757(9)	-0.0403(6)	0.7543(6)	0.030(2)
C5	0.5989(10)	-0.0121(6)	0.6814(7)	0.027(2)
C6	0.6040(15)	0.0540(8)	0.6684(10)	0.055(4)
H5	0.58790	0.08310	0.70610	0.066
C7	0.6331(16)	0.0769(8)	0.5993(9)	0.062(5)
H6	0.63450	0.12130	0.59000	0.074
C8	0.8914(11)	0.0283(7)	0.8031(7)	0.035(3)
H7	0.90550	0.05840	0.76610	0.042
C9	0.8986(11)	-0.0351(6)	0.7854(6)	0.038(3)
H8	0.91000	-0.04820	0.73660	0.045
C10	0.8884(12)	-0.0795(8)	0.8418(9)	0.049(4)
H9	0.89670	-0.12350	0.83180	0.059
C11	0.8659(11)	-0.0600(7)	0.9132(9)	0.040(3)
H10	0.85760	-0.08980	0.95160	0.048
C12	0.8561(9)	0.0069(6)	0.9252(7)	0.031(3)
C13	0.8276(8)	0.0354(5)	0.9963(7)	0.029(2)

C14	0.8048(10)	-0.0032(7)	1.0600(8)	0.047(3)
H11	0.80490	-0.04830	1.05750	0.057
C15	0.7819(11)	0.0294(8)	1.1274(7)	0.054(4)
H12	0.76780	0.00550	1.17000	0.064
C16	0.6600(16)	0.0336(10)	0.5446(10)	0.077(6)
H13	0.68360	0.04780	0.49880	0.092
C17	0.6502(14)	-0.0336(7)	0.5606(8)	0.044(4)
H14	0.66160	-0.06330	0.52260	0.052
C18	0.5617(8)	-0.2052(5)	0.5127(5)	0.024(2)
C19	0.4306(8)	-0.1970(5)	0.5408(5)	0.023(2)
C20	0.5788(9)	-0.2244(6)	0.4396(6)	0.037(3)
H15	0.50970	-0.23300	0.40250	0.044
C21	0.7012(10)	-0.2303(7)	0.4239(6)	0.047(3)
H16	0.71660	-0.24550	0.37660	0.057
C22	0.8020(9)	-0.2133(7)	0.4799(6)	0.042(3)
H17	0.88500	-0.21560	0.46950	0.05
C23	0.7779(8)	-0.1930(5)	0.5506(6)	0.025(2)
C24	0.8709(9)	-0.1720(5)	0.6176(6)	0.026(2)
C25	0.7806(11)	0.0953(8)	1.1301(6)	0.048(3)
H18	0.76710	0.11670	1.17450	0.057
C26	0.7995(9)	0.1298(6)	1.0663(6)	0.037(3)
H19	0.79430	0.17480	1.06740	0.045
C27	1.0200(7)	0.1912(5)	0.7955(5)	0.022(2)
C28	1.1161(8)	0.1685(5)	0.8636(5)	0.021(2)
C29	1.0463(9)	0.2137(6)	0.7260(6)	0.036(3)
H20	1.12920	0.21820	0.71600	0.044
C30	0.9426(11)	0.2294(7)	0.6709(6)	0.048(3)
H21	0.95730	0.24300	0.62280	0.058
C31	0.8196(9)	0.2251(6)	0.6861(6)	0.034(3)
H22	0.75160	0.23690	0.64970	0.041
C32	0.8010(8)	0.2032(5)	0.7557(5)	0.0220(19)
C33	0.6762(8)	0.1935(5)	0.7841(6)	0.027(2)

N1	0.5771(7)	-0.1054(4)	0.7563(5)	0.0263(18)
N2	0.8642(10)	0.0522(4)	0.8733(7)	0.0244(17)
N3	0.6265(13)	-0.0549(4)	0.6248(8)	0.0296(16)
N4	0.6567(6)	-0.1890(4)	0.5643(4)	0.0187(16)
N5	0.8255(7)	0.1007(5)	1.0017(4)	0.0275(19)
N6	0.8978(6)	0.1831(5)	0.8121(5)	0.041(3)
O1	0.6340(6)	-0.2413(4)	0.7172(4)	0.0281(16)
O2	0.8778(6)	0.2375(4)	0.9622(4)	0.0290(16)
O3	1.2288(9)	-0.1267(6)	0.6789(6)	0.081(4)
O4	0.4736(8)	0.1265(5)	0.9315(5)	0.063(3)
O5	0.4349(7)	-0.1723(4)	0.6056(4)	0.0312(18)
O6	0.3349(6)	-0.2156(4)	0.4969(4)	0.0359(18)
O7	0.8259(6)	-0.1516(4)	0.6744(4)	0.0304(17)
O8	0.9868(6)	-0.1758(4)	0.6110(5)	0.0401(19)
O9	1.0694(7)	0.1490(4)	0.9201(4)	0.0302(18)
O10	1.2299(6)	0.1712(4)	0.8554(4)	0.0387(19)
O11	0.6796(7)	0.1675(4)	0.8497(4)	0.030(2)
O12	0.5791(6)	0.2105(4)	0.7408(4)	0.0355(18)

Table 14.2: Anisotropic displacement parameters of Aqua(2,2'-bipyridine-k^2N,N')(pyridine 2,6-dicarboxylato-k^3N,O,O) nickel(II) dihydrate, [Ni(H_2O)(2,2'-bipy)(2,6-pda)](H_2O)$_2$ (14), in Å2.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0214(5)	0.0243(7)	0.0177(6)	0.0017(5)	0.0060(4)	-0.0016(6)
Ni2	0.0210(5)	0.0216(7)	0.0208(6)	-0.0004(5)	0.0046(4)	0.0025(6)
C1	0.044(6)	0.051(9)	0.025(5)	-0.005(5)	0.010(4)	-0.010(5)
C2	0.043(6)	0.077(11)	0.026(6)	0.001(6)	0.011(5)	-0.007(6)
C3	0.039(6)	0.080(12)	0.039(7)	-0.003(6)	0.016(5)	-0.039(7)
C4	0.039(6)	0.049(8)	0.043(7)	0.017(5)	0.009(5)	-0.017(6)
C34	0.028(5)	0.031(7)	0.032(5)	0.003(4)	0.010(4)	-0.009(5)
C5	0.030(5)	0.013(6)	0.037(6)	0.002(4)	0.002(4)	-0.005(5)
C6	0.075(10)	0.034(9)	0.057(10)	0.003(7)	0.007(8)	-0.016(7)
C7	0.075(10)	0.032(9)	0.070(12)	0.005(7)	-0.016(10)	0.016(7)
C8	0.034(6)	0.032(8)	0.039(7)	-0.015(5)	0.003(5)	-0.015(5)
C9	0.049(6)	0.037(8)	0.027(5)	-0.001(5)	0.004(5)	-0.013(5)
C10	0.039(7)	0.035(9)	0.069(10)	0.011(6)	-0.002(7)	-0.011(7)
C11	0.028(5)	0.027(7)	0.063(9)	-0.010(5)	-0.004(6)	0.002(6)
C12	0.017(5)	0.038(8)	0.037(6)	-0.002(4)	0.002(4)	0.001(5)
C13	0.017(4)	0.019(6)	0.047(6)	0.000(4)	-0.002(4)	0.010(5)
C14	0.041(6)	0.040(8)	0.059(8)	0.001(5)	0.000(6)	0.030(7)
C15	0.046(7)	0.078(12)	0.039(7)	0.004(7)	0.008(5)	0.026(7)
C16	0.080(11)	0.076(15)	0.070(11)	-0.016(9)	-0.004(9)	0.042(11)
C17	0.066(9)	0.029(8)	0.037(7)	-0.009(6)	0.009(6)	0.007(6)
C18	0.024(4)	0.028(6)	0.017(4)	-0.002(4)	-0.002(3)	-0.009(4)
C19	0.022(4)	0.025(6)	0.020(4)	-0.001(4)	0.000(3)	0.007(4)
C20	0.027(5)	0.057(8)	0.027(5)	-0.001(5)	0.009(4)	-0.008(5)
C21	0.032(6)	0.082(11)	0.030(6)	-0.009(6)	0.013(4)	-0.017(6)
C22	0.028(5)	0.061(9)	0.039(6)	-0.003(5)	0.014(4)	-0.016(6)
C23	0.020(4)	0.027(6)	0.028(5)	0.003(4)	0.006(4)	-0.004(4)
C24	0.026(5)	0.025(6)	0.028(5)	0.005(4)	0.004(4)	-0.001(4)
C25	0.051(7)	0.067(10)	0.028(6)	0.002(6)	0.018(5)	0.006(6)

C26	0.046(6)	0.040(8)	0.029(5)	0.001(5)	0.015(4)	-0.009(5)
C27	0.016(4)	0.028(6)	0.026(5)	-0.001(4)	0.017(3)	0.002(4)
C28	0.015(4)	0.020(6)	0.028(5)	0.001(3)	0.005(3)	0.007(4)
C29	0.029(5)	0.055(8)	0.030(5)	0.002(5)	0.019(4)	0.009(5)
C30	0.051(7)	0.073(10)	0.023(5)	0.004(6)	0.010(5)	0.026(6)
C31	0.023(5)	0.045(8)	0.035(6)	0.007(4)	0.002(4)	0.008(5)
C32	0.025(4)	0.018(5)	0.021(4)	0.002(4)	0.000(4)	0.000(4)
C33	0.026(5)	0.027(6)	0.027(5)	-0.002(4)	-0.002(4)	0.001(4)
N1	0.030(4)	0.023(5)	0.028(4)	0.004(3)	0.012(3)	-0.006(4)
N2	0.018(4)	0.020(4)	0.034(4)	-0.001(4)	0.002(3)	-0.003(5)
N3	0.033(4)	0.026(4)	0.031(4)	0.002(5)	0.006(3)	-0.003(5)
N4	0.022(3)	0.019(4)	0.017(4)	0.006(3)	0.009(3)	-0.010(3)
N5	0.024(4)	0.037(6)	0.021(4)	-0.002(4)	0.002(3)	0.001(4)
N6	0.008(3)	0.070(7)	0.041(5)	0.019(4)	-0.011(3)	-0.048(5)
O1	0.024(3)	0.030(4)	0.030(4)	0.000(3)	0.004(3)	0.009(3)
O2	0.023(3)	0.034(5)	0.032(4)	-0.005(3)	0.009(3)	-0.002(3)
O3	0.059(6)	0.105(10)	0.079(7)	-0.011(6)	0.011(5)	-0.045(7)
O4	0.052(5)	0.096(9)	0.045(5)	0.012(5)	0.014(4)	0.020(5)
O5	0.026(4)	0.039(5)	0.029(4)	0.003(3)	0.010(3)	-0.001(4)
O6	0.025(3)	0.056(6)	0.027(4)	-0.008(3)	0.004(3)	0.002(4)
O7	0.032(3)	0.030(5)	0.029(4)	0.001(3)	0.004(3)	-0.005(4)
O8	0.023(3)	0.040(5)	0.058(5)	0.001(3)	0.005(3)	-0.009(4)
O9	0.029(3)	0.033(5)	0.028(3)	0.007(4)	0.004(3)	0.007(4)
O10	0.023(3)	0.046(5)	0.048(4)	0.004(3)	0.009(3)	0.016(4)
O11	0.020(3)	0.044(6)	0.028(4)	-0.001(3)	0.007(3)	0.014(4)
O12	0.022(3)	0.050(5)	0.033(4)	0.009(3)	-0.001(3)	-0.005(4)

Table 15.1: Atomic parameters and equivalent temperature coefficients U_{eq} (10^{-4} pm^2) of Aqua(2,2'-bipyridine-k^2N,N')(pyridine 2,6-dicarboxylato-k^3N,O,O) nickel(II) dihydrate, $[Nd(2,6\text{-}pda)_3][Nd(2,6\text{-}pda)(H_2O)_6]_2(H_2O)_7$ (15)

Atom	x/a	y/b	z/c	U_{eq}
Nd01	0.42025(5)	0.05179(5)	0.77809(4)	0.04407(19)
Nd02	0.06282(5)	0.56346(5)	0.72538(4)	0.03079(16)
Nd03	0.47795(5)	0.51347(5)	0.74940(3)	0.0370(12)
O1	0.5246(8)	0.6443(7)	0.6125(5)	0.0282(11)
O2	0.5582(8)	-0.0605(8)	0.8671(5)	0.0350(12)
O4	0.4970(7)	0.6775(7)	0.7784(5)	0.0405(12)
O5	0.3027(7)	0.5163(7)	0.7216(5)	0.0349(12)
O6	0.8593(7)	0.4096(7)	0.7685(5)	0.0397(13)
O7	0.3406(7)	0.4711(7)	0.8901(5)	0.048
O8	0.5165(8)	0.3083(7)	0.7699(5)	0.0413(12)
O9	0.3452(8)	0.2019(7)	0.8612(5)	0.0358(12)
O10	0.5659(8)	0.1512(7)	0.7258(5)	0.043
O11	0.4178(7)	-0.1444(7)	0.7981(5)	0.0433(13)
O12	0.0569(8)	0.4446(7)	0.6280(5)	0.052
O13	0.1096(7)	0.5988(7)	0.7174(5)	0.0494(15)
O14	-0.0858(8)	0.5863(9)	0.8655(5)	0.059
O15	0.0797(8)	0.3756(7)	0.7976(5)	0.0417(13)
O16	0.3878(9)	0.0512(8)	0.6523(6)	0.05
O17	-0.2817(8)	0.6466(9)	0.8049(5)	0.0289(11)
N100	0.5768(8)	0.4277(8)	0.6196(6)	0.0401(13)
O19	0.6148(8)	-0.0675(8)	0.6958(5)	0.048
O20	0.3001(8)	0.4129(8)	1.0283(5)	0.0399(12)
O22	-0.1238(7)	0.7793(7)	0.6913(5)	0.048
O23	0.2010(8)	0.1013(7)	0.8233(5)	0.0461(13)
O24	0.3267(8)	0.2584(8)	0.6946(5)	0.0360(12)
O25	0.6948(7)	0.4572(7)	0.7261(5)	0.070(2)
N1	0.2963(9)	0.6991(9)	0.7537(6)	0.083
N2	0.0066(8)	0.6670(8)	0.5755(6)	0.043(3)
N3	0.3315(9)	-0.0173(8)	0.9324(6)	0.052
N4	0.5672(8)	0.4152(8)	0.8790(6)	0.030(2)
O26	0.1480(8)	0.4155(8)	0.5019(5)	0.027(2)
O27	0.5960(8)	0.6873(8)	0.4753(5)	0.055(4)
O28	-0.1078(9)	0.9465(8)	0.6100(6)	0.066
O29	0.6082(8)	-0.1495(8)	0.9874(5)	0.062(5)
C040	0.1985(11)	0.894(1)	0.7664(8)	0.074
H040	0.20080	0.95970	0.77220	0.035(3)
C042	0.5971(10)	0.3161(10)	0.6278(7)	0.042

C043	0.6854(10)	0.3878(10)	0.8693(7)	0.038(3)
C044	0.5468(11)	0.3386(11)	1.0235(7)	0.045
H044	0.49850	0.32110	107.560	0.049(4)
C045	0.0196(11)	0.7829(11)	0.5528(8)	0.059
O101	0.0359(9)	0.1584(10)	0.9206(7)	0.040(3)
C048	0.3590(12)	-0.1156(11)	1.0688(7)	0.048
H048	0.40960	-0.15620	0.43730	0.031(3)
C049	0.4029(11)	-0.0784(10)	0.9854(7)	0.029(2)
C050	0.2017(10)	0.5973(10)	0.7273(7)	0.0578(16)
C051	0.6826(11)	0.3345(11)	0.4833(8)	0.069
H051	0.71700	0.30340	0.43730	0.0498(15)
C052	0.1956(10)	0.7069(11)	0.7428(7)	0.06
C053	0.7522(10)	0.4194(10)	0.7813(7)	0.0426(13)
C054	0.6624(10)	0.4497(11)	0.4751(7)	0.0432(13)
H054	0.68540	0.49620	0.42400	0.0418(13)
C055	0.0692(10)	0.6089(11)	0.5170(7)	0.05
C056	0.5347(11)	-0.0983(10)	0.9435(7)	0.0559(16)
C057	0.6072(10)	0.4928(10)	0.5450(7)	0.067
C058	0.1065(11)	0.6582(12)	0.4346(8)	0.0696(18)
H058	0.14760	0.61420	0.39550	0.083
C060	0.2969(10)	0.7932(11)	0.7662(7)	0.0463(13)
C061	0.4997(10)	0.3926(10)	0.9546(7)	0.056
C062	0.413(1)	0.7741(9)	0.7815(6)	0.0483(14)
C063	0.557(1)	0.2534(10)	0.7136(7)	0.0481(14)
C064	0.0911(10)	0.8366(10)	0.6244(8)	0.058
C065	0.6699(11)	0.3108(12)	1.0126(8)	0.0535(15)
H065	0.70350	0.27590	105.790	0.064
C066	0.6506(11)	0.2674(11)	0.5606(8)	0.0654(19)
H066	0.66500	0.18990	0.56750	0.078
C067	0.5746(10)	0.6172(10)	0.5427(7)	0.0452(14)
C068	0.0945(10)	0.4785(11)	0.5511(7)	0.054
C070	0.3683(10)	0.4271(10)	0.9593(7)	0.0427(13)
C071	0.7394(11)	0.3356(11)	0.9348(8)	0.0436(13)
H071	0.82060	0.31780	0.92630	0.052
C072	0.2120(11)	0.0145(10)	0.9624(8)	0.0536(15)
C075	0.0790(12)	0.7781(12)	0.4129(8)	0.0611(16)
H075	0.10330	0.81540	0.35840	0.073
C077	0.0163(12)	0.8405(12)	0.4722(8)	0.0427(13)
H077	-0.00180	0.91990	0.45840	0.051
C078	0.2352(12)	-0.0897(12)	1.0978(8)	0.0428(13)
H078	0.20320	-0.11930	115.280	0.0527(9)
C082	0.0924(11)	0.8041(11)	0.7455(8)	0.126(3)
H082	0.02400	0.80420	0.73880	0.177(4)
C085	0.1615(13)	-0.0211(12)	1.0453(8)	0.119(2)

H085	0.07900	0.00130	106.490	0.0602(10)
C088	0.1430(11)	0.0951(11)	0.8976(8)	0.0760(12)
C500	0.0915(10)	0.8939(12)	0.7574(9)	0.0582(9)
H500	0.02200	0.95920	0.76010	0.0742(12)
O200	-0.2156(8)	0.6382(7)	0.6420(5)	0.0386(7)
O500	-0.2089(8)	1.0076(8)	0.7423(6)	0.0403(7)
O602	-0.1759(9)	0.8256(8)	0.8736(6)	0.0444(7)
O603	0.2000(9)	0.1854(9)	0.5832(7)	0.0399(7)
O604	0.0263(10)	0.1855(9)	0.7323(7)	0.0489(8)
O601	0.4742(10)	0.8748(8)	0.5784(7)	0.0409(7)
O615	0.1221(9)	0.4467(10)	0.9083(7)	0.0410(7)
O755	0.3265(13)	0.0424(13)	0.4723(8)	0.0366(7)

Table 14.2: Anisotropic displacement parameters of $[Nd(2,6\text{-}pda)_3][Nd(2,6\text{-}pda)(H_2O)_6]_2(H_2O)_7$ (**15**), in Å2.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd01	0.0210(3)	0.0179(3)	0.0148(3)	-0.0075(2)	0.0055(2)	0.0046(2)
Nd02	0.0165(3)	0.0202(3)	0.0134(3)	-0.0089(2)	0.0028(2)	0.0048(2)
Nd03	0.0177(3)	0.0179(3)	0.0120(3)	-0.0092(2)	0.0039(2)	0.0035(2)
O1	0.029(4)	0.022(4)	0.016(4)	-0.009(4)	-0.001(3)	-0.004(3)
O2	0.030(5)	0.031(5)	0.015(4)	-0.011(4)	-0.009(3)	-0.003(3)
O4	0.021(4)	0.025(4)	0.022(4)	-0.007(3)	-0.009(3)	-0.009(3)
O5	0.022(4)	0.023(4)	0.020(4)	-0.012(3)	-0.005(3)	-0.008(3)
O6	0.021(4)	0.023(4)	0.023(4)	-0.013(3)	-0.005(3)	-0.003(3)
O7	0.022(4)	0.031(4)	0.020(4)	-0.012(4)	-0.009(3)	-0.007(4)
O8	0.031(4)	0.023(4)	0.018(4)	-0.015(4)	-0.005(3)	-0.005(3)
O9	0.034(5)	0.022(4)	0.021(4)	-0.017(4)	-0.006(4)	-0.005(3)
O10	0.029(4)	0.018(4)	0.027(4)	-0.011(3)	-0.005(4)	-0.006(3)
O11	0.026(4)	0.025(4)	0.028(5)	-0.011(4)	-0.009(4)	-0.010(4)
O12	0.032(5)	0.028(4)	0.016(4)	-0.014(4)	-0.006(3)	-0.007(3)
O13	0.023(4)	0.028(4)	0.028(4)	-0.018(4)	-0.010(4)	-0.004(4)
O14	0.022(4)	0.044(5)	0.023(4)	-0.007(4)	-0.007(4)	-0.013(4)
O15	0.032(5)	0.027(4)	0.029(5)	-0.022(4)	-0.011(4)	-0.004(4)
O16	0.046(6)	0.025(4)	0.029(5)	-0.008(4)	-0.020(4)	-0.010(4)
O17	0.021(4)	0.047(6)	0.022(4)	-0.005(4)	-0.009(3)	-0.019(4)
N100	0.019(5)	0.017(4)	0.021(5)	-0.011(4)	-0.004(4)	0.000(4)
O19	0.027(4)	0.032(5)	0.017(4)	-0.008(4)	-0.007(3)	-0.012(4)
O20	0.023(4)	0.036(5)	0.017(4)	-0.014(4)	-0.002(3)	-0.006(4)
O22	0.025(4)	0.018(4)	0.021(4)	-0.009(3)	-0.001(3)	-0.002(3)
O23	0.029(5)	0.023(4)	0.025(4)	-0.006(4)	-0.011(4)	-0.007(4)
O24	0.032(5)	0.032(5)	0.015(4)	-0.012(4)	-0.003(3)	-0.004(4)
O25	0.021(4)	0.031(4)	0.012(4)	-0.016(4)	-0.001(3)	-0.002(3)
N1	0.027(5)	0.022(5)	0.019(5)	-0.006(4)	-0.008(4)	-0.005(4)
N2	0.016(4)	0.020(5)	0.015(4)	-0.010(4)	-0.001(4)	-0.002(4)

N3	0.026(5)	0.017(4)	0.019(5)	-0.009(4)	-0.008(4)	-0.002(4)
N4	0.021(5)	0.016(4)	0.016(4)	-0.011(4)	-0.004(4)	-0.003(4)
O26	0.031(5)	0.033(5)	0.019(4)	-0.008(4)	-0.003(4)	-0.014(4)
O27	0.036(5)	0.030(5)	0.014(4)	-0.018(4)	-0.003(4)	0.000(3)
O28	0.041(5)	0.019(4)	0.040(6)	-0.019(4)	-0.003(4)	-0.005(4)
O29	0.028(5)	0.032(5)	0.023(4)	-0.009(4)	-0.011(4)	-0.004(4)
C040	0.025(6)	0.021(6)	0.038(7)	-0.015(5)	-0.009(5)	-0.009(5)
C042	0.022(6)	0.022(6)	0.018(5)	-0.010(5)	-0.006(4)	-0.002(5)
C043	0.017(5)	0.021(5)	0.018(5)	-0.005(4)	-0.005(4)	-0.009(4)
C044	0.026(6)	0.030(6)	0.015(5)	-0.013(5)	-0.001(5)	-0.003(5)
C045	0.024(6)	0.027(6)	0.026(6)	-0.012(5)	-0.009(5)	-0.007(5)
O101	0.029(5)	0.057(7)	0.043(6)	-0.008(5)	-0.011(5)	-0.011(5)
C048	0.033(7)	0.024(6)	0.018(6)	-0.013(5)	-0.006(5)	-0.005(5)
C049	0.030(6)	0.019(5)	0.020(6)	-0.007(5)	-0.008(5)	-0.008(5)
C050	0.025(6)	0.023(5)	0.014(5)	-0.012(5)	-0.008(4)	-0.005(4)
C051	0.027(6)	0.031(6)	0.023(6)	-0.012(5)	-0.003(5)	-0.014(5)
C052	0.022(6)	0.027(6)	0.013(5)	-0.012(5)	-0.003(4)	-0.003(4)
C053	0.015(5)	0.022(5)	0.019(5)	-0.010(4)	0.000(4)	-0.005(4)
C054	0.024(6)	0.031(6)	0.016(5)	-0.017(5)	-0.004(4)	-0.006(5)
C055	0.014(5)	0.031(6)	0.020(6)	-0.009(5)	-0.006(4)	-0.004(5)
C056	0.029(6)	0.017(5)	0.019(6)	-0.007(5)	-0.007(5)	-0.005(4)
C057	0.020(5)	0.025(6)	0.018(5)	-0.010(5)	-0.007(4)	-0.003(5)
C058	0.021(6)	0.040(7)	0.021(6)	-0.015(5)	0.000(5)	-0.011(5)
C060	0.020(5)	0.029(6)	0.018(5)	-0.008(5)	-0.005(4)	-0.011(5)
C061	0.021(5)	0.021(5)	0.015(5)	-0.008(4)	-0.002(4)	-0.007(4)
C062	0.029(6)	0.018(5)	0.011(5)	-0.016(5)	-0.007(4)	-0.001(4)
C063	0.017(5)	0.022(6)	0.019(5)	-0.005(4)	-0.003(4)	-0.007(5)
C064	0.022(6)	0.018(5)	0.028(6)	-0.011(5)	-0.007(5)	-0.003(5)
C065	0.026(6)	0.036(7)	0.020(6)	-0.011(5)	-0.012(5)	-0.004(5)
C066	0.028(6)	0.027(6)	0.024(6)	-0.014(5)	-0.004(5)	-0.009(5)
C067	0.025(6)	0.024(6)	0.016(5)	-0.017(5)	-0.007(4)	0.001(4)
C068	0.017(5)	0.030(6)	0.023(6)	-0.009(5)	-0.006(4)	-0.011(5)
C070	0.023(6)	0.025(6)	0.016(5)	-0.010(5)	-0.003(4)	-0.007(5)

C071	0.023(6)	0.030(6)	0.024(6)	-0.009(5)	-0.006(5)	-0.006(5)
C072	0.027(6)	0.023(6)	0.027(6)	-0.011(5)	-0.010(5)	-0.005(5)
C075	0.031(7)	0.037(7)	0.020(6)	-0.021(6)	-0.005(5)	0.006(5)
C077	0.032(7)	0.028(6)	0.025(6)	-0.017(5)	-0.007(5)	0.000(5)
C078	0.035(7)	0.031(7)	0.020(6)	-0.015(6)	-0.001(5)	-0.005(5)
C082	0.024(6)	0.029(6)	0.033(7)	-0.014(5)	-0.006(5)	-0.013(5)
C085	0.031(7)	0.037(7)	0.028(7)	-0.019(6)	-0.003(5)	-0.007(6)
C088	0.027(6)	0.027(6)	0.028(7)	-0.014(5)	-0.007(5)	-0.003(5)
C500	0.013(5)	0.038(7)	0.056(9)	-0.020(5)	-0.010(5)	-0.017(6)
O200	0.031(5)	0.025(4)	0.017(4)	-0.019(4)	-0.007(3)	-0.002(3)
O500	0.028(5)	0.028(5)	0.046(6)	-0.013(4)	-0.007(4)	-0.017(4)
O602	0.033(5)	0.032(5)	0.039(6)	-0.009(4)	-0.010(4)	-0.013(4)
O603	0.033(5)	0.034(5)	0.047(6)	-0.010(4)	-0.019(5)	-0.008(5)
O604	0.051(6)	0.030(5)	0.048(6)	-0.009(5)	-0.028(5)	-0.012(5)
O601	0.052(6)	0.026(5)	0.038(6)	-0.011(5)	-0.010(5)	-0.011(4)
O615	0.036(6)	0.051(7)	0.044(6)	-0.012(5)	-0.018(5)	-0.009(5)
O755	0.069(9)	0.071(9)	0.036(7)	0.003(7)	-0.016(6)	-0.020(6)

Erklärung

„Ich versichere, dass ich die von mir vorgelegte Dissertation selbstständig angefertigt, die benutzen Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit – einschließlich Tabellen, Karten, Abbildungen -, die anderen Werken im Wortlaut oder dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe; dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie – abgesehen von unten angegebenen Teilpublikationen – noch nicht veröffentlich worden ist sowie, dass ich eine solche Veröffentlichung vor Abschluss des Promotionsverfahrens nicht vornehmen werde. Die Bestimmungen der Promotionsordnung sind mir bekannt. Die von mir vorgelegte Dissertation ist von Prof. Dr. Gerd Meyer betreut worden.“

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