The Synthesis and Characterization of Two Novel Cubane-like Clusters $[M_2Cu_2S_4(PPh_3)_2(SCH_2CH_2S)_2]$ (M = Mo and W)

Zhu Nianyong, Zheng Yifan, and Wu Xintao*

Fuzhou Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

New members of the cubane-like cluster family with the core $[M_2Cu_2S_4]^{4+}$ (M = Mo and W) have been synthesized and characterized; the crystal structure of the molybdenum complex shows that it contains one Mo–Mo bond [2.8576(7) Å] and four Mo–Cu bonds [av. 2.810(1) Å] approximately with C_{2v} symmetry.

Research on synthetic analogues of the redox sites of iron–sulphur proteins has led to studies on homometallic cubane-like clusters with the $M_4(\mu_3\text{-}S)_4$ core.[1] Also, a variety of methods have been used to synthesize heterometallic cubane-like clusters $M^1{}_2M^2{}_2S_4$[2] and $M^1{}_3M^2S_4$.[3] The unit-construction method,[4] using reactive fragments as building blocks, is a more convenient method for obtaining clusters, and we have synthesized cluster compounds with cores $[M_3CuS_4]$ (M = Mo[5] or W[6]) and $[MoCu_3S_3Br]$.[7c,d] We now report the synthesis of new members of the cubane-like cluster family with the $[M_2Cu_2S_4]^{4+}$ (M = Mo or W) core using this method. There is extensive research on Mo–Cu–S[8] complexes which exhibit rich structural variations. The title clusters $[M_2Cu_2S_4(PPh_3)_2(edt)_2]$ (**1**; M = Mo) and (**2**; M = W) (H_2edt = ethane-1,2-dithiol) complete the series of M–Cu–S (M = Mo or W) cubane-like clusters for the series M_3CuS_4, $M_2Cu_2S_4$, and MCu_3S_3E (E = Cl[7a,b] or Br[7c,d]).

$[M_2Cu_2S_4(PPh_3)_2(edt)_2]$
(**1**) M = Mo
(**2**) M = W
$[Et_4N]_2[Mo_2S_4(edt)_2]$
(**3**) M = Mo
(**4**) M = W

The dinuclear molybdenum complex $[Et_4N]_2[Mo_2S_4(edt)_2]$ (**3**) was prepared by the method of Stiefel *et al.*[9] The compound has two terminal and two μ_2-bridging sulphido ligands. It was used as a reactive building block in a reaction with $Cu(PPh_3)_3Cl$[10] (2 mol. equiv.; all preparations under dinitrogen atmosphere) to give complex (**1**). Dark red crystals of (**1**), which are stable in air, were obtained from MeCN–CH_2Cl_2. Satisfactory elemental analyses were obtained. The cluster (**1**) was characterized by *X*-ray crystallography,† and IR and UV-VIS spectroscopy.‡

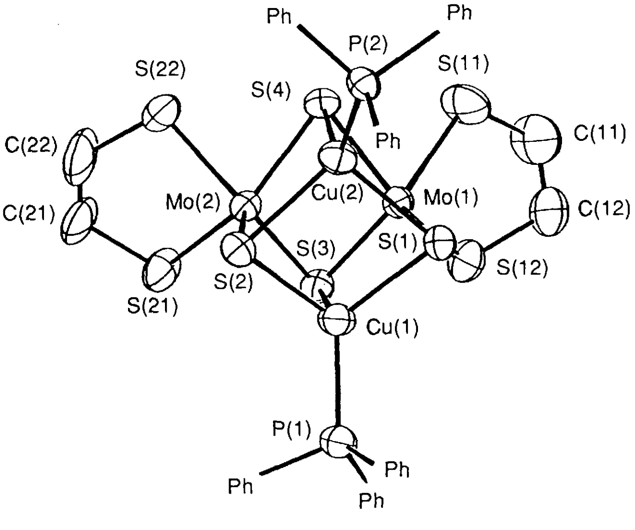

Figure 1. Perspective view of the molecule $[Mo_2Cu_2S_4(PPh_3)_2(edt)_2]$. Selected bond distances (Å): Mo(1)–Mo(2), 2.8576 (7); Mo(1)–Cu(1), 2.782(2); Mo(1)–Cu(2), 2.831(1); Mo(2)–Cu(1), 2.827(1); Mo(2)–Cu(2), 2.7985(9); Cu(1)–Cu(2), 3.095(2); Mo(1)–S(1), 2.199(2); Mo(1)–S(3), 2.330(2); Mo(1)–S(4), 2.359(2); Mo(2)–S(2), 2.199(2); Mo(2)–S(3), 2.347(2); Mo(2)–S(4), 2.354(2); Cu(1)–S(1), 2.363(2); Cu(1)–S(2), 2.420(2); Cu(1)–S(3), 2.274(2); Cu(2)–S(1), 2.420(2); Cu(2)–S(2), 2.372(2); Cu(2)–S(4), 2.252(2).

The isomorphous compound $[W_2Cu_2S_4(PPh_3)_2(edt)_2]$ (**2**) was synthesized by the same method from $[Et_4N]_2[W_2S_4(edt)_2]$[9] (**4**) and a solution in CH_2Cl_2–EtOH of $CuCl_2{\cdot}2H_2O$ and PPh_3 (2:3). Dark orange crystals§ were obtained on diffusion into CH_2Cl_2–EtOH.

The ORTEP drawing of cluster (**1**) is shown in Figure 1. The idealized symmetry of the molecule is C_{2v}, as for the dinuclear molybdenum complex.[11] Each Mo is co-ordinated by three μ_3-sulphido ligands and two sulphur atoms from the bidentate edt ligand, the five sulphur atoms maintaining the tetragonal-pyramidal (TP) geometry. Each Cu atom is tetrahedrally co-ordinated by three bridging μ_3-sulphido atoms and one P atom from the PPh_3 ligand. In both TP fragments the Mo atom is 0.66 Å out of the basal plane, a distance which is shorter than that (0.72 Å)[11] in the cluster (**3**). The change from terminal sulphur to bridging μ_3-sulphido increases the Mo–S bond length slightly from an average of 2.10 to 2.20 Å, unlike in the cluster $[Mo_2Co_2S_4(S_2CNEt_2)_2(MeCN)_2(CO)_2]$[2f] in which there was a greater change in Mo–S bond length. The bonds of two of the Cu atoms to these terminal sulphur atoms (av. 2.39 Å) are longer than the other two Cu–S bonds (av. 2.26 Å). The cubane-like cluster core $\{Mo_2Cu_2S_4\}$ is distorted; the dihedral angle between the Mo(1)/Mo(2)/S(3) and

---

† *Crystal data*: $C_{40}H_{38}Cu_2Mo_2P_2S_8$ (**1**), orthorhombic, space group $P2_12_12_1$, a = 11.676(2), b = 12.385(2), c = 31.576(6) Å, U = 4566.3 Å^3, Z = 4, D_c = 1.68 g cm^{-3}, μ = 19 cm^{-1}, F(000) = 2312, T = 296 K, crystal dimensions 0.45 × 0.3 × 0.2 mm^3; λ(Mo-K_α) = 0.71073 Å, $2\theta_{max}$ = 50°, CAD-4 k-geometry diffractometer, $\omega/2\theta$ scan, scan rate varied from 1 to 7° min^{-1} (in ω), scan width 0.40° + 0.35° tan θ. The structure analysis is based on 3624 observed reflections with $I > 3\sigma(I)$; the intensities were corrected for absorption using empirical scan data, and for Lorentz and polarization factors. The structure was solved by direct methods using MULTAN11/82 and was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-H atoms (487 variables). Final R = 0.043, R_w = 0.046, S = 3.40. $(\Delta/\sigma)_{max}$ = 0.47. The final difference electron density synthesis showed maximum features of 0.47 and −0.49 e Å^{-3}. All calculations were performed on a VAX 785 computer using the SDP package, with scattering factors taken from international tables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ UV-VIS λ_{max}: (**1**), 230 (ε 60), 315 (26), and 510 (8.9) nm; (**2**), 230 (ε 37), 275 (37), and 428 (10.6) nm; (**3**), 228 (ε 37), 306 (26), and 445 (24) nm; (**4**) 235 (ε 24), 284 (20), and 362 (6.6) nm.

§ Approximate cell constants: a = 11.76, b = 12.50, c = 31.74 Å, α = 89.7, β = 89.8, γ = 89.5°, U = 4665 Å^3.

Mo(1)/Mo(2)/S(4) plane is 156° and that between the Cu(1)/S(1)/S(2) and Cu(2)/S(1)/S(2) planes is 157°. The Mo···Mo distances in clusters (**1**) and (**3**) are nearly identical. It seems that the $Mo_2(\mu_2\text{-}S)_2S_2(edt)_2$ unit remains unchanged except for a slight increase in some bond lengths and differences in some dihedral angles. The apparent C–C distances of 1.22 and 1.45 Å from the edt ligand are unrealistically short for single bonds, owing to thermal motion.[7c,11]

The cyclic voltammograms¶ of clusters (**1**)—(**4**) have been recorded in the range 0.0 to −1.7 V. The two dinuclear complexes (**3**) and (**4**) have no reduction or oxidation wave in this range, but clusters (**1**) and (**2**) display a reduction wave at −0.76 and −1.2 V, respectively in CH_2Cl_2, but no corresponding reversible oxidation was apparent for the two clusters.

The reactions of the compounds (**3**) and (**4**) with Ag and other metals are under investigation.

This research was supported by grants from the Structural Chemistry Research Laboratory of the Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, and the National Science Foundation of China.

Received, 4th January 1990; Com. 0/00081G

References

1 B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 3523; J. A. Ibers and R. H. Holm, *Science*, 1980, **209**, 223, and references cited therein; C. T.-W. Chu, F. Y.-K. Lo, and L. F. Dahl, *J. Am. Chem. Soc.*, 1982, **104**, 3409.

2 (a) H. Brunner and J. Wachter, *J. Organomet. Chem.*, 1982, **240**, C41; (b) M. D. Curtis and P. D. Williams, *Inorg. Chem.*, 1983, **22**, 2661; (c) H. Brunner, H. Kauermann, and J. Wachter, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 549; (d) T. B. Rauchfuss, T. D. Weatherill, S. R. Wilsin, and J. P. Zebrowski, *J. Am. Chem. Soc.*, 1983, **105**, 6508; (e) H. Brunner, N. Janietz, J. Watcher, T. Zahn, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 133; (f) T. R. Halbert, S. A. Cohen, and E. I. Stiefel, *Organometallics*, 1985, **4**, 1689.

3 R. E. Palermo, R. Singth, J. K. Bashkin, and R. H. Holm, *J. Am. Chem. Soc.*, 1984, **106**, 2600, and references therein; T. Shibahara, H. Akashi, and H. Kuroya, *ibid.*, 1986, **108**, 1342; B. A. Averill, *Struct. Bonding*, 1983, **53**, 59; A. A. Pasynskii, I. L. Eremenko, B. Orazsakhatov, V. T., Kalinnikov, G. G. Aleksandraov, and Y. T. Struchkov, *J. Organomet. Chem.*, 1981, **212**, 367; I. L. Eremenko, A. A. Pasynskii, B. Orazsakhatov, O. G. Ellert, V. M. Novotortsev, V. T. Kalinnikkov, M. A. Porai-Koshits, A. S. Antsyshkina, L. M. Dikareva, and V. N. Ostrikova, *Inorg. Chim. Acta*, 1983, **73**, 225.

4 X.-T. Wu and J.-X. Lu, *Jiegou Huaxue* (*J. Struct. Chem.*), 1989, **8**, in the press.

5 X.-T. Wu, S.-F. Lu, N.-Y. Zhu, Q.-J. Wu, and J.-X. Lu, *Inorg. Chim. Acta*, 1987, **133**, 39; S.-F. Lu, N.-Y. Zhu, X.-T. Wu, Q.-J. Wu, and J.-X. Lu, *J. Mol. Struct.*, 1989, **197**, 15.

6 H.-Q. Zhan, Y.-F. Zheng, X.-T. Wu, and J.-X. Lu, *Inorg. Chim. Acta*, 1989, **156**, 277; Y.-F. Zheng, H.-Q. Zhan, X.-T. Wu, and J.-X. Lu, *Transition Met. Chem.*, 1989, **12**, 161.

7 (a) A. Müller, H. Bögge, and U. Schimanski, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 654; (b) *Inorg. Chim. Acta*, 1983, **69**, 5; (c) X.-T. Wu, Y.-F. Zheng, S.-W. Du, and N.-Y. Zhu, *Transition Met. Chem.*, 1989, **12**, 157; (d) X.-T. Wu, Y.-F. Zheng, and S.-W. Du, *Acta Crytallogr., Sect. C*, 1989, **45**, 1070.

8 S. Sarkar and S. B. S. Mishra, *Coord. Chem. Rev.*, 1984, **59**, 239.

9 W. H. Pan, T. Chandler, J. H. Enemark, and E. I. Stiefel, *Inorg. Chem.*, 1984, **23**, 4265.

10 S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051.

11 G. Bunzey and J. H. Enemark, *Inorg. Chem.*, 1978, **17**, 682.

¶ 2 mM solutions in 0.1 M Bu_4NClO_4 *vs.* standard calomel electrode in CH_2Cl_2 solution with a platinum electrode (scan rate 0.1 V/s).