

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 $^1\text{SCH}_2\text{CH}_2\text{S}^-$ 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), Jiang F.L., Liu H.Q., et al. in this reaction the dithiolate edt^{2-} ($^1\text{SCH}_2\text{CH}_2\text{S}^-$) 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.

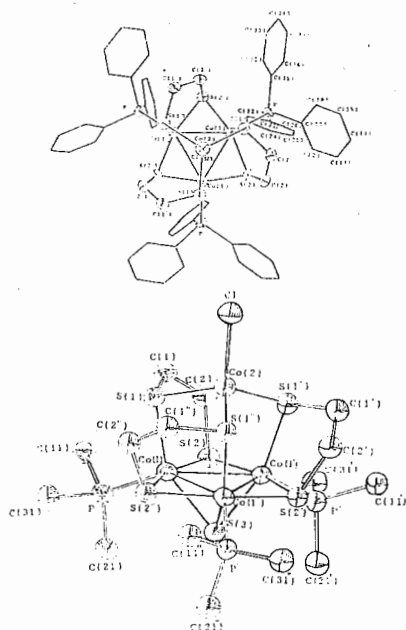


Fig.1 top and side views of $(\text{Co}_4(\mu_3\text{S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$.

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 $(M_4S_4)^{2+}$ 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.

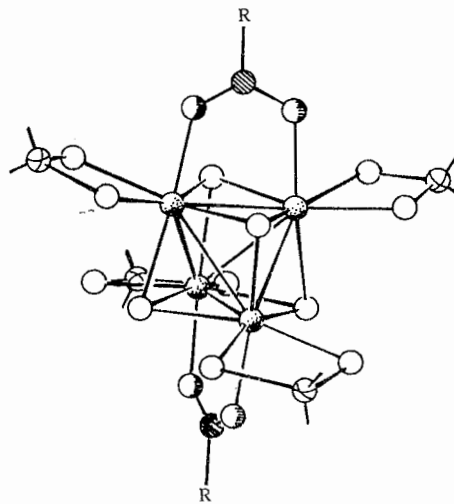


Fig. 1.



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. Ihmaime, 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