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Different Acetate Bonding Modes and the Smallest Monoatomic Cu–O–Cu Bridge Angle in $[Cu_3(O_2CMe)_4(H_2O)(bipy)_3][PF_6]_2$ (bipy = 2,2′-bipyridine)

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The reaction of 2,2′-bipyridine (bipy) with $[Cu_2(O_2CMe)_4(H_2O)_2]$ in ethanol followed by NH_4PF_6 yields an unique trinuclear copper(II) species, $[Cu_3(O_2CMe)_4(H_2O)(bipy)_3][PF_6]_2$, the crystal structure of which shows the smallest monoatomic acetate bridge Cu–O–Cu angle of 92.9(1)° and four different acetate co-ordination modes; in methanol glass at 77 K it exhibits an X-band ESR spectrum characteristic of a strongly coupled dicopper(II) unit and a normal copper(II) centre.

Christou *et al.*[1] have recently shown that the dimeric core of copper(II) acetate undergoes a facile conversion on reaction with 2,2′-bipyridine (bipy) to form weakly coupled ferromagnetic dicopper(II) complexes $[Cu_2(O_2CMe)_3(bipy)_2]ClO_4$ and $[Cu_2(OH)(O_2CMe)(H_2O)(bipy)_2][ClO_4]_2$. In this communication we present an unprecedented type of core conversion in which an unique higher-nuclearity copper(II) complex, $[Cu_3(O_2CMe)_4(H_2O)(bipy)_3][PF_6]_2$ **1** is formed† from a reaction of copper(II) acetate with bipy. Complex **1** exemplifies rare acetato bridging modes of bonding.

Complex **1** was characterised by determination of its crystal structure (Fig. 1).‡,[2] In the trinuclear unit the geometry around the copper(II) centres is tetragonally elongated square pyramidal with a 4 + 1 $CuN_2O_2\cdots O$ chromophore. The Cu(1)Cu(2) unit is bridged by three acetato ligands displaying different bridging modes. Atom Cu(3) is bonded to an unidentate and a bridging acetato ligand. The Cu(1)···Cu(2), Cu(1)···Cu(3) and Cu(2)···Cu(3) distances are 3.196(1), 6.277(1) and 4.568(1) Å, respectively. It appears from the structural data that atom Cu(3) exists as an isolated paramagnetic centre weakly interacting with the strongly coupled Cu(1)Cu(2) moiety. The terminal O_2CMe ligand is involved in a strong intramolecular hydrogen-bonding interaction with the aqua ligand [O(8)···O(9) 2.505(7) Å]. The trinuclear units are linked *via* intermolecular hydrogen bonds involving bridging acetato-*O* and the aqua ligands into a one-dimensional chain polymeric species [O(4)···O(9′) 2.619(5), Cu(1)–Cu(3′) 5.620(1) Å].

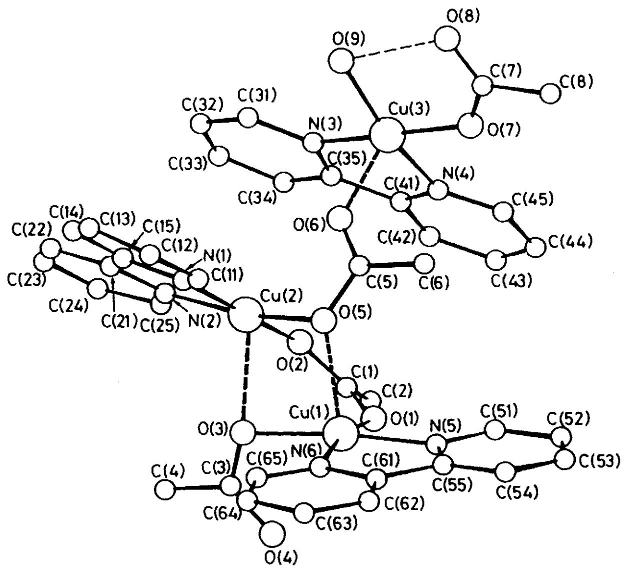

Fig. 1 A view of the trinuclear complex cation $[Cu_3(O_2CMe)_4(H_2O)(bipy)_3]^{2+}$. Selected distances (Å) and angles (°): Cu(1)–O(1) 1.946(3), Cu(1)–O(3) 1.994(4), Cu(1)–O(5) 2.276(2), Cu(1)–N(5) 1.994(5), Cu(1)–N(6) 1.985(4), Cu(2)–O(2) 1.953(3), Cu(2)–O(3) 2.400(3), Cu(2)–O(5) 1.965(4), Cu(2)–N(1) 1.985(3), Cu(2)–N(2) 2.001(4), Cu(3)–O(6) 2.258(4), Cu(3)–O(7) 1.938(4), Cu(3)–O(9) 1.971(3), Cu(3)–N(3) 1.980(4) and Cu(3)–N(4) 2.004(3), Cu(1)–O(3)–Cu(2) 92.9(1), Cu(1)–O(5)–Cu(2) 97.5(1)

An interesting structural feature is the narrow Cu(1)–O(3)–Cu(2) and Cu(1)–O(5)–Cu(2) angles. The former [92.9(1)°] is the smallest known[1,3–7] in monoatomic bridged dicopper(II) complexes. The bridging angles (φ) are in the region of those

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† The complex $[Cu_2(O_2CMe)_4(H_2O)_2]$ (0.20 g, 0.5 mmol) was treated with a magnetically stirred ethanol (10 cm^3) solution of bipy (0.16 g, 1.0 mmol). The resulting mixture was heated to 50 °C for 5 min with stirring, followed by cooling to ambient temperature. The salt NH_4PF_6 (0.16 g, 1.0 mmol) was then added. The resulting solution was filtered and the filtrate kept for 12 h at 25 °C. A sky-blue crystalline solid,[1] formulated as $[Cu_2(O_2CMe)_3(bipy)_2]PF_6$ from the elemental analysis and isolated as a major product in 50% yield, was filtered off and the filtrate allowed slowly to evaporate. Dark blue rectangular crystals of **1** were obtained in *ca.* 10% yield. They were washed with cold EtOH–water (1:1) and dried *in vacuo* over P_4O_{10} [Found (Calc.): C, 37.2 (37.9); H, 3.3 (3.2); N, 6.4 (7.0)%].

‡ *Crystal data.* $C_{38}H_{38}Cu_3F_{12}N_6O_9P_2$, $M = 1203.3$, triclinic, space group $P\bar{1}$, $a = 11.529(1)$, $b = 12.121(2)$, $c = 17.153(2)$ Å, $\alpha = 82.01(1)$, $\beta = 79.42(1)$, $\gamma = 89.62(1)°$, $U = 2332.9(5)$ Å^3, $Z = 2$, $D_c = 1.71$ g cm^{-3}, $T = 290$ K, $4 \leqslant 2\theta \leqslant 50°$, $\mu = 15.3$ cm^{-1}, $F(000) = 1210$, $R(R') = 0.0577$ (0.0638) for 4791 reflections with $I > 3\sigma(I)$, weighting scheme $w = 1/[\sigma^2|F_o| + 0.007\,483|F_o|^2]$. Intensity data, collected on an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, λ = 0.7107 Å), were corrected for Lorentz, polarization and absorption effects. The structure was solved and refined by use of the SHELX 76 program[2a] with Fourier syntheses and full-matrix least squares. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

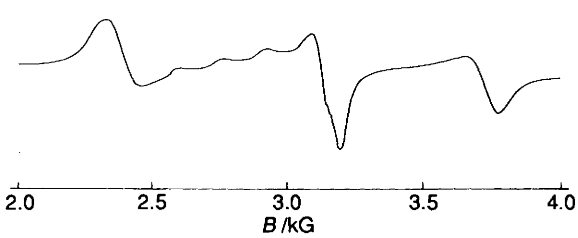

Fig. 2 The ESR spectrum of complex **1** in methanol glass at 77 K (microwave frequency 9.05 GHz, microwave power 2 mW, modulation frequency 100 kHz and modulation amplitude 4 × 1 G on a Varian-E-line Century series X-band spectrometer)

expected[8,9] for ferromagnetic coupling. The three-atom acetato bridge may, however, provide[9,10] a superexchange pathway for an antiferromagnetic coupling.

The ESR spectrum of complex **1**, recorded at X-band in frozen methanol, exhibits well resolved resonances which correspond to $\Delta M_s = \pm 1$ giving $g_{\parallel}$ and $g_{\perp}$ values of 2.28 and 2.06, respectively (Fig. 2, $A_{\parallel} = 160$, $A_{\perp} = 12$ G; G = 10^{-4} T). That $g_{\parallel} > g_{\perp}$ is consistent with the X-ray structure. The polycrystalline ESR spectra at 298 and 77 K display an isotropic signal with g_{av} 2.21. The ESR spectrum in frozen methanol also shows two additional isotropic signals near 2390 and 3730 G with g 2.70 and 1.74, respectively (Fig. 2). The significantly high intensity and large separation of these two signals indicate[11] the presence of a strongly coupled dimeric unit in the trinuclear complex. Preliminary results showing a μ_{eff} per Cu value of 2.02 at 297 K suggest a ferromagnetic coupling in the Cu(1)Cu(2) moiety. A detailed ESR analysis and variable-temperature magnetic susceptibility measurements on complex **1** are currently in progress.

Acknowledgements

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