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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)

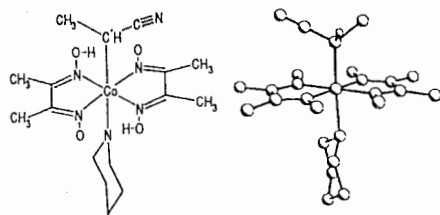


Table 1. Crystal Data (1-ce-pip)
Space Group $P2_12_12_1$, $Z=8$

| Initial | 100:0 | 85:15 | 76:24 | 66:34 | 50:50 |
|------------------|-----------|-----------|-----------|-----------|-----------|
| 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 | 71:29 | 69:31 | 69:31 |
|------------------|-----------|-----------|------------|
| 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).