07.02 - Metal Clusters and Metal Coordination Analysis

MS-07.02.01 POLYMETALLOORGANOXYANOLOATES - A NOVEL CLASS OF THE ORGANOSILICON METAL COMPLEXES. By V.A. Ivanov, S.V. Lindeman, Yu.T. Strachkov, O.I. Shegelgolzhina, 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 polymeric organosiloxanates are based on stereoregular macrocyclic polydentate polyoxoammonium of a new type: [SiR(O')(O)R]_n (R=Ph, Et, Vin; n=6, 8, 12). The size of the macrocyclic ligand depends on the number of coordinated metal ions (transient oxidation state, coordination number). For d-metal ions, 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 steric interference between metal cationic groups and siloxanate 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 (H_C=O or O_H) 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 alkali metal ions, which ensure complex electroneutrality and in many cases are coordinated by the siloxane macrocyclic 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 molecules always belong to a similar symmetry class. The largest organosiloxanolate ligands (n=12) with tris(endo)-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 Cu^{2+} cations enveloping them as a tennis-ball seam. By salting out with Me_3SiCl the complexes studied are destroyed and all three types of ligands obtained as trisethylsilyle derivatives [SiR(O)(OSiMe)_2]-n, which according to an X-ray study (for n = 6 and 12) have the same configuration as the starting siloxanolate ligands. Thus the preparation of large stereo-regular 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(lll) HYDROLYSIS PRODUCTS. By Erik Larsen1, S. Larsen2, T.A. Larsen3, G. Poulsen1, J. Springborg1 and Dong Ni Wang1.

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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(ami-}

nomethyl)ethane (tame) is used to block the remaining three coordination sites on cobalt(III). Using 3-thia-1,6-hexaenamide (= aeaps) it was found that Co(tacn)(aeaps)_{3}^{3+} with base gives a species with a carbon-cobalt bond. This species was characterized by X-ray crystallography, by ^{15}C and ^{59}Co 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}^{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-pentaenamide (= daas) has been used to give Co(tacn)(daas)_{3}^{3+}. Under equilibrium conditions with strong base this ion does not produce a carbon co-ordinate 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.
07-Crystallography of Organometallic and Coordination Compounds

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

A crystal of [B-1-cyanoethyl][piperidino]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 cyanocobaloxime (ce) group with S configuration. When both crystals, chiral and racemic, were exposed to visible light, the B ce groups were gradually changed to the orderer racemates whereas the A molecules remained unaltered.

In racemic crystal:

$$ (A, B) = (R, S) \rightarrow (R, R + S) $$

In chiral crystal:

$$ (A, B) = (R, R) \rightarrow (R, S + R) $$

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][piperidino]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)

<table>
<thead>
<tr>
<th>Space Group</th>
<th>$P2_12_12_1$</th>
<th>$Z = 8$</th>
</tr>
</thead>
</table>

Initial

<table>
<thead>
<tr>
<th>$R_{(Total)}$</th>
<th>$R_{(Total)}$</th>
<th>$R_{(Total)}$</th>
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</thead>
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$S\%/(Site Bi)$

| 0.50 | 0.50 | 0.50 |

$\alpha/\AA$

| 11.740(6) | 11.740(1) | 11.750(2) |

$\beta/\AA$

| 30.940(6) | 30.940(8) | 30.790(7) |

$\gamma/\AA$

| 13.390(6) | 13.390(6) | 13.390(6) |

$V/\AA^3$

| 4117(1) | 4117(1) | 4117(1) |


We are interested in structure-reactivity relationships in a series of complexes of the type trans-[PtX(η)(η'SR)2]X, where X = Cl or Br; η is the thioether and Y = ary 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 stereo 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 $I_1$ to $I_2$ or D and in that case for which thioether and ary ligands? The bond length Pt-X as well as the steric blocking is best studied by diffusion methods in the solid state. Complexes trans-[PtCl2(η)(η'SR)2] and [PtCl2(η)(η'SR)2] with the thioethers dimethylsulfoxide and 1,4-dioxane have been structurally characterized previously. The average Pt-Cl distance in the trans-compounds is 2.39 Å and in the cis-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 BF3 ion to the Pt(II) center in [PCIS(MEO2)2]. The title compound crystallizes in the space group $P2_1'2_12_1$ with $a = 10.164(1), b = 13.046(3), c = 29.939(3)$ Å, $\beta = 94.99(1)^\circ$ and $Z = 8$. The coordination geometry is distorted square planar with Pt-S distances 2.38-2.39, 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 NI(II) IMIDO AND POLYMERIZED NI(II) COMPLEXES. AN EXAMPLE OF METALLOCENE ANALOGUES. By C. Wilson*, J. A. K. Howard, V. C. Gibson, A. D. Poole, P. W. Dyer, S. Bahar, A. Whittle, Department of Chemistry, University of Durham South Road, Durham DH1 3LE, UK

There has been considerable recent interest in Group 4 metalloocene derivatives as precursors to well defined, Ziegler-Natta polymerisation catalysts and stoichiometric reagents as 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, 759), similarly for Group 6 bis(imido) fragments (II) (Schofield, J. Am. Chem. Soc., 1990, 112, 7879).