

07-Crystallography of Organometallic and Coordination Compounds

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 Co₂ and S₂ 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 'SCH₂CH₂S' 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-} ('SCH₂CH₂S') 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.

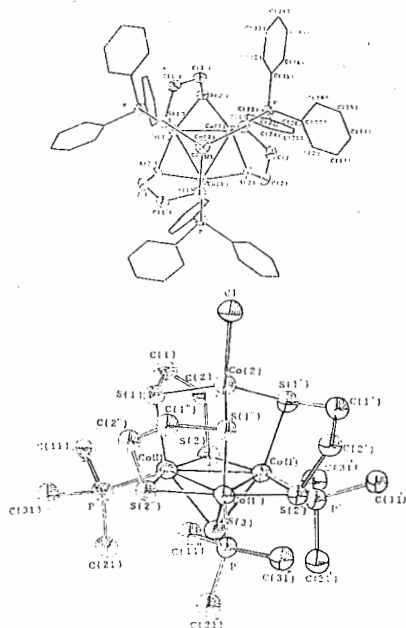


Fig.1 top and side views of $(\text{Co}_4(\mu_3\text{S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$.

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 $(M_4S_4)^{2+}$ 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.

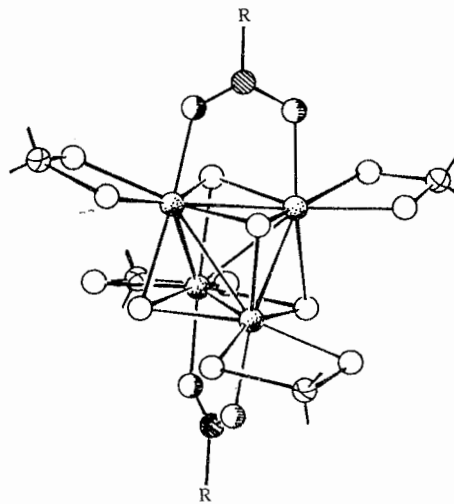


Fig. 1.



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 "M₄S₄ box" is

PS-07.03.17 SYNTHESIS AND STRUCTURE OF RETEOMETALLIC CLUSTER COMPLEX (Et₃N)₃[VS₄(CuSPh)₃(CudtcEt₂)] 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

07-Crystallography of Organometallic and Coordination Compounds

217

the synthesis and structure of $(Et_3N)_3[VS_4(CuSPh)_3(CudtcEt_2)]$ in which four copper atoms were added to the $[VS_4]^{3-}$. The title compound was obtained by reaction of $(NH_4)_3VS_4$ with $CuCl$ in a solution of dimethylformamide (DMF) containing $NaSPh$, $NadtcEt$, and Et_3NCl . The reaction mixture was stirred for 20 hours and then filtered. After standing for several days at room temperature black crystals were collected and used for X-ray diffraction.

Crystal data were collected on an Enraf-Nonius CAD4 diffractometer. The space group is $P1$ with $a = 10.391(2)$, $b = 12.391(2)$, $c = 12.586(5) \text{ \AA}$; $\alpha = 78.67(2)^\circ$, $\beta = 82.48(2)^\circ$, $\gamma = 81.59(2)^\circ$; $V = 1563.1 \text{ \AA}^3$ and $Z = 1$. 4538 reflections with $I > 3\sigma(I)$ were used for the structure determination and gave a final R of 0.039 and R_w of 0.042.

The structure is shown in Figure 1. The unit cell contains only one molecule, a $[VS_4(CuSPh)_3(CudtcEt_2)]^{3-}$ anion and three $[Et_3N]^+$ cations. The anion is formed of a central VS_4 tetrahedron surrounded by a tetragon of four copper atoms. The VS_4 core has retained the ideal geometry of free tetrathiovanadate with S-V-S angles and V-S bond lengths ranging from $108.2(1)$ to $110.9(1)^\circ$ and $2.171(3)$ to $2.220(3) \text{ \AA}$ respectively. Each copper atom is bound across an edge of the VS_4 tetrahedron with a u_3 -S coordination to each sulfur atom. The Cu- u_3 -S bond lengths are quite similar. The VS_4Cu_4 aggregate approximates D_{2d} symmetry which is also observed for MoS_4Cu_4 and WS_4Cu_4 cores. The V-Cu mean distance of $2.611(2) \text{ \AA}$ implies intermetallic contacts between heterometallic atoms. Four copper atoms have two types of geometries. One is trigonal with an SPh group coordinated, the other is a distorted tetrahedron with a chelating Et_3dtc group. The Cu-S_{ph} bond lengths ($2.166(1)$ - $2.182(1) \text{ \AA}$) are the same as those in $[PhSCuS_2MoS_2]^{2-}$, but shorter than that in $[Cu(SPh)_2]^{2-}$ ($2.30(4) \text{ \AA}$), moreover Cu-S_{ac} bond lengths are equivalent to those in $[WS_4(Cudtc)_2]^{2-}$. These may be attributed to transfer of charge from Cu^I to V^V , similar to dislocation from Cu^I to M^{VI} ($M=Mo, W$) for $Mo(W)$ -Cu-S cluster complexes.

Further studies on spectroscopic characterization and electrochemistry for this compound are in process.

We gratefully acknowledge the support of the Chinese National Natural Science foundation and the Natural science Fund of the Chinese Academy of Sciences.

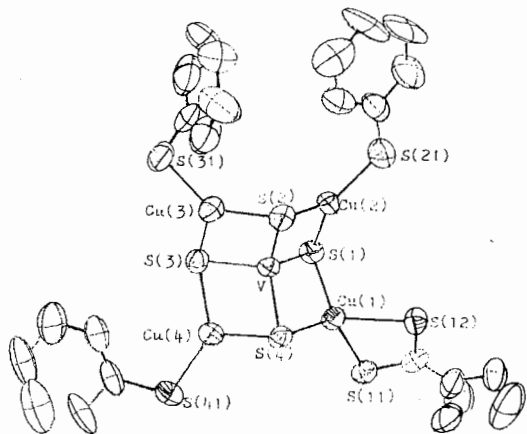


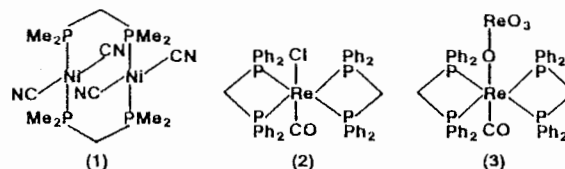
Figure 1. Structure of $[VS_4(CuSPh)_3(CudtcEt_2)]^{3-}$

PS-07.03.18 STRUCTURAL CHEMISTRY OF TRANSITION METAL — DIPHOSPHINOMETHANE COMPLEXES. Ljubica Manojlović-Muir,* Kenneth W. Muir, and Moira-Ann Rennie, Chemistry Department, The University, Glasgow G12 8QQ, Scotland.

Crystallographic studies of the title compounds have been instrumental

in the development of their chemistry: mononuclear, binuclear and cluster complexes displaying a wealth of different types of molecular architecture have now been characterised. The structural diversity displayed by these complexes is to a large extent a consequence of the remarkable stereochemical flexibility of the diphosphinomethane ligand (Chaudret, B., Delavaux, B., Poilblanc, R., *Coord. Chem. Rev.*, 1988, **86**, 191; Puddephatt, R.J., Manojlović-Muir, Lj., Muir, K.W., *Polyhedron*, 1990, **9**, 2767).

Our continuing interest in the binding modes of diphosphinomethane ligands (Manojlović-Muir, Lj., Muir, K.W., Davis, W.M., Mirza, H.A., Puddephatt, R.J., *Inorg. Chem.*, 1992, **31**, 904) has prompted the syntheses and structural characterisation of the Ni(0) complex $[Ni_2(CN)_4(\mu-dmpm)_2]$, **1**, the Re(I) complex $[ReCl(CO)(dppm)_2]$, **2**, and the novel mixed-valence Re(I) - Re(VII) complex $[Re(CO)(ReO_4)(dppm)_2]$, **3**, ($dmpm = Me_2PCH_2PMe_2$, $dppm = Ph_2PCH_2PPh_2$). Full details of the molecular geometry and bonding in **1**, **2** and **3** will be presented.



PS-07.03.19 $[M_3(\mu_3-CO)(Ph_2PCH_2PPh_2)_3]^{2+}$ CLUSTERS OF PALLADIUM AND PLATINUM AND THEIR REACTIONS WITH MOLECULES AND IONS. TRACKING DOWN AN ELUSIVE ANION. Kenneth W. Muir,* Ljubica Manojlović-Muir and James Fullard, Chemistry Department, The University, Glasgow G12 8QQ, Scotland.

The chemical processes which occur during the addition of a small molecule or ion to triangular cluster complexes $[M_3(\mu_3-CO)(\mu-dppm)_3]^{2+}$, ($M = Ni, Pd$ or Pt ; $dppm = Ph_2PCH_2PPh_2$), successfully mimic related reactions at metal surfaces; they can therefore be used to model the behaviour of such surfaces during heterogeneous catalysis. We have previously described complexes arising from the addition of thiocyanide, cyanide, alkynes, phosphines and phosphites, and trihalostannate(II) to triangular $dppm$ clusters of the platinum group metals (Puddephatt, R.J., Manojlović-Muir, Lj., Muir, K.W., *Polyhedron*, 1990, **9**, 2767; Manojlović-Muir, Lj., Muir, K.W., Mirza, H.A., Puddephatt, R.J., *Organometallics*, 1992, **11**, 3340).

We now report *inter alia* the mode of coordination of iodide, $Re(CO)_3$ and $AuPPh_3$ to the $[M_3(\mu_3-CO)(\mu-dppm)_3]$ framework. The gold-phosphine complex $[Pt_3(\mu_3-AuPPh_3)(\mu-dppm)_3][PF_6]$ crystallises in the cubic space group $Fd\bar{3}$ (No. 203) with $a = 40.69 \text{ \AA}$. The cation geometry has been clearly established from data collected at room temperature and refined to $R = 0.057$; however, there is little evidence for the presence, let alone position, of the counterion. The results of a refinement based on new data collected at 123 K will be presented.