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S(1) of m.i.t. along the edges of the Co6 trigonal pyramid. The molecular structure possesses a crystallographic C3 symmetry with the rotation axis passing through the atom Cl, Co(2), S(2) and the centre of the base plane. The planes of Co(1) and S(1) are very near each other with the axial μ-S(3) atom 1.84(2) Å and 1.52(2) 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(1) Å and Co(1)-S(2) and Co(1)-S(3) bond lengths (2.202(3) Å and 2.323(2) Å) are slightly shorter than the corresponding ones in [Co6(S2)(O-xylyl)]3+ (Hemmel G., Angew. Chem. Int.Ed.Engl., 1983, 22, 333. Role R.I., Inorg. Chem., 1983, 22, 305). Co(1)-S(1) and Co(2)-S(1) distances being different from those in general metal-phenanthroline complexes for different lengths 2.249(2) and 2.328(6) Å, respectively. The N-OH spectrum with a broad peak at high field for SCH2CH2R confirms the paramagnetic character of 1. Unlike a recent report (Jiang F.C., Liu H.Q., et al. J. Organomet. Chem., 1993, in press; Jiang F.C., Liu H.Q., et al. J. Organomet. Chem., 1993, in press), this reaction does not simply generate C6H5(SCH2CH2R)2 complexes and may be considered a lithiation of the bridging sulphur atom through cleavage of the S-C bond.

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Fig. 1 Top and side view of [Co6(S2)(O-xylyl)]3+. Copyright © 1993 International Union of Crystallography. c216


The cubane-like metalloporphyrin 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. Inoue, A. Perrin, H. Ben-Yakhch, O. Pensa, R. Chevrel, P. Goeggel, M. Potel, J. Chim. Phys., 1981, 78, 212–214). The structural analysis of large quantity of this kind of crystals indicates that the “M5S3 box” is shown to possess flexibility. It allows a change of (M4) 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 future chemistry and as a good electron transfer agents.

The crystal structure of two new compounds containing (M5S3)3+ cubane-type cluster core with 11 (M4) cluster electrons are reported in this paper. The alteration of the M–M bond lengths, the cuboid volume and the symmetry with different d electron number for some (M5S3)3+ and (M3S3)3+ clusters are compared.

The crystal data are as follows: 1 [(Mn3S3) (CH3COO)2]; (OC(OH)2)2; (OC(OH)2)2; (OC(OH)2)2; (CH3COO)2] M = 1496, 01, orthorhombic Pbcn, a = 24.300(8), b = 25.4595(5) Å, c = 19.1310(4) Å, V = 10385.5 Å3, Z = 8, D = 1.79 g/cm3, F(000) = 5584, μ(MnKα) = 15.51 cm–1. R = 0.068 for 244 reflections. 2 [(Mn3S3) (CH3COO)2]; (OC(OH)2)2; (OC(OH)2)2; (CHOH)2] M = 1456, 87, orthorhombic Pbcn, a = 24.465(7) Å, b = 21.773(6) Å, c = 18.880(3) Å, V = 10057 Å3, Z = 8, D = 1.32 g/cm3, F(000) = 5700, μ(MnKα) = 38.82 cm–1. R = 0.058 for 2758 reflections. The molecular configuration of 1 and 2 is depicted in Figure 1.

Fig. 1. M (M = Mn, W)
 ○ S
 ○ P
 ○ C
 ○ O

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

It is well known that "tetrahedralligates" [M5]3+ bind as multideterminate ligands to a wide variety of metal ions and neutral molecules. Among the latter, CuCl showed a cluster to a large number of compounds by successive addition across the six metal ions. As we have shown, three and six copper atoms were added to [V2]3+ cluster. We here report here...
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The synthesis and structure of \( \{V_8(Si_{2}P_2)_{12}\} \) were studied where four copper atoms were added to the \( \{V_8\} \) unit. The title compound was obtained by reaction of \( \text{NH}_4\text{VS}_2 \) with \( \text{CuCl} \) in a solution of dimethylformamide (DMF) containing \( \text{N}_{2} \text{H}_4\text{PS}_2 \) and \( \text{N}_{2} \text{H}_4\text{SCN} \). 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 CAD-4 diffractometer. The space group is \( P\bar{1} \) with \( a = 10.39(2) \), \( b = 12.39(2) \), \( c = 12.58(5) \AA \), \( \alpha = 78.67(2) \), \( \beta = 82.48(2) \), \( \gamma = 81.59(2) \) \(^\circ\). \( V = 1562.1 \AA^3 \) and \( Z = 4 \). 4538 reflections with \( \|\theta\| < 15^\circ \) were used for the structure determination and gave a final \( R \) of 0.039 and \( R_1 \) of 0.042.

The structure is shown in Figure 1. The unit cell contains only one molecule, a \( \{V_8(Si_{2}P_2)_{12}\} \) unit and three \( \{\text{CuCl}\}^+ \) cations. The anion is formed of a central \( V_8 \) tetrahedron surrounded by a tetragon of four copper atoms. The \( V_8 \) core has retained the ideal geometry of free tetrachloroanide with S-V-S angles and V-S bond lengths ranging from 108.4(1) to 110.9(1) \(^\circ\) and 2.71(3) to 2.720(3) \( \AA \) respectively. Each copper atom is bound across an edge of the \( V_8 \) tetrahedron with a \( V_8 \)-Cu bond coordination to each sulfur atom. The \( \text{Cu}_{\text{s}-\text{s}} \) bond lengths are quite similar. The \( \text{V}_{\text{Cu}} \) aggregate approximates \( D_{4h} \) symmetry which is also observed for \( \text{Nd}_{2} \text{Cu}_{2} \) and \( \text{V}_{\text{Cu}} \) cores. The V-Cu near distance of 2.611(2) \( \AA \) implies intermetallic contacts between heterometallic atoms. Four copper atoms have two types of geometries. One is trigonal with a \( S_{6h} \) group coordinated; the other is a distorted tetrahedron with a chelating ligand group. The Cu-S bond lengths (2.166(1) to 2.182(1) \( \AA \)) are in agreement with those in \( \text{VCu}_{2} \) complexes. These may be attributed to transfer of charge from \( \text{Cu}^+ \) to \( \text{V}^3+ \). The N-H...N distances range from 1.86 to 2.40 \( \AA \), consistent with the observed \( V_8 \)-Cu-S cluster complexes.

Further studies on spectroscopic characterisation and electrochemistry for this compound are in progress.

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Figure 1. Structure of \( \{V_8(Si_{2}P_2)_{12}\} \) unit.

PS-07.03.19 \( \{M_{3}(\mu-\text{CO})(P_{4}P_{3}C_{2}H_{4}P_{2}H_{4})\}^{\text{iii}} \) CLUSTERS OF PALADIUM AND PLATINUM AND THEIR REACTIONS WITH MOLECULES AND IONS. TRACKING DOWN AN ELUSIVE ANION. Kenneth W. Mair,*,† Ljudica Manojlovic-Muir and James Fulillard, 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 \( \{M_{3}(\mu-\text{CO})(\mu-\text{dppm})\}^{\text{iii}} \), \( M = \text{Ni, Pd or Pt; dppm = } P_{4}P_{3}C_{2}H_{4}P_{2}H_{4} \), successfully mimic related reactions at metal surfaces; they can therefore be used to model the behavior of such surfaces during heterogeneous catalysis. We have previously described complexes arising from the addition of thiocyanate, cyanide, alkynes, phosphines and phosphonates, and triblockates to \( \{M_{3}(\mu-\text{CO})(\mu-\text{dppm})\}^{\text{iii}} \) clusters of the platinum group metals (Puddephatt, R.J., Manojlovic-Muir, L.J., Mair, K.W., Polyhedron, 1990, 9, 2367; Manojlovic-Muir, L.J., Mair, K.W., Mirza, H.A., Puddephatt, R.J., Inorg. Chem., 1992, 31, 904) and \( \{M_{3}(\mu-\text{CO})(\mu-\text{dppm})\}^{\text{iii}} \) clusters of the platinum group metals.

We now report \( \text{inter alia} \) the mode of coordination of iodide, \( \text{ReCO}_{3} \) and \( \text{AuPPh}_{3} \) to the \( \{M_{3}(\mu-\text{CO})(\mu-\text{dppm})\}^{\text{iii}} \) framework. The gold-phosphine complex \( \{P_{4}P_{3}C_{2}H_{4}P_{2}H_{4}(\mu-\text{dppm})\}^{\text{iii}} \) crystallises in the cubic space group \( Fd\overline{3} \) (No. 206) with \( a = 40.69 \text{ Å} \). The cation geometry has been carefully 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.