

07-Crystallography of Organometallic and Coordination Compounds

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Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1987). *Inorg. Chim. Acta*, **134**, 87–93; Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 201–207. The title compound was obtained by slow evaporation of methanol solution containing Cu(II) 4-chlorobenzoate and 2-dimethylamino-ethanol. Blue crystals of $[\text{Cu}_4(\text{C}_7\text{H}_4\text{ClO}_2)_4(\text{C}_4\text{H}_{10}\text{NO})_4] \cdot 2\text{CH}_3\text{OH}$ are triclinic, space group $P\bar{1}$, $a=14.056(4)$, $b=14.704(4)$, $c=15.335(3)$ Å, $\alpha=106.27(2)$, $\beta=105.76(2)$, $\gamma=102.24(2)^\circ$, $Z=2$, $V=2782(1)$ Å³, $D_x=1.495$ Mg m⁻³, $M_r=1293.1$, final R value 0.039 for 5563 significant reflections.

The structure consists of discrete molecules. The Cu and bridging ethanolato O atoms form a cubane-type Cu_4O_4 core in which the short Cu–O bonds form an eight-membered ring folded in a boat-like conformation.

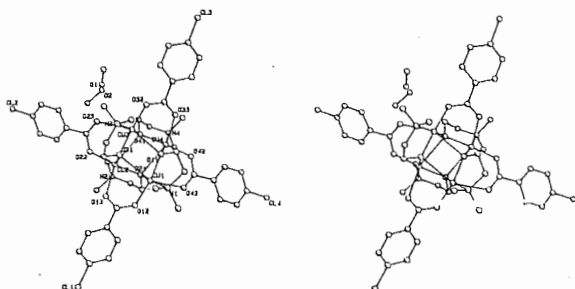


Fig. 1. Stereoview of the molecule.

Within the Cu_4O_4 core the long Cu–Cu distances are 3.664 and 3.796 Å and the four short Cu–Cu distances range from 3.096 to 3.191 Å. Each Cu atom is surrounded by two ethanolato oxygen atoms, a carboxyl oxygen atom and an amino nitrogen atom in a nearly square-planar arrangement with average Cu–O and Cu–N bonds of 1.936 and 2.055 Å. The axial sites of each Cu atom are occupied by an ethanolato oxygen and an oxygen atom of the carboxylate group with Cu–O distances of 2.409–2.815 Å.

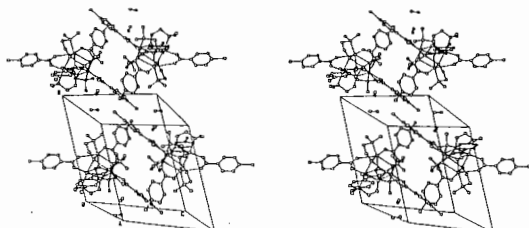


Fig. 2. Stereoscopic view of the packing.

PS-07.03.13 CRYSTAL STRUCTURE OF A TRINUCLEAR SULFIDOTUNGSTATE ANION. By Masood Parvez*, P. Michael Boorman and Meiping Wang, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.

We have been exploring the controlled polymerization of WS_4^{2-} anions by alkylation reactions. The $\text{W}_3\text{S}_9^{2-}$ anion has been previously reported as a product of the reaction between WS_4^{2-} and alkyl halides. We have found that the complex $\text{Cl}_3\text{W}(\mu\text{-SEt}_2)_3\text{WCl}_3$ (**1**) is an effective ethylating agent, and will cause the trimerization of WS_4^{2-} to $\text{W}_3\text{S}_9^{2-}$. From ¹H NMR data we have evidence that the $\text{W}_3\text{S}_9^{2-}$ anion can itself be alkylated, hence we wished to see if clusters of higher nuclearity could be prepared this way. One product of the reaction between **1** and $[\text{PPh}_4]_2[\text{W}_3\text{S}_9]$ in a mixture of MeCN and N,N-dimethylformamide (DMF) was isolated and subjected to an X-ray crystal structure determination. It has been shown to be $[\text{PPh}_4]_2[\text{S}_2\text{W}(\mu\text{-S})_2\text{W}(\text{DMF}) (\text{S}) (\mu\text{-S})_2\text{WS}_2]$, rather than a cluster of higher nuclearity as was

anticipated. The structure has some interesting features, however, in that the sulfide and DMF ligands on the central tungsten are disordered over the two axial sites.

Crystal data. $\text{S}_9\text{W}_3(\text{C}_3\text{H}_6\text{NO}) \cdot 2(\text{C}_{24}\text{H}_{20}\text{P})$, monoclinic, space group $P2_1/n$, $a = 9.863(2)$, $b = 14.618(3)$, $c = 18.795(3)$ Å, $\beta = 97.98(1)^\circ$, $V = 2683.6(8)$ Å³, $Z = 2$, $R = 0.072$ for 3813 observed data ($I > 3\sigma(I)$) collected on a Rigaku AFC6S at 150(1) K.

PS-07.03.14 CRYSTAL STRUCTURE OF DIAMINE COMPLEXONATES OF COBALT WITH ALKALINE-EARTH CATIONS by L.A.Zassourskaya*, T.N.Polynova, V.B.Rybakov, M.A.Porai-Koshits. Department of Chemistry, Moscow State University, 119899, Moscow, Russia.

X-ray structure analysis and crystal chemistry investigation of $\text{M}'[\text{ML}]_2 \cdot n\text{H}_2\text{O}$ complexonates (M' —alkaline-earth cation, $\text{M}=\text{Co(II)}$, Co(III) , $\text{L}=(\text{edta})^{4-}$, $(\text{Hedta})^{3-}$, where edta—ethylenedia-minetetraacetic acid) were carried out in order to study the role of M' in the formation of their crystal structure. The active interaction between M' and the ligand leads to change the structural function of the complexon carboxylate groups. The interaction of M' with a single carbonyl oxygen atom leads change the structural function of the complexon carboxylate groups. The interaction of M' with a single carbonyl oxygen atom leads to the formation of an island structure. So, $[\text{Mg}(\text{CoHedta}(\text{NO}_2))_2 \cdot 9\text{H}_2\text{O}]$ consists of heterometallic binuclear complexes $[\text{Mg}(\text{H}_2\text{O})_5\text{CoHedta}(\text{NO}_2)]^+$ and $[\text{CoHedta}(\text{NO}_2)]^-$ anions. If M' is connected with several carbonyl atoms chain ($\text{Ba}(\text{Coedta})_2 \cdot 8\text{H}_2\text{O}$) or layer ($\text{Ca}(\text{CoHedta}(\text{CN})_2 \cdot 6\text{H}_2\text{O})$) structures are formed. Even more interesting are isostructural layer compounds $\text{M}'[\text{CoHedta}]_2 \cdot 6\text{H}_2\text{O}$, where $\text{M}'=\text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} . Besides water molecules M' coordinates both carbonyl and carboxyl oxygen atoms forming four-membered cycles. The structure of $\text{Ca}(\text{Coedta})_2 \cdot 7\text{H}_2\text{O}$ is the most peculiar among calcium complexonates, because in it Ca^{2+} cation is completely hydrated and therefore plays the role of "outer sphere" cation. The wide diversity in the nature of the interaction between M' and carboxylate groups makes the investigation of the compounds of such type important.

PS-07.03.15 SYNTHESIS AND CRYSTAL STRUCTURE OF TETRACOBALT CLUSTER COMPLEX $[\text{Co}_4(\mu_3\text{-S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$. By F. L. Jiang*, Z. Y. Huang, B. S. Kang, M. C. Hong and H. Q. Liu, State Key Lab. of Struct. Chem. and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A new tetracobalt compound $[\text{Co}_4(\mu_3\text{-S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$ (**1**) was prepared by reacting $\text{CoCl}(\text{PPh}_3)_2$ and Na_2edt ($\text{H}_2\text{edt}=1,2$ ethanedithiol) in acetonitrile, and structurally characterized by X-ray diffraction methods. Compound **1** crystallizes in the trigonal space group $P\bar{3}$ with $a=16.505(8)$, $c=13.401(6)$ Å, $V=3162(3)$ Å³, $Z=2$ and $R(\text{w})=0.046$ (0.064) for 2636 reflections ($I > 3\sigma(I)$). The cluster contains four cobalt atoms in the form of a trigonal pyramid. The basal Co_3 triangle is capped by $\mu_3\text{-S}(3)$ below, and also di-bridged by $\text{S}(2)$ of edt^{2-} in each edge of the triangle, while the triangle is bridged to the apical $\text{Co}(2)$ above by another

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S(1) of edt^{2-} along the edges of the Co_4 trigonal pyramid. The molecular structure possesses a crystallographic C_3 symmetry with the rotation axis passing through the atoms Cl, Co(2), S(3) and the centre of the basal plane. The planes of Co₃ and S₃ are very near each other with the axial μ_3 -S(3) atom 1.54(2) Å and 1.50(0) Å away from them, respectively, and can be regarded as an irregular hexagon as shown in Figure 1.

The Co-Co bond lengths (2.741(2) Å) and Co(1)-S(2) and Co(1)-S(3) bond lengths (2.202(2) Å, 2.232(2) Å) are slightly shorter than the corresponding ones in $[\text{Co}_4\text{S}_2(\text{S}_2\text{-o-xy})_2]^{2-}$ (Henkel G., *Angew. Chem. Int. Ed. Engl.*, 1983, 22, 313. Holm R.H., *Inorg. Chem.*, 1983, 22, 309). Co(1)-S(1) and Co(2)-S(1) distances being different from those in general metal-ethanedithiolate complexes are of different lengths 2.249(2) and 2.328(8) Å, respectively. The ^1H NMR spectrum with a broad peak at high field for $[\text{SCH}_2\text{CH}_2\text{S}]$ confirm the paramagnetic character of 1. Unlike a recent report (Jiang F.L., Liu H.Q., et al. *J. organometal. Chem.*, 1993, in press. Jiang F.L., Liu H.Q., et al. *Jiegou Huxue*, in press), in this reaction the dithiolate edt^{2-} ($[\text{SCH}_2\text{CH}_2\text{S}]$) functions not only as a ligand but also provides the bridged sulphur atom through a cleavage of the C-S bond. We are grateful to the National Science Foundation for financial support.

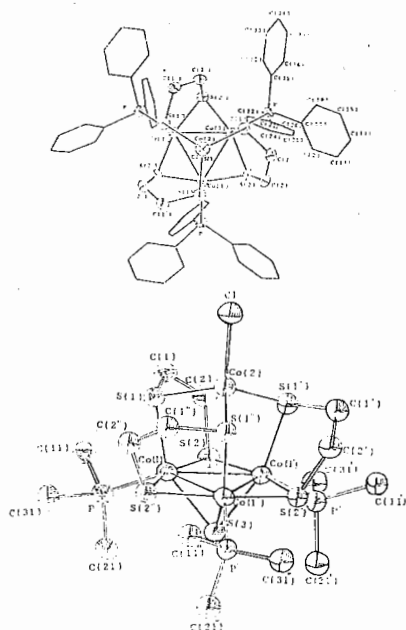


Fig.1 top and side views of $(\text{Co}_4(\mu_3\text{S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$.

shown to possess flexibility. It allows a change of (M_4) bonding electron number from 9 to 12 while the fundamental molecular configuration still remains unchanged. This is the reason why the cluster compounds can act as a reservoir for redox chemistry and as a good electron transfer agents.

The crystal structures of two new compounds containing $(M_4S_4)^{3+}$ cubane-type cluster core with 11 (M_4) cluster electrons are reported in this paper. The alteration of the M-M bond lengths, the cuboid volumes and the symmetry with different d electron-number for some $(M_4S_4)^{3+}$ and $(M_4S_4)^{4+}$ clusters are compared.

The crystal data are as follows: 1 $(\text{Co}_4\text{S}_4)(\text{C}_2\text{H}_5\text{COO})_2[(\text{OC}_2\text{H}_5)_2\text{PS}_2]_3[(\text{OC}_2\text{H}_5)_2\text{P}(\text{S})\text{SH}]$ $M_r=1400.01$, orthorhombic Pbcu, $a=24.230(8)$ Å, $b=22.403(5)$ Å, $c=19.131(8)$ Å, $V=10385(6)$ Å³, $Z=8$, $D_c=1.79\text{g/cm}^3$, $F(000)=5584$, $\mu(\text{MoK}\alpha)=15.51\text{cm}^{-1}$, $R=0.068$ for 2443 reflections. 2 $(\text{Mo}_4\text{WS}_4)(\text{CH}_3\text{COO})_2[(\text{OC}_2\text{H}_5)_2\text{PS}_2]_3[(\text{OC}_2\text{H}_5)_2\text{P}(\text{S})\text{SH}]$ $M_r=1459.87$, orthorhombic Pbcu, $a=24.465(7)$ Å, $b=21.773(6)$ Å, $c=18.880(8)$ Å, $V=10057$ Å³, $Z=8$, $D_c=1.93\text{g/cm}^3$, $F(000)=5720$, $\mu(\text{MoK}\alpha)=36.92\text{cm}^{-1}$, $R=0.059$ for 2758 reflections.

The molecular configuration of 1 and 2 is depicted in Figure 1.

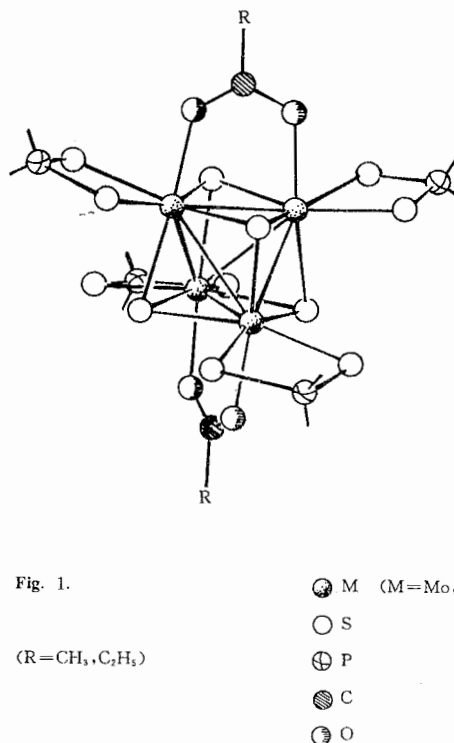
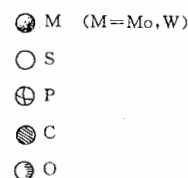


Fig. 1.

(R=CH₃, C₂H₅)



PS-07.03.16 THE CONFIGURATION FLEXIBILITY OF CUBANE LIKE STRUCTURE. By Shao-fang Lu*, Qiang-jin Wu and Jian-quan Huang, Fujian Institute of Research on the structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China.

The cubane-type molybdenum cluster compounds have proved to be of biological significance and their potentiality for application in catalysis and superconductivity has attracted attention (M. Sergent, C. Perrin, S. Ihmaine, A. Perrin, H. Ben. Yaich, O. Pena, R. Chevrel, P. Gougcon, M. Potel, *J. Chim. Phys.*, 1991, 88, 2123-2142). The structural analysis of large quantity of this kind of crystals indicates that the " M_4S_4 box" is

PS-07.03.17 SYNTHESIS AND STRUCTURE OF RETEOMETALLIC CLUSTER COMPLEX $(\text{Et}_3\text{N})_3[\text{VS}_4(\text{CuSPh})_3(\text{CudtcEt})_2]$ By Yu Yang*, Liangren Huang and Qiutian Liu, State Key Lab. of Struct. Chem. and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

It is well known that tetrathiometalates $[\text{MS}_4]^{2-}$ bind as multidentate ligands to a wide variety of metal ions and neutral molecules. Among the latter, CuCl led to a large number of compounds by successive addition across the six edges of the MS_4 (M=Mo, W) tetrahedron. As we known, three and six copper atoms were added to $[\text{VS}_4]^{3-}$. We report here