

Abstract

The subject of the presented work is the synthesis, as well as spectroscopic and structural investigation of vanadium- and zinc complexes of polydentate ligands with alcoholate- and tetrazolate functional groups. Variation of the reaction conditions allowed excellent control over the nuclearity and charge of the vanadium complexes. For the 2,6-substituted pyridinediols (R = H, pydimH₂; R = CH₃, pydipH₂; R = Ph, pyphenH₂), all three examples of the so called oxido-pincer-ligands possessing an ONO-donor set, anionic complexes [VO₂(ONO)]⁻ (with alkali metal as counter ion) could be obtained. For the ligands pydip²⁻ and pyphen²⁻ subsequent conversion into neutral [VOCl(ONO)]-type complexes was accomplished and monitored using NMR-spectroscopy. It could be shown, that this conversion follows a pathway via binuclear [V₂O₃(ONO)₂] complexes. Investigations into electrochemistry and EPR-spectroscopy showed the formation of a mixed-valent species upon one electron reduction of [V₂O₃(pyphen)₂] with strong delocalisation of the electron. In contrast, the analogous compounds of pydip²⁻ and pydim²⁻ showed strong localisation of the electron at one vanadium centre. Additionally, a series of tetrazole-ligands (2-tetrazolepyridine, PytzH; 2,6-ditetrazolepyridine, PydtzH₂ and 8-hydroxo-2-tetrazolequionoline, HyChtzH₂) was synthesised and the ligands were successfully reacted with vanadium, titanium and zinc. The resulting complexes were characterised using NMR, IR- and UV/Vis-spectroscopy. Importantly, the free tetrazole ligands as well as the resulting complexes showed emission. This was studied in detail. A special focus was laid on the NNN-pincer ligand PydtzH₂, which is a bioisosteric analogue of the ONO-pincer ligand PydicH₂ (2,6-pyridine dicarboxylic acid) with similar physicochemical properties. Interestingly, Pydtz²⁻ did not show very similar reactivity towards Titanium, Vanadium and Zinc compared to pydic²⁻. The compounds Na[Zn(Pydtz)₂·6H₂O] and K[VO₂(Pydtz)(H₂O)](CH₃OH) represent the first known complexes of Pydtz²⁻ that were structurally characterised, and the latter is the first known metal complex of a chelating tetrazole ligand containing an early transition metal. Moreover, the chiral bidentate ON-ligands (2-fenchyl-pyridine, fenpyH and menthyl-pyridine, menpyH) were employed in the synthesis of the compound [Zn(menpy)₃][ZnCl₄], containing the chiral [Zn(menpy)₃]²⁺ complex, as well as [V₃O₆(phenpy)₃]. Both structures were determined by single crystal x-ray diffraction.