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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)

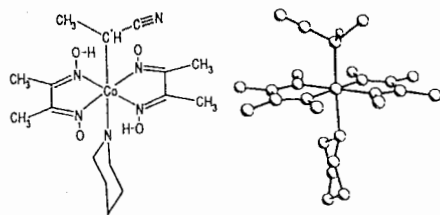


Table 1. Crystal Data (1-ce-pip)
Space Group $P2_12_12_1$, $Z=8$

Initial					
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. Löfvqvist 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).

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The geometry around the metal centre predicted by this isolobal 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 inter alia alkyl, phosphine, carbonyl, olefin and acetylene ligands (Gibson, *J. Chem. Soc. Dalton Trans.*, 1992, 739; Gibson and Howard, *J. Chem. Soc. Chem Commun.*, 1992, 1666). Experimental and predicted geometries can now be compared as a result of recent x-ray crystallographic studies.

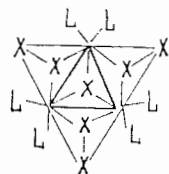


MS-07.02.06 SPECIFIC NON-BONDED INTERACTIONS IN THE CRYSTAL STRUCTURES OF $M_3 X_7^{4+}$ AND $M_3 X_4^{4+}$ ($M = Mo, W, X = O, S, Se$) CLUSTERS.

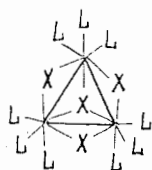
By A. V. Virovets* and N. V. Podberezskaya, Institute of Inorganic Chemistry Siberian Division of Russian Academy of Sciences, Novosibirsk, Russia.

At the present time many crystal structures containing $M_3(\mu_3-X)(\mu-X_2)_3^{4+}$ and $M_3(\mu_3-X)(\mu-X_2)_3^{4+}$ cluster cores (usually abbreviated as $M_3 X_7^{4+}$ and $M_3 X_4^{4+}$) are known.

One half of the X atoms in the $(\mu-X_2)$ ligands of the $M_3 X_7^{4+}$ core lie near to the M_3 plane (X_{eq}) and the rest ones deviate from it to the side opposite relative to the (μ_3-X) ligand (X_{ax}). Analysis of the non-bonded contacts (NDC) in the crystal structures of those clusters allowed to reveal and classify some specific interactions playing an outstanding role in the formation of crystal packing and being fallen outside the investigators' view previously (Virovets A. V. & Podberezskaya N. V., *Zh.*



formation of an NBC but usually lengthen them. Non-bonded X...Y distances in the axial contacts and X...X in dimers were essentially shorter than the sum of Van der Waals radii of the X and Y atoms.



Struct. Khim., 1993, 34, N.2, 150-164). Practically all $M_3 X_4^{4+}$ crystal structures include the Y atom which is equidistant from the three X_{ax} atoms and lies in an extension of the X-X bonds in the X_2 ligands ($Y...X-X$ angles are about 160-180°). The Y atom may enter both into the counterion or even uncharge ion. Those non-bonded contacts have been suggested to call '3X_{ax}...Y' contacts or simply axial contacts. In some crystal structures of the $M_3 X_4^{4+}$ clusters centrosymmetric dimers are formed in which cluster cores face to one another by the $(\mu-X)_3$ planes. Those dimers have been classified by the relative positions of components and a number of short X...X contacts into three types: 6 (X...X), 5 (X...X) and 2 (X...X). It has been found that Coulomb repulsions of uncharge ions do not prevent the

MS-07.02.07 STRUCTURES OF Cu(II) COMPLEXES WITH DEPROTONATED OXIMES. By Tian-Huey Lu* and Tahir H. Tahirov, Department of Physics; Hung Luh and Chung-Sun Chung, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, China.

In order to study the influence of the different electron and steric factors to coordination center and the

role of oxime groups in Cu(II) complexes with general formula (1) and its derivatives, by changing the length and volume of N,N' bridged R in the central chelate ring, the double chemical bonds to single bonds in the terminal chelate rings and the nature of anion, we have studied the structures of: (A) Isothiocyanato[3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1-)]copper(II), $Cu(NCS)(C_{12}H_{21}N_4O_2)$, orthorhombic, $a=7.532(1)$, $b=12.652(2)$, $c=17.985(4)$ Å, $Pn2_1a$, $Z=4$, 1928 refl., $R=0.034$; (B) Thiocyanato[3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato(1-)]copper(II), $Cu(NCS)(C_{11}H_{19}O_2N_4)$, triclinic, $a=7.275(3)$, $b=7.711(7)$, $c=14.293(1)$ Å, $\alpha=90.152(7)$, $\beta=98.77(1)$, $\gamma=100.49(2)^\circ$, $P1$, $Z=2$, 4193 refl., $R=0.062$; (C) Isothiocyanato[3,6,6,9-tetramethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime(1-)]copper(II), $Cu(NCS)(C_{13}H_{23}N_4O_2)$, monoclinic, $a=8.099(2)$, $b=10.638(2)$, $c=19.870(2)$ Å, $\beta=92.70(2)^\circ$, $P2_1/n$, $Z=4$, 4073 refl., $R=0.030$; (D) Aqua[meso-3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(1-)]copper(II) thiocyanate, $[Cu(H_2O)(C_{13}H_{27}N_4O_2)] \cdot SCN$, monoclinic, $a=7.692(1)$, $b=12.028(2)$, $c=20.235(3)$ Å, $\beta=93.03(1)^\circ$, $P2_1/n$, $Z=4$, 2223 refl., $R=0.034$; (E) Tetraperchlorato tetrakis[u-3-methyl-6-amino-4-aza-3-hexene-2-one-oximato(1-)-u-O-N'-N''-N''']tetracopper(II) hydrate, $[Cu(ClO_4)(C_6H_{12}N_3O)]_4 \cdot H_2O$, tetragonal, $a=12.440(3)$, $c=14.851(7)$ Å, $P4_2/n$, $Z=2$, 1614 refl., $R=0.068$; and (F) bis[μ -3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1-)- μ -O,N',N'',N''']dicopper(II) diperchlorate, which

