

07-Crystallography of Organometallic and Coordination Compounds

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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.

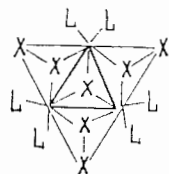


MS-07.02.06 SPECIFIC NON-BONDED INTERACTIONS IN THE CRYSTAL STRUCTURES OF $M_3X_7^{4+}$ AND $M_3X_4^{4+}$ ($M=Mo, W, X=O, S, Se$) CLUSTERS.

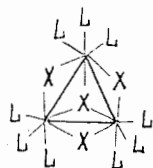
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At the present time many crystal structures containing $M_3(\mu_3-X)(\mu-X_2)_3^{4+}$ and $M_3(\mu_3-X)(\mu-X_2)_3^{4+}$ cluster cores (usually abbreviated as $M_3X_7^{4+}$ and $M_3X_4^{4+}$) are known.

One half of the X atoms in the $(\mu-X_2)$ ligands of the $M_3X_7^{4+}$ 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.*



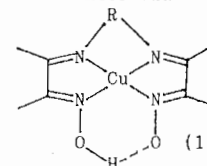
formation of an NBC but usually lengthen them. Non-bonded X...Y distances in the axial contacts and X...X in dimers were essentially shorter than the sum of Van der Waals radii of the X and Y atoms.



Struct. Khim., 1993, 34, N.2, 150-164). Practically all $M_3X_4^{4+}$ 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 $M_3X_4^{4+}$ 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, $a=7.275(3)$, $b=7.7110(7)$, $c=14.293(1)$ Å, $\alpha=90.152(7)$, $\beta=98.77(1)$, $\gamma=100.49(2)^\circ$, $P\bar{1}$, $Z=2$, 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

