07-Crystallography of Organometallic and Coordination Compounds

MS-07.02.03  EACENTIC-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)(pyridinedio)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 cyanohydrin (ce) group with S configuration. When both crystals, chiral and racemic, were exposed to visible light, the B ce group was 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 60 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)(pyridinedio)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 pyridine 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>
<tbody>
<tr>
<td>R:S (Total)</td>
<td>100:30</td>
<td></td>
</tr>
<tr>
<td>N(Site 1)</td>
<td>50:15</td>
<td>36:16</td>
</tr>
<tr>
<td>V/A</td>
<td>11.736(6)</td>
<td>11.739(2)</td>
</tr>
<tr>
<td>b/A</td>
<td>31.046(8)</td>
<td>30.740(7)</td>
</tr>
<tr>
<td>c/A</td>
<td>11.390(3)</td>
<td>11.377(3)</td>
</tr>
<tr>
<td>V/A</td>
<td>417(10)</td>
<td>4107(2)</td>
</tr>
</tbody>
</table>


We are interested in structure-reactivity relationships in a series of complexes of the type trans-PtX(Y)Cl(S$_2$)$_2$, X=thioether and Y=thioether similar to those of the Pt-Bond length. Reaction rates and reaction mechanisms in solution for the substitution of X, as a function of electronic effects (variation of Y) and stereoblocking (variation of the substituents R are studied. In particular, we are interested in the following questions: When will Z be the most substitution labile ligand? When will this reaction mechanism change from $I_4$ to $I_4$ or $D_4$ 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(S$_2$)$_2$ and PtCl(S$_2$)$_2$ (with the thioethers dimethylsulfide 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 2.25 Å reflecting a large 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 phenylcarbon was achieved by a phenyl migration procedure from a BPh$_4$ en to the Pt(II) center in [PCIS][MCl$_y$]. The title compound crystallizes in the space group $P2_1$ with $a=10.164(1), b=13.046(3), c=29.939(3)$ Å, $\beta=94.39(1)^\circ$ and Z=8. The coordination geometry is distorted square planar with Pt-Cl distances 2.36-2.40, Pt-C=1.99 and Pt-Cl=2.40 Å. Thus the coordinated phenyl has a dynamic 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 NITRIUM IMIDO AND POLYEMETHEN BIS (IMIDO) COMPLEXES : METALLOCENE ANALOGUES. By C. Wilson, J. A. 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 metallocene derivatives as precursors to well-defined Ziegler-Natta polymerisation catalysts and stoichiometric reagents for 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, 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 (Schrock, J. Am. Chem. Soc., 1990, 112, 7820).
The geometry around the metal centre predicted by this isostructural relationship has been probed through the synthesis and subsequent crystallographic studies of a range of half-sandwich niobium imido and molybdenum bis(imido) complexes containing alkyl, phosphine, carbonyl, olefin and acetylene ligands (Gibson, J. Chem. Soc. Dalton Trans., 1992, 739; Gibson and Howard, J. Chem. Soc. Chem. Commun., 1992, 169). Experimental and predicted geometries can now be compared as a result of recent x-ray crystallographic studies.

![Chemical structure](image)

**MS-07.02.06 SPECIFIC NON-BONDED INTERACTIONS IN THE CRYSTAL STRUCTURES OF M₆X₆⁺ AND M₄X₄⁺ (M=Mo, W, X=O, S, Se) CLUSTERS.** By A. V. Virovets and N. V. Podberezskaya, Institute of Inorganic Chemistry Siberian Division of Russian Academy of Sciences, Novosibirsk, Russia.

At the present time many crystal structures containing M₆(X₆⁻) and M₄(X₄⁻) clusters are known. One of the main directions in the study of these clusters is the analysis of non-bonded interactions, particularly in the metal-ligand region of the crystal structure, which can influence the formation of an NMC but also the structure of the metal centre. The distances in the axial and equatorial ligands and X...X in dimers were especially chosen.

**Struct. Khim., 1993, 34, N.2, 150-164.** Practically all M₆X₆⁺ crystal structures include the Y atom which is equidistant from the three X₆ atoms and lies in an equatorial ligand in the X₆ ligands (Y...X...Y angles are about 160-180°). The Y atom may enter both into the coordination sphere or even uncharged ion. Those non-bonded contacts have been suggested to form Y...X...Y contacts or simply axial contacts. In some crystal structures of the M₆X₆⁺ cluster centrosymmetric dimers are formed in which cluster cores face to one another by the (X₆)₈ planes.

Those dimers have been classified by the relative positions of the components of the cluster and a number of short X...X contacts into three types: (5(X...X), 5(X...Y) and 2(X...X)). It has been found that Coulomb repulsions of uncharged ions do not prevent the formation of the dimers.