

Abstract

The subject of the presented work is the synthesis and investigation of dinitrosyl complexes of iron as well as carbonylnitrosyl complexes of cobalt with nitrogen containing chelating ligands.

A series of Aryl-BIAN-iron dinitrosyl $[\text{Fe}(\text{Aryl-BIAN})(\text{NO})_2]$ and Aryl-BIAN-cobalt carbonylnitrosyl $[\text{Co}(\text{Aryl-BIAN})(\text{CO})(\text{NO})]$ complexes was successfully synthesised, in which the following Aryl-BIAN derivatives were used: Ph-BIAN, Mes-BIAN, 4-ⁱPr-Ph-BIAN, 2-Me-Ph-BIAN and 4-NO₂-Ph-BIAN (Aryl-BIAN = Bis(N-arylimino)-acenaphthene). The compounds were characterised using IR-, UV/Vis- and EPR spectroscopy as well as spectroelectrochemical UV/Vis-experiments. For $[\text{Fe}(\text{Mes-BIAN})(\text{NO})_2]$ and $[\text{Co}(\text{Mes-BIAN})(\text{CO})(\text{NO})]$ additional magnetic measurements were carried out. The nitrosyl ligand could be identified as NO⁺ (IR-spectroscopy) in all cases. The Aryl-BIAN ligands are neutral (UV/Vis-absorption spectroscopy), hence the oxidation states of the metals are Fe^{-II} and Co^{-I}. UV/Vis-, electrochemical as well as spectroelectrochemical investigations on both the iron and the cobalt complexes showed the reversible reduction of the complexes to be ligand centred (diimine- π^*), while the oxidations are metal centred.

The second part of this work deals with the synthesis and characterisation of iron dinitrosyl and cobalt carbonylnitrosyl complexes with various other α -diimine ligands. The α -diimines applied were bpy (2,2'-bipyridine), phen (1,10-Phenanthroline), pyphen (Dipyrido[3,2-*f*:2',3'-*h*]quinoxalin) and dppz (Dipyrido[3,2-*a*:2',3'-*c*]phenazin). The reversible reductions could again be proven to be ligand centred by performing electrochemical as well as UV/Vis-spectroelectrochemical measurements, while the oxidations were again metal centred.

A comparison of all systems investigated in this work and the well studied complexes with diazabutadiene ligands (R-DAB) reveals significant differences in the ligand-metal interaction between the strong donors (and poor π -acceptors) such as bpy and phen and the excellent π -acceptors (but poor σ -donors) such as Aryl-BIAN, R-DAB and dppz. The two extremely electron rich systems $[\text{Fe}(\text{NO})_2]$ and $[\text{Co}(\text{CO})(\text{NO})]$ are very well suited for the assessment of those effects.