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An unusual tetranuclear copper(II) acetate structure with an open cubane Cu_4O_4 framework

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The tetranuclear copper(II) complex $[\{Cu(O_2CMe)(OMe)\}_4]$ has been found to contain an unusual open cubane Cu_4O_4 framework defined by two interpenetrating copper and oxygen planes rather than two tetrahedra; it also shows strong antiferromagnetic coupling.

There has been considerable interest in the chemistry of multinuclear copper(II) complexes, much of which stems from the involvement of such species in biological processes and in inorganic materials.[1] In the presence of bridging acetate groups numerous higher nuclearity metal complexes having various structures and unique magnetic properties have been observed. They include a tetranuclear manganese(III) complex of 4-methyl-2,6-bis(salicylideneaminomethyl)phenol which has two incomplete cubanes sharing faces and the recently reported new class of pentanuclear copper(II) acetate complexes with imidazole.[2,3] In addition, tetrameric nickel(II) and cobalt-(II) and -(III) acetate complexes have been reported in which a cubane-like configuration is defined by two interpenetrating tetrahedra of metal and methoxide ions with the acetates bridging two metal ions on opposite faces of the cube.[4,5] The magnetic studies of these acetate-bridged tetra- or penta-nuclear complexes indicate an overall ferromagnetic or antiferromagnetic behaviour. In this Communication a novel tetranuclear copper(II) complex $[\{Cu(O_2CMe)(OMe)\}_4]$ with an open cubane Cu_4O_4 framework that resulted from the incorporation of OMe^- ions into the copper(II) acetate structure is described.

The complex was prepared[†] by the reaction of copper(II) acetate monohydrate and sodium methoxide. The structure[‡] of $[\{Cu(O_2CMe)(OMe)\}_4]$ is illustrated in Fig. 1. Each unit cell contains four such tetramers situated in a special position along the C_2 axis. The C_2 axis intersects the centre of the Cu(1)–O(5)–Cu(1′)–O(5′) and Cu(2)–O(6)–Cu(2′)–O(6′) face. The compound adopts an open cubane-like arrangement of copper(II) and methoxide ions; the acetates bridge two crystallographically independent copper atoms Cu(1) and Cu(2) in a manner reminiscent of the dimeric copper(II) acetate structure. Thus, each copper atom is found in a distorted square-planar environment [if the Cu $\cdots$ Cu separations of 2.958(1) to 2.970(1) Å are regarded as non-bonding] that includes two *cis* carboxylate oxygen atoms and two *cis* methoxide oxygen atoms. The dibridged Cu(1) $\cdots$ Cu(2) distance [2.958(1) Å] is 0.342 Å longer than the comparable distance in copper(II) acetate monohydrate.[7] This elongation of the Cu(1) $\cdots$ Cu(2) distance leads to an opening of the O(1)–C(1)–O(2) and O(3)–C(3)–O(4) angles to 124.8(5) and 125.6(5)°, respectively. Other distances and angles within the tetramer are much as expected.

The most intriguing feature of this cubane-like structure is its unusual Cu_4O_4 framework. The two symmetry-related copper and two bridging methoxide oxygen atoms, taken alternately,

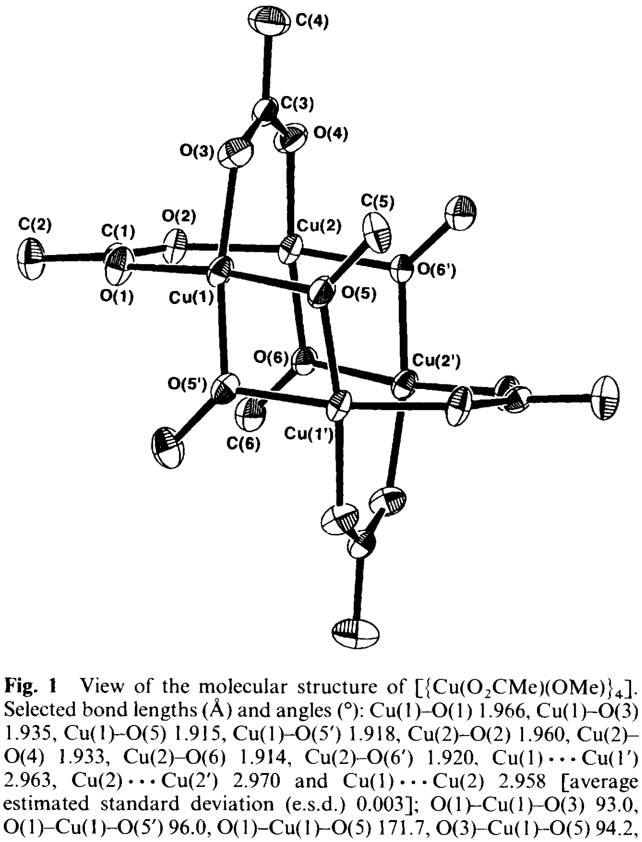

Fig. 1 View of the molecular structure of $[\{Cu(O_2CMe)(OMe)\}_4]$. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.966, Cu(1)–O(3) 1.935, Cu(1)–O(5) 1.915, Cu(1)–O(5′) 1.918, Cu(2)–O(2) 1.960, Cu(2)–O(4) 1.933, Cu(2)–O(6) 1.914, Cu(2)–O(6′) 1.920, Cu(1) $\cdots$ Cu(1′) 2.963, Cu(2) $\cdots$ Cu(2′) 2.970 and Cu(1) $\cdots$ Cu(2) 2.958 [average estimated standard deviation (e.s.d.) 0.003]; O(1)–Cu(1)–O(3) 93.0, O(1)–Cu(1)–O(5′) 96.0, O(1)–Cu(1)–O(5) 171.7, O(3)–Cu(1)–O(5) 94.2, O(3)–Cu(1)–O(5′) 169.9, O(5)–Cu(1)–O(5′) 76.5, Cu(1)–O(5)–Cu(1′) 101.3, O(2)–Cu(2)–O(4) 92.6, O(2)–Cu(2)–O(6) 95.9, O(2)–Cu(2)–O(6′) 171.3, O(4)–Cu(2)–O(6′) 94.6, O(4)–Cu(2)–O(6) 170.1, O(6)–Cu(2)–O(6′) 76.6 and Cu(2)–O(6)–Cu(2′) 101.5 (average e.s.d. 0.2)

[†] A methanol solution (6 cm^3) of copper(II) acetate monohydrate (30 mg, 0.15 mmol) was treated with sodium methoxide (4.1 mg, 0.15 mmol) in the same solvent (4 cm^3). The mixture was stirred for 1 h and a blue precipitate was gradually deposited. Removal of the precipitate by filtration gave a clear blue filtrate which was transferred to a glass tube and layered with diethyl ether. After standing at room temperature for 6 months dark blue brick crystals of $[\{Cu(O_2CMe)(OMe)\}_4]$ were isolated (Found: C, 23.90; H, 4.30. Calc. for $C_6H_{12}Cu_2O_6$: C, 23.45; H, 3.95%).

[‡] Crystal data. $C_6H_{12}Cu_2O_6$, $M = 307.25$, monoclinic, space group $C2/c$, crystal size 0.40 × 0.20 × 0.20 mm, $a = 11.341(2)$, $b = 9.851(3)$, $c = 18.164(2)$ Å, $\beta = 94.33(1)°$, $U = 2023(1)$ Å^3, $Z = 8$, $D_c = 2.017$ g cm^{-3}, $\mu = 12.32$ cm^{-1}, $F(000) = 1232$. Data were collected on a Rigaku AFC5R four-circle diffractometer (graphite-monochromated Mo-Kα radiation, λ 0.710 69 Å, ω–2θ scans, 293 K). All data were corrected for Lorentz and polarization effects and for absorption. The structure was solved by a combination of direct and Fourier-difference methods using the TEXSAN computer program.[6] It was refined on F with all non-H atoms anisotropic, 1612 reflections were measured as observed applying the condition $I > 3.00\sigma(I)$, 127 parameters, $R = 0.038$, $R' = 0.051$ with weights based on counting statistics. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/51.

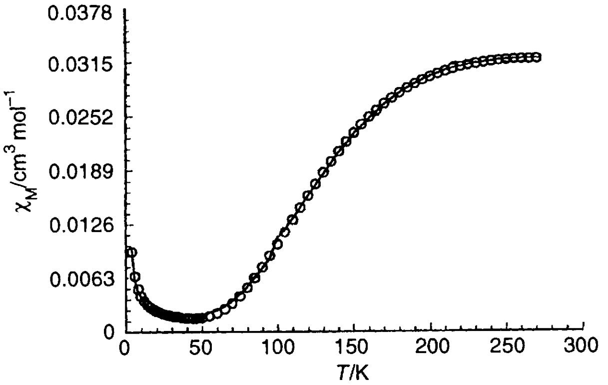

Fig. 2 Temperature-dependent molar magnetic susceptibility of a powdered sample of the compound $[\{Cu(O_2CMe)(OMe)\}_4]$; the solid line represents the best calculated fit of the data

define the four corners of each of the two closed cubane faces. These two planes are almost parallel to each other with a dihedral angle of 1.37° between them. Within the open cubane Cu_4O_4 framework the Cu–O distances differ relatively little between Cu(1) and Cu(2) as shown in Fig. 1. The Cu(1)–O(OMe) bonds at 1.918(4) and 1.915(4) Å, and the Cu(2)–O(OMe) at 1.920(4) and 1.914(4) Å are strikingly similar. Likewise, the bond angles O–Cu–O and Cu–O–Cu of 76.5(2) and 101.3(2)° for Cu(1) and 76.6(2) and 101.5(2)° for Cu(2). Therefore, the tetranuclear structure is unique in the sense that it can be thought of as two copper(II) acetate dimers associated by four methoxide groups.

Cubane-type structures have been found for a number of different bridging groups and metal ions, such as Zn^{II}, Ni^{II}, Co^{II}, Co^{III}, Cu^{I} and Ag^{I}, and in organometallic complexes of Mn, Re and Se.[4,5,8] Some oxygen-bridged copper(II) tetramers with 2,2′-bipyridyl, 2-diethylaminoethanolate or dialkylaminoethanolate anions having cubane-like structures are also known.[9,10] For each of these tetranuclear cubane structures with a Cu_4O_4 core, without a single exception, the metal ions always occupy the corners of a distorted tetrahedron. In contrast, the four copper atoms in the present tetramer $[\{Cu(O_2CMe)(OMe)\}_4]$ are located on a diagonal plane across the cube. To our knowledge, this is the first example of a cubane-like configuration defined by two interpenetrating copper and oxygen planes rather than two tetrahedra.

The temperature dependence of the magnetic susceptibility of the complex was measured for a solid sample in the temperature range 4–270 K. The data shown in Fig. 2 are displayed as molar susceptibility *versus* temperature. The susceptibility data show a maximum at 270 K and below this temperature down to 40 K the susceptibility decreases. The rise of the susceptibility at lower temperature is due to paramagnetic impurities. This behaviour is characteristic of an overall antiferromagnetic interaction with a singlet ground state. The magnetic data were analysed using the Van Vleck equation.[11] Considering chemically similar environments to be magnetically equivalent, three parameters are needed to take into account the exchange interactions. The best least-squares-fit parameters are $g = 2.313(5)$, $J_1 = -153.5(10)$ cm^{-1}, $J_2 = -150.2(10)$ cm^{-1}, $J_3 = -150(1)$ cm^{-1} and $\chi_p = 0.274(3)\%$. The discrepancy value, defined as $R = \Sigma[(\chi_{obs} - \chi_{calc})/\sigma\chi_{obs}]^2$, is 0.4162. The results are comparable with those of oxygen-bridged copper(II) tetranuclear complexes.[10,11b] The three J values are also in good agreement with the expected value of −143.7 cm^{-1} from a correlation between J and the Cu–O–Cu angle.[12] This indicates that the correlation of J values with Cu–O–Cu angles in hydroxo-bridged copper(II) dimers as postulated by Hatfield and co-workers[12] can be successfully applied to the methoxy-bridged system. The large antiferromagnetic intratetramer interaction observed in the present work could be attributed to the good overlap between the square-planar copper(II) magnetic orbitals *via* the bridging oxygen atoms.

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Received 6*th February* 1996; *Communication* 6/00867D