

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.

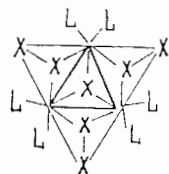


MS-07.02.06 SPECIFIC NON-BONDED INTERACTIONS IN THE CRYSTAL STRUCTURES OF $M_3 X_7^{4+}$ AND $M_3 X_4^{4+}$ ($M = Mo, W, X = O, S, Se$) CLUSTERS.

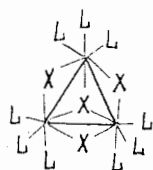
By A. V. Virovets* and N. V. Podberezskaya, Institute of Inorganic Chemistry Siberian Division of Russian Academy of Sciences, Novosibirsk, Russia.

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.*



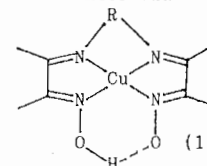
formation of an NBC but usually lengthen them. Non-bonded X...Y distances in the axial contacts and X...X in dimers were essentially shorter than the sum of Van der Waals radii of the X and Y atoms.



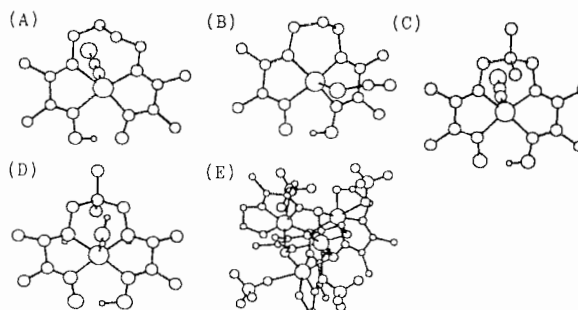
Struct. Khim., 1993, 34, N.2, 150-164). Practically all $M_3 X_4^{4+}$ crystal structures include the Y atom which is equidistant from the three X_{ax} atoms and lies in an extension of the X-X bonds in the X_2 ligands ($Y...X-X$ angles are about 160-180°). The Y atom may enter both into the counterion 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, $a=7.275(3)$, $b=7.7110(7)$, $c=14.293(1)$ 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



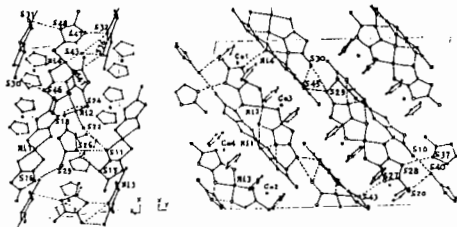
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belongs to a series of Cu(II) complexes. (F) was reported earlier (Wang, Wang, Wang & Chung, Acta Cryst., 1990, C46, 1770-1772). The coordination geometry about Cu(II) ion in all complexes, except (E), is five-coordinated and distorted square-pyramidal with four N atoms of the diazadioxime in equatorial positions. The axial position is occupied by different atoms: isothiocyanate N atom in (A) and (C), thiocyanate S atom in (B), water O atom in (D) and bridging oxime O atom in (F). The six-coordinated polyhedron in (E) is distorted square-bipyramidal with amine-, imine-, oxime N and bridging oxime O atoms equatorial, perchlorate O and another bridging oxime O atoms axial. The complexes (A)-(C) are mononuclear, meanwhile (E) is tetranuclear and (F) is binuclear. The central part of tetranuclear complex (E) is dodecahedron formed by four Cu, four oxime N and four bridging oxime O atoms. Present research shows that the electron and steric factors govern coordination in the axial position of Cu(II) and the oxime O atoms, which participate in forming the intramolecular H-bonds in mononuclear complexes (A)-(C), or bonding with Cu(II) atoms in tetranuclear (E) and binuclear (F) complexes. [Work was supported by National Science Council, Taiwan, China].

07.03 - Metal Clusters

PS-07.03.01 INTERMOLECULAR INTERACTIONS IN A CONDUCTING COBALTOCENIUM SALT OF A NICKEL-DMIT COMPLEX. Q.Fang*, Institute of Crystal Materials, Shandong Univ. 250100, China; J.H.Cai, Fuzhou Lab. of Structure Chemistry, Chinese Academy of Sciences, 350002, China.

$Zx[M(\text{dmit})_2]$ ($H_2\text{dmit}=4,5\text{-dimercapto-1,3-dithiole-2-thione}$) is known for its electrical conductivity or superconductivity. The anionic interaction, indicated by S...S distances shorter than the Van der Waals separation 3.70Å, significantly affects the conducting ability of this kind of complex. The views of (010), (001) of our synthesized conducting complex $[\text{Co}(\text{CsH}_5)_2][\text{Ni}(\text{dmit})_2]$ are as follows:



Four independent anions in the cell are abbreviated as $[\text{Ni}]_i$ ($i=1,2,3,4$). $[\text{Ni}]_1$ and $[\text{Ni}]_2$ connected by 5 pairs of S...S contacts (average dist. 3.56(1) Å) form ... $[\text{Ni}]_1[\text{Ni}]_2[\text{Ni}]_1[\text{Ni}]_2$... zigzag chains or stacks along the [001] direction. $[\text{Ni}]_3$ and $[\text{Ni}]_4$ form another stack (average dist. of 6 pairs of S...S is 3.59(1) Å). Two types of stacks are further connected by 5 S...S contacts (S10, S40; S29, S30; S20, S40; and S28, S37; S29, S45 with average dist. 3.54(1) Å) forming two-dimensional (111) sheets. Furthermore, the neighboring sheets are weakly connected by S27...S43 (3.60(1) Å) showing the characteristics of a three-dimensional anionic network. Cobaltocenium takes an eclipsed D_{5h} configuration.

PS-07.03.02 SYNTHESSES AND STRUCTURES OF A NEW CLASS OF OCTANUCLEAR MIXED-METAL CLUSTERS: $[\text{M}'\text{M}_3\text{O}_4(\text{O}_2\text{CC}_2\text{H}_5)_8]_2\text{Na}_2$ ($\text{M}'=\text{Cr}, \text{V}, \text{M}=\text{Mo}, \text{W}; \text{M}'=\text{Mo}, \text{M}_3=\text{MoW}_2$) By Li Xu*, Huang Liu, Duangcao Yan, Jinshun Huang, and Qianer Zhang, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P.R.China

A new class of octanuclear cluster compounds formulated as $[\text{M}'\text{M}_3\text{O}_4(\text{O}_2\text{CC}_2\text{H}_5)_8]_2\text{Na}_2$ ($\text{M}'=\text{Cr}, \text{V}, \text{M}=\text{Mo}, \text{W}; \text{M}'=\text{Mo}, \text{M}_3=\text{MoW}_2$) have been prepared and structurally characterized. The black crystals of the title compounds were obtained from the redox reactions of $\text{M}'(\text{CO})_6$ with Na_2MoO_4 (or $\text{M}(\text{CO})_6$ with NaVO_3) in propionic anhydride solution. The five iso-structural compounds don't dissolved in many solvents such as water, most common acids (e.g., HCl), bases (e.g., NaOH) and organic solvents (e.g., DMF, THF, EtOH, CH_3CN). X-ray structure analyses of them revealed the existence of a cluster anion $[(\text{C}_2\text{H}_5\text{CO}_2)_8\text{M}_3\text{O}_4\text{M}'\text{M}_3(\text{O}_2\text{CC}_2\text{H}_5)_8]^{2-}$, in which the two M_3O_4 units are connected by two M' atoms through four $\text{M}'-\mu_3\text{O}$ (from $\mu_2\text{O}$ in the two M_3O_4 units) and eight $\text{M}'-\text{O}_{\text{ca}}$ (bridging $\text{C}_2\text{H}_5\text{CO}_2$) bonds to form a centro-symmetric structure as shown in Fig.1. The M_3O_4 unit is similar to the well-known M_3O_4 triclusters except for a carboxylic bridge spanning two M atoms. Bonds lengths and angles in the former are similar to the ones in the latter but $\text{M}-\mu_3\text{O}$ bond lengths (from $\mu_2\text{O}$ atoms in the M_3O_4 units) become significantly ca. 0.03-0.06 Å longer. Each metal atom has distorted octahedral coordination geometry. A small range of $\text{M}'-\text{O}$ distances indicates M'^{III} rather than M'^{II} which is expected to show a much range because of Jahn-Teller distortion. Thus, by deduction M atoms have formal oxidation states of IV, which is also supported by the similarity of the M-M distances in the five compounds to the ones in the M_3O_4 triclusters. There is an interesting nearly planar $\text{M}_3\text{M}'_2\text{O}_2$ eight-membered cycle with C_i symmetry in the center of the structure. The deviations of the eight atoms from the least-squares plane defined by them range from ca. 0.04 to 0.32 with the average of ca. 0.14 Å. In addition there are four approximate $\text{M}'\text{M}_2\text{O}$ planes. The long M'-M distances (3.5-3.8 Å) attest to the absence of M'-M bondings. Each Na atom is coordinated to five O atoms from two anions in an uncommon distorted trigonal bipyramidal arrangement with the unusually short Na-O average distance of 2.31 Å which suggests some extent of Na-O covalent bonding, consequently, the cluster anions are connected by Na atoms to constitute an infinite chain structure. So we suppose that they are best regarded as extended species rather than simple ionic complexes. This is also supported by their insolubilities in many solvents.

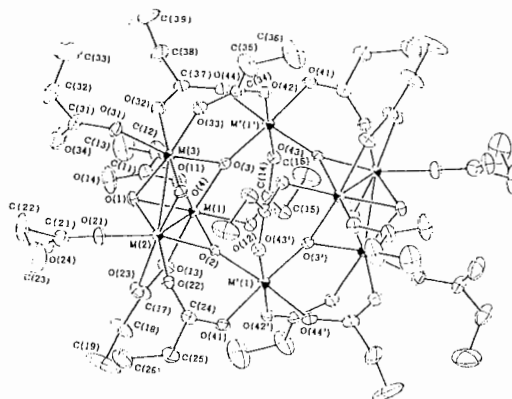


Fig.1 The structure of $[\text{M}'\text{M}_3\text{O}_4(\text{O}_2\text{CC}_2\text{H}_5)_8]^{2-}$.