

07-Crystallography of Organometallic and Coordination Compounds

207

07.02 - Metal Clusters and Metal Coordination Analysis

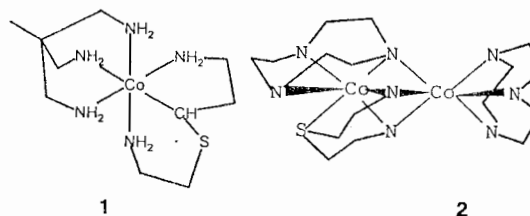
MS-07.02.01 POLYMETALLOORGANOSILOXANOLATES - A NOVEL CLASS OF THE ORGANOSILICON METAL COMPLEXES. By V.A.Igonin, S.V.Lindeman, Yu.T.Struchkov*, O.I.Shechegolikhina, A.A.Zhdanov. A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

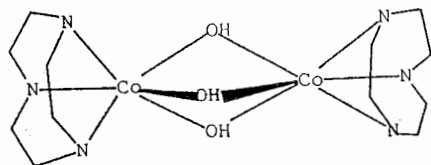
A representative series of the products of interaction between Na or K organosiloxanates and salts of bivalent transition metals (Mn, Co, Ni, Cu) or trivalent lanthanides (La, Nd, Gd, Dy) is structurally investigated by X-ray diffraction. These polymetallic organosiloxanates are based on stereoregular 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.





3

MS-07.02.03 RACEMIC-TO-CHIRAL TRANSFORMATION IN A COBALOXIME CRYSTAL. By T. Nemoto*, H. Uekusa and Y. Ohashi, Department of Chemistry, Tokyo Institute of Technology, Japan

A crystal of (R-1-cyanoethyl)(piperidine)cobaloxime has a chiral space group ($P2_12_12_1$) and has two crystallographically independent molecules, A and B, in the asymmetric unit. The racemic crystal has an isomorphous structure to the chiral one. But the B molecule has the cyanoethyl (ce) group with S configuration. When both crystals, chiral and racemic ones, were exposed to visible light, the B ce groups were gradually changed to the disordered racemates whereas the A molecules remained unaltered.

In racemic crystal : (A, B) = (R, S) \rightarrow (R, R + S)
In chiral crystal : (A, B) = (R, R) \rightarrow (R, R + S)

This means that racemic crystals were changed to chiral ones. In order to examine the disordering process of the B ce group more quantitatively, several crystals with different R:S compositions were crystallized from solutions with different R:S ratios.

The ratios of R:S for the obtained crystals were determined by crystal structure analysis. They are very similar to the ratios in solutions. Then the crystals were exposed to a Xe-lamp. After about 40 hours irradiation, cell parameters of each crystal changed to the same values. The R:S ratio was determined again. It became 70:30 not 75:25. This difference is well explained by the reaction cavity.

The crystal of racemic (1-cyanoethyl)(pyrrolidine)cobaloxime has space group $P1$, $Z=4$. This crystal has two R molecules and two S molecules in the unit cell. One of these appears to be changed to disordered racemates as observed in the piperidine complex. Further study is now in progress.

Fig. 1. Molecular structure (1-ce-pip B-S)

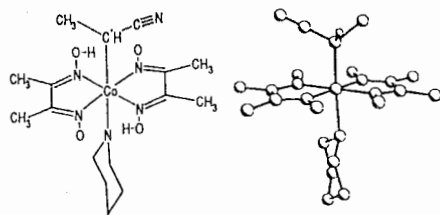


Table 1. Crystal Data (1-ce-pip)
Space Group $P2_12_12_1$, $Z=8$

Initial					
R:S (Total)	100:0	85:15	76:24	66:34	50:50
S/(Site B)	0.	30.(2)	48.2(7)	67.(4)	100.
a/Å	11.743(6)	11.734(1)	11.725(2)	11.717(2)	11.707(2)
b/Å	31.045(4)	30.946(5)	30.790(7)	30.73(1)	30.723(7)
c/Å	11.395(3)	11.339(2)	11.377(3)	11.394(4)	11.414(3)
V/Å ³	4121(2)	4117(1)	4107(2)	4102(2)	4105(2)

Final			
R:S (Total)	71:29	69:31	69:31
S/(site B)	58.(1)	62.(2)	62.(2)
a/Å	11.720(1)	11.725(1)	11.7215(7)
b/Å	30.768(5)	30.754(5)	30.761(3)
c/Å	11.380(2)	11.384(2)	11.384(1)
V/Å ³	4103(2)	4105(2)	4105(1)

MS-07.02.04 cis/trans-INFLUENCES IN Pt(II)-COMPLEXES. STRUCTURE OF trans-Chlorobis(dimethylsulfide)(phenyl)-platinum(II). By Å. Oskarsson*, V. Yu. Kukushkin, K. Lövgqvist and L.-I. Elding, Inorg. Chem. 1, Chemical Center, University of Lund, P.O.Box 124, S-221 00 Lund, Sweden.

We are interested in structure-reactivity relationships in a series of complexes of the type $trans-[Pt(X)(Y)(SR_2)_2]$, X=halide, SR_2 =thioether and Y=any ligand suitable to tune the Pt-X bond length. Reaction rates and reaction mechanisms in solution for the substitution of X, as a function of electronic effects (variation of Y) and steric blocking (variation of the substituents R) are studied. In particular, we are interested in the following questions: When will X be the most substitution labile ligand? When will this reaction mechanism change from I_a to I_d or D and in that case for which thioether and Y ligands?

The bond length Pt-X as well as the steric blocking is best studied by diffraction methods in the solid state. Complexes $trans-[PtCl_2(SR_2)_2]$ and $[PtCl(SR_2)_3]^+$ with the thioethers dimethylsulfide and 1,4-thioxane has been structurally characterized previously. The average Pt-Cl distance in the *trans*-compounds is 2.29 Å and in the *trans*-compounds 2.32 Å, reflecting a larger *trans*-influence of S as compared to Cl. A carbon is expected to have a much larger *trans*-influence than S and in order to further increase the Pt-Cl bond length we have synthesized and determined the crystal structure of the title compound.

The substitution of a thioether-sulfur with a phenyl-carbon was achieved by a phenyl migration procedure from a BPh_4^- ion to the Pt(II) centre in $[PtCl(SMe_2)_3]^+$. The title compound crystallizes in the space group $P2_1/m$ with $a=10.106(1)$, $b=13.046(3)$, $c=20.939(2)$ Å, $\beta=94.39(1)^\circ$ and $Z=8$. The coordination geometry is distorted square planar with Pt-S distances 2.28-2.30, Pt-C=1.99 and Pt-Cl=2.40 Å. Thus the coordinated phenyl has a dramatic effect on the Pt-Cl distance, and to our knowledge the Pt-Cl distance of 2.40 Å is the longest one observed so far.

MS-07.02.05 HALF-SANDWICH NIOBIUM IMIDO AND MOLYBDENUM BIS (IMIDO) COMPLEXES: METALLOCENE ANALOGUES by C. Wilson*, J. A. K. Howard, V. C. Gibson, A. D. Poole, P. W. Dyer, S. Bahar, B. Whittle, Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

There has been considerable recent interest in Group 4 metallocene derivatives as precursors to well defined Ziegler Natta polymerisation catalysts and stoichiometric reagents organic synthesis. By comparison of the shapes and energies of the frontier orbitals for these species with those of Group 5 half-sandwich imido fragments (I), they can be regarded as being pseudo-isolobal and valence isoelectronic (Gibson, J. Chem. Soc. Dalton. Trans. 1992, 739), similarly for Group 6 bis (imido) fragments (II) (Schrock, J. Am. Chem. Soc., 1990, 112, 6728).