A Novel Tetranuclear Thiolato-copper Cluster Anion with a Two-dimensional Molecular Interaction

Gen-etsu Matsubayashi* and Akito Yokozawa

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

Bis(*N*-methylpyridinium) tris[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]tetracopper(I) has dimerized anion units with interanionic Cu–S and S–S contacts which further interact with each other through several nonbonded S–S contacts to form a two-dimensional molecular sheet in the solid as shown by an X-ray crystal structure determination.

Many planar bis(dmit)–metal complexes [metal = Ni, Pd, Pt and Au; dmit = $C_3S_5^{2-}$, 4,5-dimercapto-1,3-dithiole-2-thionato(2−)] exhibit good electrical conductivities,[1–3] and some become superconductors at low temperatures.[1,2,4] Two- or three-dimensional, close intermolecular contacts of the sulphur atoms produce conduction pathways in the crystals. Although nonplanar dmit–metal complexes also are expected to behave as new conductors having multi-dimensional dmit–dmit interactions in the solid, few nonplanar dmit–metal complexes have been studied.[5–7] We have isolated a bulky tetranuclear copper(I)–dmit cluster complex and clarified its molecular and crystal structure; the cluster anion units are dimerized and have a two-dimensional molecular interaction through Cu–S and nonbonded S–S contacts.

The reaction of an acetonitrile solution of $[Cu(MeCN)_4][ClO_4]$ with a methanol solution containing an equimolar amount of Na_2dmit[8] in the presence of excess of [mpy]I (mpy = *N*-methylpyridinium) or $NBu^n{}_4Br$ gave dark brown microcrystals of $[mpy]_2$- or $[NBu^n{}_4]_2[Cu_4(dmit)_3]$.† Crystals of $[mpy]_2[Cu_4(dmit)_3]$ suitable for an X-ray structure analysis‡ were obtained by recrystallization from acetone.

As illustrated in Fig. 1, the molecular structure of the anion consists of a distorted tetrahedron of copper atoms. Cu(1), Cu(2) and Cu(3) atoms are chelated by the dmit ligands and bridged by another dmit-sulphur atom to form a trigonal-planar array of sulphur atoms, while the Cu(4) atom is coordinated with three dmit-sulphur atoms only through the bridging mode forming also a trigonal planar array of sulphur atoms. A similar Cu_4S_6 cluster structure containing dithiolato-chelate ligands was observed for the $[Cu_4\{o\text{-}(SCH_2)_2\text{-}$

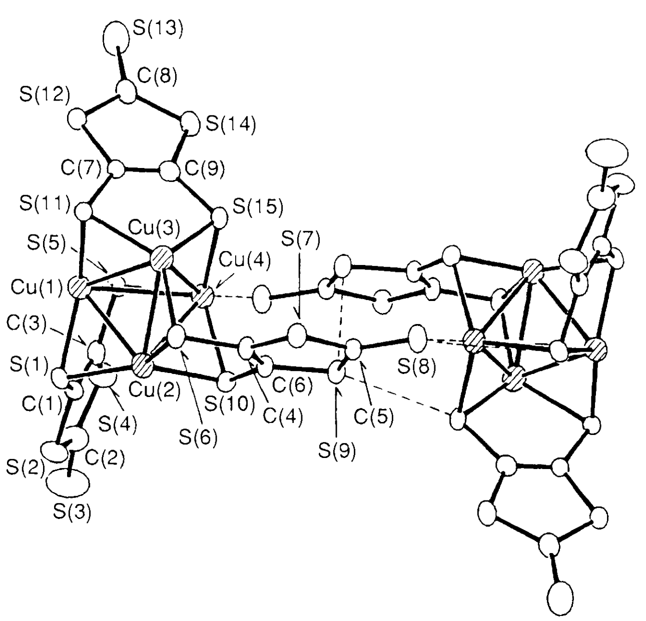

Fig. 1 Perspective view of the dimerized anion moieties of $[mpy]_2[Cu_4(dmit)_3]$ with atom numbering. Bond lengths (Å): Cu(1)–Cu(2) 2.608(2), Cu(1)–Cu(3) 2.773(2), Cu(2)–Cu(3) 2.756(2), Cu(1)–Cu(4) 3.150(2), Cu(2)–Cu(4) 2.965(2), Cu(3)–Cu(4) 3.133(2), Cu(1)–S(1) 2.262(3), Cu(1)–S(5) 2.312(3), Cu(1)–S(11) 2.211(3), Cu(2)–S(1) 2.233(3), Cu(2)–S(6) 2.286(3), Cu(2)–S(10) 2.280(3), Cu(3)–S(6) 2.244(3), Cu(3)–S(11) 2.289(3), Cu(3)–S(15) 2.298(4), Cu(4)–S(5) 2.353(3), Cu(4)–S(10) 2.368(3), Cu(4)–S(15) 2.333(3), Cu(4)–S(8′) 2.495(3).

---

† Satisfactory elemental analyses were obtained.

‡ *Crystal data*: $C_{21}H_{16}Cu_4N_2S_{15}$, M_r = 1031.4, triclinic, space group $P\bar{1}$, a = 11.558(2), b = 13.914(2), c = 11.111(2) Å, α = 98.50(2), β = 106.67(2), γ = 91.80(1)°, U = 1687.8(6) Å^3, Z = 2, D_c = 2.030(1) g cm^{-3}, μ(Cu-Kα) = 113.5 cm^{-1}, $F(000)$ = 1024. Data were collected on a Rigaku four-circle diffractometer using Cu-Kα radiation (λ = 1.541 84 Å); 5623 independent reflections in the range $6 < 2\theta < 125°$ were collected, of which 3980 unique reflections with $|F_o| > 3\sigma(F)$ were used to solve (Patterson method) and refine (block-diagonal least-squares) the structure. An absorption correction[11] was applied (correction range, 1.01–1.67). All non-hydrogen atoms were allowed to vibrate anisotropically. Hydrogen atoms were not included. Final R = 0.068 and R_w = 0.078. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

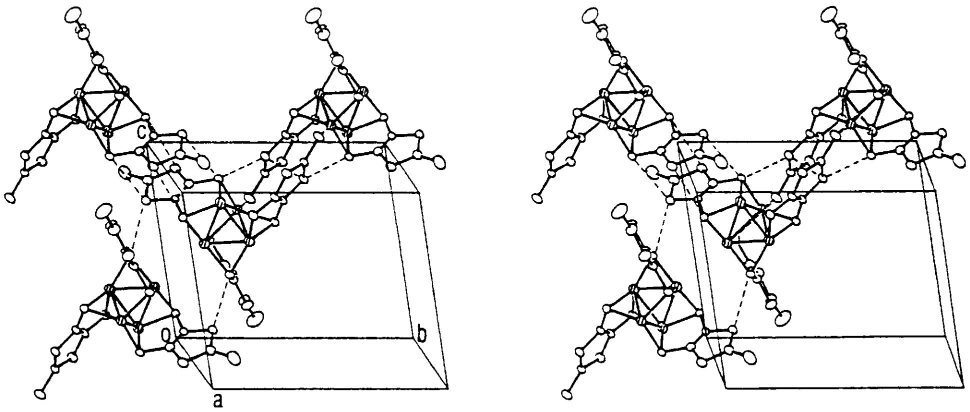

Fig. 2 Stereoview of the packing diagram of the anion moieties of $[mpy]_2[Cu_4(dmit)_3]$. Dashed lines indicate Cu–S (2.495 Å) and nonbonded S–S contacts (<3.7 Å).

$C_6H_4\}_3]^{2-}$ anion with almost equal Cu–Cu lengths (2.699–2.739 Å).[9] In the present complex, however, the Cu–Cu lengths for Cu(1), Cu(2) and Cu(3) (2.608–2.756 Å) are shorter than those for Cu(4) bonded to Cu(1)–Cu(3) (2.965–3.150 Å). The appreciable distortion of the Cu(4) atom arises from the coordination to it by a sulphur atom of another cluster anion [Cu(4)–S(8′) = Cu(4′)–S(8) = 2.495(3) Å]. The anions form a dimer unit having Cu–S and some nonbonded S–S contacts (<3.7 Å) in the solid. Fig. 2 shows the packing diagram of the anion moieties. The dimeric units further interact with each other through S–S contacts (<3.7 Å) to form a two-dimensional molecular interaction sheet, the cations being localized between the anion sheets.

The ^{13}C NMR spectrum of $[NBu^n_4]_2[Cu_4(dmit)_3]$ in $(CD_3)_2SO$ shows three signals at δ 136.0 (C=C), 138.9 (C=C) and 209.3 (C=S) due to the dmit unit. Occurrence of inequivalent C=C signals indicates the presence of two kinds of sulphur atoms bridging the metals. This signal profile is consistent with the geometry of the cluster anion in which the corresponding atoms of each half of the ligand are inequivalent. The electronic absorption spectrum of the $[Cu_4(dmit)_3]^{2-}$ anion shows an intense band at 458 nm in dimethyl sulphoxide which is ascribed to the π–π* transition of the dmit ligand.[10] In the powder reflectance spectrum of $[mpy]_2[Cu_4(dmit)_3]$, another broad band is also observed around 580 nm which arises from the above-mentioned molecular interaction.

The cyclic voltammogram of the $[Cu_4(dmit)_3]^{2-}$ anion in dimethylformamide shows low oxidation potentials (+0.45 and 0.55 V *vs.* standard calomel electrode), although the oxidation processes are irreversible. Partially oxidized copper–dmit cluster complexes may become new electrical conductors with effective molecular interactions through nonbonded S–S contacts in the solid; such complexes are currently under investigation.

This research was supported by a Grant-in-Aid for scientific Research No. 02230220 from the Ministry of Education, Science and Culture, Japan.

Received, 13th August 1990; Com. 0/03708G

References

1 M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908, and references therein.

2 L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J.-P. Legros and P. Cassoux, *Synth. Met.*, 1988, **27**, B157, and references therein.

3 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1990, 3013; 3535.

4 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishino, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 1819.

5 G. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem.*, 1988, **27**, 4744.

6 K. Akiba, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1989, **165**, 245.

7 W. E. Broderick, E. M. McGhee, M. R. Godfrey, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1989, **28**, 2904.

8 G. Matsubayashi, K. Takahashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1988, 967.

9 J. R. Nicholson, I. L. Abrahams, W. Clegg and C. D. Garner, *Inorg. Chem.*, 1985, **24**, 1092.

10 G. Matsubayashi, K. Akiba and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1990, 115.

11 A. C. T. North, D. C. Phillips and F. C. Matheus, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.