

07-Crystallography of Organometallic and Coordination Compounds

207

07.02 - Metal Clusters and Metal Coordination Analysis

MS-07.02.01 POLYMETALLOORGANOSILOXANOLATES - A NOVEL CLASS OF THE ORGANOSILICON METAL COMPLEXES. By *V.A.Igonin, S.V.Lindeman, Yu.T.Struchkov*, O.I.Shechegolikhina, A.A.Zhdanov, A.N.Nesmeyanov* Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

A representative series of the products of interaction between Na or K organosiloxanates and salts of bivalent transition metals (Mn, Co, Ni, Cu) or trivalent lanthanides (La, Nd, Gd, Dy) is structurally investigated by X-ray diffraction. These polymetallic organosiloxanates are based on stereoregular macrocyclic polydentate polyanions of a new type: $[-SiR(O^-)O-]_n$ (R=Ph, Et, Vin; n=6, 8, 12). The size of the macrocyclic ligand depends on the nature of coordinated metal ions (radii, oxidation state, coordination number). For *d*-metals, only cycles with n=6 are found; the cycles with n=8 are characteristic for lanthanide complexes, and the largest cycles with n=12 are observed only in some copper derivatives. Possibly, it is a result of stereochemical interplay between metal cationic group and siloxanolate anion. Such cationic groups in the complexes with n=6 or 8 are planar and include from 4 to 8 metal ions, sandwiched between two antiparallel co-axial macrocyclic 6- or 8-dentate organosiloxanolate ligands with all-cis-configuration and crown conformation. Most complexes of this type (excluding Cu derivatives) have an additional inner anionic ligand (Hal⁻, OH⁻ or O₂⁻) filling in the central cavity and thus stabilizing the cationic group. The exchange of inner ligands is feasible owing to the large central cavity of the macrocyclic ligands. However, the change of the inner ligand hardness results in the rearrangement of cationic layer and the shift of macrocyclic ligands relative to each other. Most of the investigated complexes include outer alkaline metal ions, which ensure complex electroneutrality and in many cases are coordinated by the siloxane macrocycle O atoms at the cavity as in crown-ether complexes. A partial replacement of complex-forming *d*-metal ions by the alkaline ions is also observed. In the complexes, which have undergone such replacement, the local symmetry of cationic group and organosiloxanolate ligand differs quite significantly, whereas in the original complexes both moieties always belong to a similar symmetry class. The largest organosiloxanolate ligands (n=12) with tris(cis)-trans-...-configuration were found only in copper complexes with globular, cavity-less structure. In such complexes the single ligand always coordinates the tetrahedral group of Cu²⁺ cations enveloping them as a tennis-ball seam. By silylation with Me₃SiCl the complexes studied are destroyed and all three types of ligands obtained as trimethylsilyl derivatives $[-SiR(OSiMe_3)O-]_n$, which according to an X-ray study (for n = 6 and 12) have the same configuration as the start-

ing siloxanolate ligands. Thus preparation of large stereoregular organosiloxane macrocycles becomes possible. Detailed stereochemistry and crystal chemistry of the new class of complexes are discussed.

MS-07.02.02 STRUCTURAL CHARACTERIZATION OF Co(III) HYDROLYSIS PRODUCTS. By *Erik Larsen¹, S. Larsen², T.A. Larsen², G. Poulsen¹, J. Springborg¹* and Dong Ni Wang¹, 1. Chemistry Department, The Royal Veterinary and Agricultural University and 2. Chemistry Department, University of Copenhagen, Denmark.

Investigations have been performed on base hydrolysis of cobalt(III) coordination compounds of ligands which coordinate through two primary amines and a thioether function. Another tridentate ligand like 1,4,7-triazacyclononane (tacn) or tris(aminoethyl)ethane (tame) is used to block the remaining three coordination sites on cobalt(III). Using 3-thia-1,6-hexanediamine (= aeaps) it was found that Co(tacn)(aeaps)³⁺ with base gives a species with a carbon-cobalt bond. This species was characterized by X-ray crystallography, by ¹³C and ⁵⁹Co NMR spectroscopy (P. Kofod, E. Larsen, S. Larsen, C.H. Petersen, J. Springborg and D.N. Wang *Acta Chem. Scand.* **46** (1992) 841) and the thermodynamics and kinetics was investigated (P. Kofod, E. Larsen, C.H. Petersen and J. Springborg *Acta Chem. Scand.* **46** (1992) 1149). A similar reaction takes place when Co(tame)(aeaps)³⁺ is treated with base and the structure of the dithionate of the ion **1** with carbon-cobalt bond will be shown. The ligand 3-thia-1,5-pentanediamine (= daes) has been used to give Co(tacn)(daes)³⁺. Under equilibrium conditions with strong base this ion does not produce a carbon coordinating cobalt(III) species. Instead it has been possible to isolate salts of two unexpected dinuclear coordination ions **2** and **3** whose structures will be displayed.

