Transition Metal Complexes of Tridentate Bisphenol Ligands and Their Reactivity towards Organic Substrates

Abstract:

The work presents an in-depth study of the transition metal complexes of tridentate bisphenol ligands and their reactivity. The synthesized compounds have been characterized by different spectroscopic methods including EPR, Mössbauer, variable temperature magnetic susceptibility measurements and electrochemical methods (CV, SQW). Different heterodonor (N, S, Se, P, PO)-containing bisphenol ligands stabilize various chelate rings and the heterodonors and the ring substituents have profound effect on the electrode potentials. Most of the complexes (30 out of 36 synthesized complexes) have been structurally characterized by X-ray crystallography. These ligands are good π-donors and stabilize higher oxidation states of the metals making strong M-O covalent bonds (e.g., with Mn(IV) and V(IV)). The ease of formation of the phenoxyl radicals by oxidation of the phenolate ligands depends upon the strength of the covalent M-O bonding and the electronegativity of heterodonor atoms.

A series of non-oxo vanadium(IV) complexes with the bisphenol ligands have been synthesized and characterized by various analytical techniques. They all show very strong covalent V-O bonds and the covalency could be related to structural parameters by EPR spectroscopy. Cr(III) and Mn(IV) complexes of a N-containing bisphenol ligand represents the first example of d^3 complexes of Cr(III) and Mn(IV) in the same ligand system which allows their distinctive metal-ligand covalent binding characteristics as probes for comparison of EPR spectroscopic properties.

The ligands form either mono or dinuclear complexes with early transition metal ions (Cr(III), Mn(III), Mn(IV), Fe(III)), but with Ni(II) and Cu(II) they form a variety of complexes depending upon the way of synthesis. A set of polynuclear Ni(II) complexes, Ni_4, Ni_5 and Ni_6 having interesting structural and magnetic properties was studied in this work.

Another part of the thesis demonstrates the formation of phenoxyl radical in C-H abstraction process in the rate-determining step of the aerial oxidation of primary alcohols and amines, catalyzed by the Cu(II) complexes of the selenobisphenol ligand. Primary amines with at least one α-hydrogen atom undergo oxidative deamination reactions in air. The oxidative deamination reaction by air is the first example of functional model study of copper enzymes, Amine Oxidases.

$$\mathbf{RCH_2NH_2 + O_2 \xrightarrow[\text{as catalyst}]{\text{Cu(II) Complex}} RCHO + NH_3 + H_2O_2}$$