Crystal Structures, Spectral and Magnetic Properties of (μ-Hydroxo)(μ-acetato)dicopper(II) Complexes containing Chelating Amines†

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The reaction of $[Cu_2(O_2CMe)_4(H_2O)_2]$ with *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen) in ethanol yielded the dicopper(II) complex $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1**. A similar reaction with *N,N*-dimethylethane-1,2-diamine (dmen) afforded a crystalline product **2** in which two dicopper(II) complexes, $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$ **2a** and $[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2$ **2b**, are cocrystallized in a 1:1 molar ratio along with $2NaClO_4$. The crystal structures of **1** and **2** have been determined. The complexes have an asymmetrically dibridged $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core. The co-ordination geometry of the metal is square planar (CuO_2N_2). The copper atoms in **2b** have a square-pyramidal CuO_3N_2 co-ordination sphere. The Cu ··· Cu distances and Cu–O–Cu angles in **1**, **2a** and **2b** are 3.339(2), 3.368(3), 3.395(7) Å, 120.1(2), 116.4(1) and 123.6(2)°, respectively. Complex **1** exhibits an axial ESR spectrum in a methanol glass giving $g_{\parallel} = 2.26$ ($A_{\parallel} = 164 \times 10^{-4}$ cm^{-1}) and $g_{\perp} = 2.04$. The ESR spectra obtained from the bulk material of the dmen product are indicative of the presence of two dimers, *viz.* complex **2a** ($g_{\parallel} = 2.25$, $A_{\parallel} = 165 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 2.03$) and **2b** ($g_{\parallel} = 2.19$, $A_{\parallel} = 184 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 2.0$). Variable-temperature magnetic susceptibility measurements on these complexes show an intramolecular antiferromagnetic coupling in the dimeric core. The fitting parameters are $J = -27.8$ cm^{-1}, $g = 2.1$ for complex **1** and $J = -10.1$ cm^{-1}, $g = 2.0$ for **2**. The magnetostructural properties of the complexes are discussed. There is a linear correlation of the $-2J$ values with the Cu ··· Cu distances among dibridged complexes having square-planar copper(II) centres.

Among several types of dinuclear copper(II) systems, antiferromagnetically coupled tetra-μ-carboxylatodicopper(II) complexes have been extensively studied.[1,2] The symmetrically dibridged species with a $[Cu_2(\mu\text{-}X)_2]^{2+}$ core (X = OH, OR or Cl) form another class of complexes[1,3,4] in which the nature and extent of spin–spin interactions depend on several factors like the Cu ··· Cu separation, Cu–X–Cu angle (φ), bridge type and the dihedral angle between the two copper-containing square planes. The magnetostructural relationship observed by Hatfield and Hodgson[3] for di-μ-hydroxo complexes shows a φ-angle dependence of the $2J$ value.

Combination of a three-atom carboxylato and a monoatomic hydroxo/alkoxo bridge has led to the emergence of a relatively new class of asymmetrically dibridged dicopper(II) complexes with a $[Cu_2(\mu\text{-}OR/OH)(\mu\text{-}O_2CR)]^{2+}$ core.[5–10] The magnetostructural properties of these complexes are of immense importance considering their relevance to the type-3 active centres, *viz.* oxyhaemocyanin which has a strong antiferromagnetically coupled and essentially diamagnetic asymmetrically dibridged $[Cu_2(\mu\text{-}OR)(\mu\text{-}O_2)]^{+}$ core.[11] In model dicopper(II) complexes the presence of a three-atom bridging ligand in addition to a monoatomic one is expected to give a Cu ··· Cu separation of ≈3.5 Å and a larger Cu–O–Cu angle suitable for promoting a strong antiferromagnetic interaction between two copper(II) centres. A question of interest is the effect of two different bridging ligands, providing two superexchange pathways, on the magnetostructural properties of the dimeric core.

Multidentate ligands with a potential alkoxo or phenoxo binding site are known[5–10] to stabilize the $[Cu_2(\mu\text{-}OR)(\mu\text{-}O_2CR)]^{2+}$ core. The chemistry of analogous hydroxo-bridged complexes is presently unknown. Recently, complexes containing a tribridged $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(\mu\text{-}H_2O/MeOH)]^{2+}$ core have been reported.[12–14] However, the additional bridge, despite being weak, exhibits a profound effect on the co-ordination geometry of the metal and the important structural parameters like the Cu ··· Cu distance and Cu–OH–Cu angle. The asymmetrically dibridged $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core can be stabilized with chelating diamines at the terminal positions. The reaction of copper(II) acetate hydrate with *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen) after addition of $NaClO_4$ affords $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1**. A similar reaction with *N,N*-dimethylethane-1,2-diamine (dmen) has led to the formation of two dicopper(II) complexes, $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$ **2a** and $[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2$ **2b**, which cocrystallize in a 1:1 molar proportion in a single crystal of the dmen product **2**. In this paper we report the crystal structures, ESR spectral and magnetic properties of complexes **1** and **2**.

Experimental

All reagents and chemicals were purchased from commercial sources and used as received.

Preparations.—$[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1**. An ethanolic solution (10 cm^3) of copper(II) acetate hydrate (0.5 mmol) was treated with tmen (1.0 mmol) with stirring for 10 min at 50 °C. After cooling to ambient temperature, an aqueous solution (10 cm^3) of $NaClO_4$ was added. Bluish violet rectangular crystalline blocks of complex **1** were obtained in ≈50% yield by slow evaporation of the solution at 25 °C for several days. The crystals were separated, washed with cold water–ethanol (1:1 v/v) and dried *in vacuo* over P_4O_{10} (Found: C, 26.7; H, 6.0; N, 9.1. $C_{14}H_{36}Cl_2Cu_2N_4O_{11}$ requires C, 26.5; H, 5.5; N, 8.8%). Single crystals suitable for X-ray studies were

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† *Supplementary data available* (No. SUP 56951, 11 pp.): magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

obtained on slow evaporation of a solution of complex **1** in dichloromethane–light petroleum (b.p. 40–60 °C).

$[Cu_2(OH)(O_2CMe)(H_2O)(dmen)_2][ClO_4]_2$ **2**. The purplish blue dmen product was prepared in ≈60% yield by following a similar procedure to that described for complex **1** (Found: C, 20.2; H, 5.1; N, 9.7. $C_{10}H_{30}Cl_2Cu_2N_4O_{12}$ requires C, 20.1; H, 5.0; N, 9.4%). Square single crystals obtained from the solution were found to contain one lattice $NaClO_4$ per dimeric unit. Complex **2** was formulated as $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$–$[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2 \cdot 2NaClO_4$ from its crystal structure.

Physical Measurements.—Elemental analyses were done using a Heraeus CHN-O Rapid instrument. Electronic, ESR and infrared spectra were recorded on Hitachi U-3400, Varian E-109 X-band and BIO-RAD FTS-7 spectrometers, respectively. Variable-temperature (45–300 K) magnetic susceptibility data were obtained on polycrystalline samples from a Faraday-type magnetometer equipped with a closed-cycle cryostat (Air Products); $Hg[Co(SCN)_4]$ was used as a calibrant. Experimental susceptibility data were corrected for diamagnetic contributions and for temperature-independent paramagnetism ($N_\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1} per dimer). The molar magnetic susceptibilities were fitted to a Bleaney–Bowers expression[15] by means of a least-squares-fitting computer program.

Crystal Structure Determinations.—*Crystal data.* $C_{14}H_{36}Cl_2Cu_2N_4O_{11}$ **1**, $M = 634.5$, orthorhombic, space group *Pbca* (no. 61), $a = 13.214(3)$, $b = 15.266(2)$, $c = 26.283(6)$ Å, $U = 5302(2)$ Å^3, $F(000) = 2624$, $Z = 8$, $D_c = 1.59$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 18.66 cm^{-1}, $T = 290$ K, transmission coefficients 0.77–1.00.

$C_{20}H_{60}Cl_6Cu_4N_8Na_2O_{32}$ **2**, $M = 1437.6$, orthorhombic, space group $Pmc2_1$ (no. 26), $a = 22.726(6)$, $b = 11.784(4)$; $c = 9.655(3)$ Å, $U = 2586(1)$ Å^3, $F(000) = 1464$, $Z = 2$, $D_c = 1.85$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.5418$ Å, μ(Cu-Kα) = 58.06 cm^{-1}, $T = 290$ K, transmission coefficients 0.90–0.98.

Data collection and processing. A bluish violet rectangular shaped crystal of complex **1** having approximate dimensions 0.4 × 0.4 × 0.2 mm was mounted on a glass fibre. The unit-cell parameters were obtained by least-squares treatment of 25 reflections in the range $20 < 2\theta < 28°$. Intensity data in the ranges $0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 31$ within $4 \leqslant 2\theta \leqslant 50°$ were measured using a ω-scan mode on an Enraf–Nonius CAD4 four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation. The data, collected with a scan width $0.60 + 0.35 \tan\theta°$ using a prescan speed of 5.5° min^{-1}, were corrected for Lorentz and polarization effects and for absorption.[16] Of 4651 unique data, 2788 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement.

A purplish blue crystal of the dmen product of approximate dimensions 0.4 × 0.4 × 0.4 mm was mounted on a glass fibre. Unit-cell dimensions were determined from setting angles of 25 reflections in the range $40 < 2\theta < 70°$ using graphite-monochromated Cu-Kα radiation. Intensity data were collected in the range 2θ 2–150° with a pre-scan speed of 5.5° min^{-1} and a scan width $0.90 + 0.15 \tan\theta°$ for reflections with $0 \leqslant h \leqslant 23$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 10$. The final scan was made at a speed calculated to satisfy the condition $\sigma(I)/I \leqslant 0.03$. The data were corrected as for **1**. 1720 Reflections, out of 2727 unique data, with $I > 3\sigma(I)$ were used for structure solution and least-squares refinement.

Structure solution and refinement. The structure of complex **1** was solved by the Patterson method which revealed the positions of two copper atoms in the crystallographic asymmetric unit. The remaining atoms were located in successive Fourier difference maps and refined by the least-squares technique. One oxygen atom of a perchlorate anion was found to be positionally disordered and two peaks were refined for it with a site occupancy factor (s.o.f.) of 0.5. Barring this disordered atom, remaining atoms were refined anisotropically.

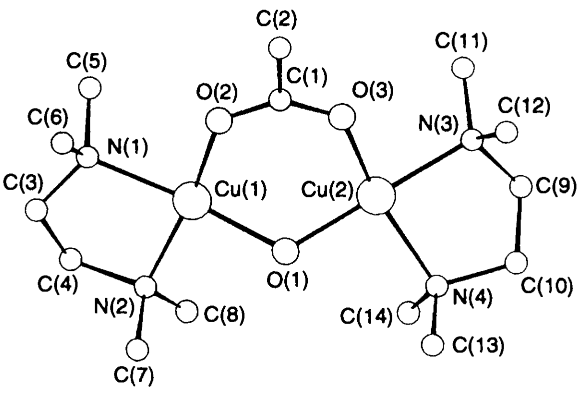


Fig. 1 A perspective view of the complex cation in $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1** showing the atom-numbering scheme

The final full-matrix least-squares refinement converged to $R = 0.067$ and $R' = 0.078$ with a weighting scheme $w = 1.0/(\sigma^2|F_o| + 0.000\,792|F_o|^2)$ using 297 parameters. The highest peak in the final Fourier difference map was of 0.9 e Å^{-3}. All calculations were carried out using a VAX88 computer and the SHELX system of programs[17] at the computer centre of the Indian Institute of Science. Atomic scattering factors were taken from ref. 18.

The metal atom positions in complex **2** were obtained from a Patterson map and the remaining atoms were located from Fourier difference maps. The observation of sodium perchlorate salt in the crystallographic asymmetric unit was not unusual as it was present in the solution used for growing single crystals of complex **2**. The structure was refined to $R = 0.088$ and $R' = 0.090$ with $w = [\sigma^2|F_o|]^{-1}$ in the final full-matrix least-squares refinement with all atoms anisotropic and 348 parameters. The crystal structure showed the presence of $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$ **2a** and $[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2$ **2b** in a 1:1 molar ratio and lattice $NaClO_4$. The final Fourier difference map showed two peaks of 1.1 e Å^{-3} situated at a distance of 1.3 Å from O(4) and 0.97 Å from C(7). The appearance of these peaks near the special positions indicated crystal-packing disorder resulting from the structural similarity of the two cationic complexes. These peaks, which on refinement as oxygen or carbon showed very high thermal parameters, were excluded from the final structural model. The higher values of the residuals and the thermal disorders observed for several atoms could be related to the crystal-packing disorder. The structure on refinement in the space group *Pma*2 or *Pmma* gave residuals 2–3% higher than those observed in $Pmc2_1$. Some bond distances and angles in the structure of **2** showed large deviations from the expected values with the other space groups. The observation of two different dimeric units in **2** in $Pmc2_1$ is in agreement with the ESR results (see below).

The positional parameters of the complexes are listed in Tables 1 and 2. No attempts were made to locate the hydrogen atoms. The perspective views of the molecules were obtained using PLUTO programs.[19]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

Crystal Structures.—A perspective view of the complex cation in $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1** is shown in Fig. 1. Selected bond distances and angles are given in Table 3. The structure consists of a discrete dimeric complex and two perchlorate anions in the crystallographic asymmetric unit. The complex has a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CR)]^{2+}$ core and terminal chelating tmen ligands. The co-ordination geometry of the copper(II) centres is essentially square planar. The Cu(1) and

Table 1 Fractional atomic coordinates for $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ with their estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.2539(1)	0.1504(1)	0.1299(0.4)
Cu(2)	0.5064(1)	0.1590(1)	0.1316(0.4)
O(1)	0.3829(3)	0.0921(3)	0.1347(2)
O(2)	0.2907(4)	0.2481(4)	0.1732(2)
O(3)	0.4589(4)	0.2551(4)	0.1733(3)
C(1)	0.3737(6)	0.2746(5)	0.1912(3)
C(2)	0.3715(6)	0.3382(6)	0.2351(4)
N(1)	0.1111(5)	0.2010(6)	0.1302(3)
C(3)	0.0423(8)	0.1366(8)	0.1068(5)
C(4)	0.0892(9)	0.0786(10)	0.0722(6)
N(2)	0.1916(5)	0.0472(4)	0.0922(3)
C(5)	0.1120(9)	0.2862(8)	0.0976(8)
C(6)	0.0755(9)	0.2184(11)	0.1834(6)
C(7)	0.1811(13)	−0.0287(7)	0.1267(5)
C(8)	0.2490(10)	0.0183(9)	0.0464(5)
N(3)	0.6365(6)	0.2287(6)	0.1244(3)
C(9)	0.7033(8)	0.1726(8)	0.0903(5)
C(10)	0.6985(7)	0.0814(8)	0.1040(5)
N(4)	0.5893(5)	0.0522(5)	0.1095(3)
C(11)	0.6225(8)	0.3161(8)	0.0997(6)
C(12)	0.6836(9)	0.2388(9)	0.1759(5)
C(13)	0.5838(9)	−0.0192(7)	0.1477(4)
C(14)	0.5510(8)	0.0191(8)	0.0585(4)
Cl(1)	0.6157(2)	−0.2430(2)	−0.0155(1)
Cl(2)	0.1286(2)	0.5167(2)	0.2650(1)
O(11)	0.6343(7)	−0.1969(6)	0.0281(4)
O(12)	0.6036(7)	−0.3304(5)	−0.0050(4)
O(13)	0.5331(8)	−0.2073(8)	−0.0397(5)
O(14)	0.7006(8)	−0.2332(7)	−0.0471(4)
O(21)	0.1238(6)	0.4520(10)	0.2266(6)
O(22)	0.1253(10)	0.4834(10)	0.3127(5)
O(23)	0.2099(13)	0.5681(11)	0.2573(7)
O(24)*	0.033(2)	0.548(2)	0.2473(10)
O(24′)*	0.079(2)	0.588(2)	0.2545(13)

* Refined with a site occupancy factor of 0.5.

Cu(2) atoms are 0.016(1) and 0.012(1) Å out of the respective O(1),O(2),N(1),N(2) and O(1),O(3),N(3),N(4) least-squares planes. The Cu(1)···Cu(2) separation is 3.339(2) Å and the Cu(1)–O(1)–Cu(2) angle is 120.1(2)°. The dihedral angle between the two CuN_2O_2 planes is 32.2(2)°. While the Cu–N distances are marginally longer than the Cu–O, Cu–O(hydroxo) and Cu–O(acetato) are essentially the same.

The crystal structure of the dmen product shows the presence of two discrete dicopper(II) complexes $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(dmen)_2][ClO_4]_2$ **2a** and $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2$ **2b** in a 1:1 molar ratio along with two $NaClO_4$. Perspective views of the complex cations are shown in Fig. 2. Selected bond distances and angles are listed in Table 4. The complexes have a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core. The Cu(1)···Cu(1′) distance is 3.368(3) Å and the Cu(1)–O(1)–Cu(1′) angle is 116.4(1)°. The co-ordination geometry of Cu(1) is essentially square planar. The metal is 0.001(1) Å out of the O(1),O(2),N(1),N(2) least-squares plane. The dihedral angle between the two square planes in **2a** is 18.1(5)°. A smaller folding of the copper planes compared to complex **1** has resulted in an increase in the Cu···Cu separation.

The co-ordination geometry of Cu(2) in complex **2b** is square pyramidal with the metal 0.004(4) Å out of the least-squares plane of O(3),O(4),N(3) and N(4). The Cu(2)···Cu(2′) distance is 3.395(7) Å and the Cu(2)–O(3)–Cu(2′) angle 123.6(2)°. The dihedral angle between the two square planes is 45.5(5)°. The observed variation of the dihedral angles in complexes **2a** and **2b** compared to that in **1** could be related to the interaction of the bridging hydroxide ligands with the lattice sodium ions and the difference in the co-ordination geometries.

Table 2 Fractional atomic coordinates for $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$–$[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2\cdot 2NaClO_4$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.4259(1)	0.2502(3)	0.1082
Cu(2)	0.0747(2)	0.2504(5)	0.4128(4)
O(1)	0.5	0.316(2)	0.181(3)
O(2)	0.4525(6)	0.0992(11)	0.109(2)
C(1)	0.5	0.051(2)	0.136(4)
C(2)	0.5	−0.074(2)	0.164(4)
N(1)	0.3823(7)	0.392(2)	0.127(2)
C(3)	0.327(2)	0.374(2)	0.054(3)
C(4)	0.317(2)	0.286(3)	−0.018(3)
N(2)	0.3450(14)	0.197(2)	0.012(3)
C(5)	0.3133(9)	0.142(2)	0.122(3)
C(6)	0.365(2)	0.112(2)	−0.114(3)
O(3)	0.0	0.308(2)	0.350(2)
O(4)	0.0473(11)	0.083(2)	0.386(3)
C(7)	0.0	0.052(4)	0.403(4)
C(8)	0.0001(9)	−0.099(4)	0.422(3)
N(3)	0.1168(10)	0.407(2)	0.406(2)
C(9)	0.1800(8)	0.391(2)	0.440(3)
C(10)	0.1786(10)	0.301(2)	0.573(2)
N(4)	0.1453(7)	0.186(2)	0.513(2)
C(11)	0.184(2)	0.110(2)	0.427(4)
C(12)	0.1315(11)	0.123(3)	0.636(3)
O(5)	0.0745(6)	0.252(2)	0.609(2)
Na(1)	0.0	0.335(2)	0.079(2)
Na(2)	0.5	0.3239(11)	0.431(2)
Cl(1)	0.0	0.4196(10)	0.7072(14)
O(11)	0.0	0.292(3)	0.676(5)
O(12)	0.0	0.430(4)	0.859(4)
O(13)	−0.0503(13)	0.488(2)	0.665(2)
Cl(2)	0.1408(4)	0.2668(9)	0.0348(11)
O(21)	0.1809(12)	0.3270(2)	0.103(3)
O(22)	0.1712(11)	0.171(3)	−0.003(4)
O(23)	0.105(2)	0.211(3)	0.138(4)
O(24)	0.120(2)	0.312(2)	−0.081(3)
Cl(3)	0.5	0.5859(7)	0.3055(10)
O(31)	0.5	0.566(2)	0.158(2)
O(32)	0.4498(7)	0.542(2)	0.373(2)
O(33)	0.5	0.690(2)	0.344(3)
Cl(4)	0.3597(3)	0.2681(6)	0.4760(7)
O(41)	0.3884(13)	0.336(2)	0.581(3)
O(42)	0.4083(7)	0.244(2)	0.398(2)
O(43)	0.3359(11)	0.173(2)	0.532(3)
O(44)	0.3229(9)	0.350(2)	0.400(2)

Table 3 Selected bond distances (Å) and angles (°) in $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$ **1** with e.s.d.s in parentheses

Cu(1)···Cu(2)	3.339(2)	Cu(2)–O(1)	1.927(4)
Cu(1)–O(1)	1.927(4)	Cu(2)–O(3)	1.936(7)
Cu(1)–O(2)	1.938(6)	Cu(2)–N(3)	2.031(8)
Cu(1)–N(1)	2.039(7)	Cu(2)–N(4)	2.048(8)
Cu(1)–N(2)	2.035(7)		
Cu(1)–O(1)–Cu(2)	120.1(2)	O(1)–Cu(2)–O(3)	95.9(2)
O(1)–Cu(1)–O(2)	95.5(2)	O(1)–Cu(2)–N(3)	177.1(3)
O(1)–Cu(1)–N(1)	173.4(3)	O(1)–Cu(2)–N(4)	92.5(3)
O(1)–Cu(1)–N(2)	91.8(2)	O(3)–Cu(2)–N(3)	86.0(3)
O(2)–Cu(1)–N(1)	86.5(3)	O(3)–Cu(2)–N(4)	159.6(3)
O(2)–Cu(1)–N(2)	169.5(3)	N(3)–Cu(2)–N(4)	86.4(3)
N(1)–Cu(1)–N(2)	85.5(3)	O(2)–C(1)–O(3)	124.3(8)

The formation of a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core from $[Cu_2(\mu\text{-}O_2CMe)_4(H_2O)_2]$ involves an opening of the tetra-μ-acetato cage [equation (1), L = tmen or dmen]. While

$$[Cu_2(O_2CMe)_4(H_2O)_2] + 2L + 2NaClO_4 \xrightarrow[H_2O]{EtOH} [Cu_2(OH)(O_2CMe)L_2][ClO_4]_2 + 2NaO_2CMe + MeCO_2H + H_2O \quad (1)$$

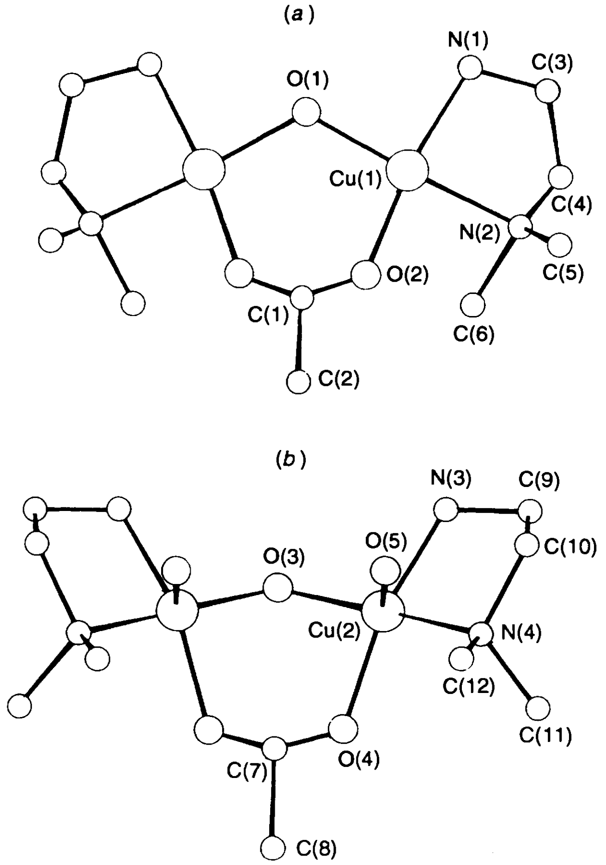


Fig. 2 Perspective views of the cationic complexes $[Cu_2(OH)(O_2CMe)(dmen)_2]^{2+}$ (*a*) and $[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2]^{2+}$ (*b*) showing the atom labelling schemes

Table 4 Selected bond distances (Å) and angles (°) in complex **2** with their e.s.d.s in parentheses

Cu(1) ··· Cu(1′)	3.368(3)	Cu(2) ··· Cu(2′)	3.395(7)
Cu(1)–O(1)	1.981(14)	Cu(2)–O(3)	1.926(12)
Cu(1)–O(2)	1.879(14)	Cu(2)–O(4)	2.08(2)
Cu(1)–N(1)	1.95(2)	Cu(2)–N(3)	2.08(2)
Cu(1)–N(2)	2.15(3)	Cu(2)–N(4)	2.02(2)
Na(2) ··· O(1)	2.42(3)	Cu(2)–O(5)	1.89(2)
Na(1) ··· O(3)	2.64(3)		
Cu(1)–O(1)–Cu(1′)	116.4(1)	Cu(2)–O(3)–Cu(2′)	123.6(2)
O(1)–Cu(1)–O(2)	95.5(4)	O(3)–Cu(2)–O(4)	91.7(7)
O(1)–Cu(1)–N(1)	93.7(6)	O(3)–Cu(2)–O(5)	108.0(5)
O(1)–Cu(1)–N(2)	172.7(8)	O(3)–Cu(2)–N(3)	94.8(6)
O(2)–Cu(1)–N(1)	166.9(7)	O(3)–Cu(2)–N(4)	169.2(6)
N(1)–Cu(1)–N(2)	82(1)	O(4)–Cu(2)–O(5)	98(1)
O(2)–C(1)–O(2′)	119.9(9)	O(4)–Cu(2)–N(3)	167(1)
Cu(1)–O(1) ··· Na(2)	111.5(1)	O(4)–Cu(2)–N(4)	86.6(9)
Cu(2)–O(3) ··· Na(1)	110.8(1)	O(5)–Cu(2)–N(3)	91.2(9)
N(3)–Cu(2)–N(4)	89.1(8)	O(5)–Cu(2)–N(4)	61.8(8)
		O(4)–C(7)–O(4′)	139(2)

copper(II) acetate is known[1,2] to form diaxial adducts with unidentate ligands, earlier attempts to incorporate a bidentate ligand at the axial and/or equatorial sites of the core led to the conversion of the cage structure into a new core with a reduced number of acetate ligands.[10,12,20-22]

Infrared and Visible Spectra.—The IR spectra of the tmen and dmen complexes show medium-intensity ν(OH) stretching vibrations of the hydroxo bridge at 3460 and 3350 cm^{-1}, respectively. The ν(NH) vibration of the dmen complex occurs at 3300 cm^{-1}. For this complex a broad band centred at *ca.* 3560 cm^{-1} is due to the bound aqua ligand. An intense band at 1567 cm^{-1} for complex **1** and at 1585 cm^{-1} for **2** is assignable to the ν_{asym}(OCO) vibration of the bridging acetate. The perchlorate anions in the complexes display a very strong band at ≈1100 cm^{-1}. The visible spectra of the complexes in methanol exhibit a broad and featureless d–d band at 643 nm (ε 180 dm^3 mol^{-1} cm^{-1}) for complex **1** and at 566 nm (ε 160 dm^3 mol^{-1} cm^{-1}) for **2**.

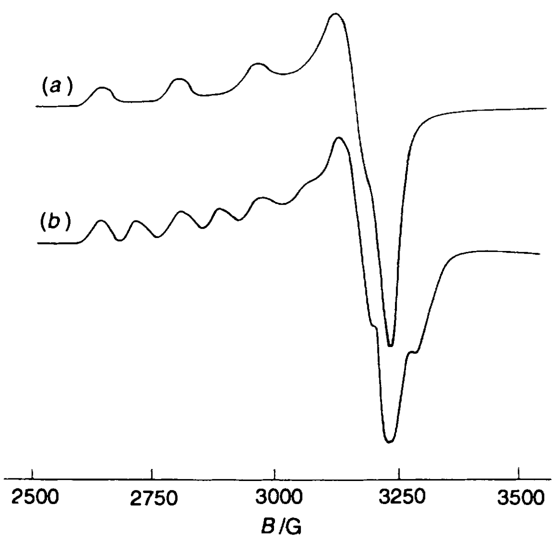


Fig. 3 The X-band ESR spectra of complexes **1** (*a*) and **2** (*b*) in methanol glasses at 77 K; G = 10^{-4} T

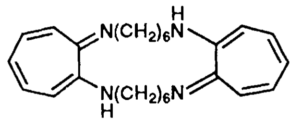
Electron Spin Resonance.—While the room-temperature polycrystalline X-band ESR spectrum of complex **1** shows an isotropic signal giving g_{av} 2.15, **2** displays only the $g_{\perp}$ component (2.07) of an axial spectrum in the polycrystalline phase. The ESR spectrum of **1** in a methanol glass displays axial signals giving $g_{\parallel}$ = 2.26 ($A_{\parallel}$ = 164 × 10^{-4} cm^{-1}) and $g_{\perp}$ = 2.04 [Fig. 3(*a*)]. The spectrum recorded for the dmen product in a methanol glass exhibits well resolved axial signals indicating the presence of two different complexes in the bulk material [Fig. 3(*b*)]. A comparison of the spectral data with those of the tmen product suggests that the signals corresponding to $g_{\parallel}$ = 2.25 ($A_{\parallel}$ = 165 × 10^{-4} cm^{-1}) and $g_{\perp}$ = 2.03 are due to complex **2a** which is structurally similar to **1**. The other axial spectrum, giving $g_{\parallel}$ = 2.19 ($A_{\parallel}$ = 184 × 10^{-4} cm^{-1}) and $g_{\perp}$ = 2.0, is assignable to complex **2b** having square-pyramidal copper(II) centres. The ESR spectral results obtained from the bulk material of the dmen product are in agreement with its single-crystal structure.

Magnetic Behaviour.—The magnetic susceptibilities of the complexes **1** and **2** were measured in the temperature range 45–300 K. A theoretical fit of the experimental data to the Bleaney–Bowers susceptibility expression[15] is shown as the solid line in Fig. 4. For complex **1** the μ_{eff} value per copper(II) decreases from 1.74 at 293 K to 1.60 at 47 K. A non-linear least-squares fit of the susceptibility data gave $J = -27.8$ cm^{-1} and g = 2.10. Complex **2** shows a μ_{eff} value of 1.78 at 293 K and 1.70 per Cu at 47 K. The theoretical fitting of the susceptibility data gave $J = -10.1$ cm^{-1} and g = 2.03. The low magnitude of J for complexes **1** and **2** indicates a weak antiferromagnetic interaction in the $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core.

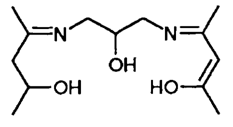
Discussion

The magnetostructural data on (μ-hydroxo/alkoxo)(μ-acetato)-dicopper(II) complexes along with their tribridged analogues are compared in Table 5. Complexes with a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(\mu\text{-}X)]^{2+}$ (X = H_2O or MeOH) core have a

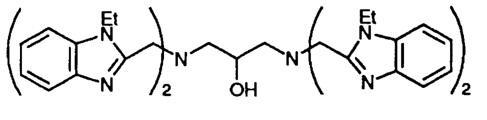
Table 5 Comparison of structural and magnetic parameters of asymmetrically bridged dicopper(II) complexes



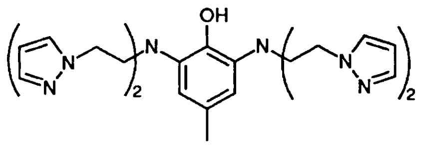
H_2L^1



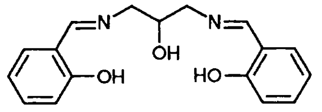
H_3L^2



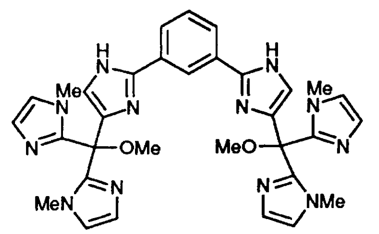
HL^3



HL^4



H_3L^5



L^6

Complex[a]	Cu···Cu/Å	Cu–O–Cu[b]/°	δ[c]/°	$-2J$/cm^{-1}	Ref.
$[Cu_2(\mu\text{-}OR)(\mu\text{-}O_2CMe)]^{2+}$ core					
3 $[Cu_2(OMe)(O_2CMe)L^1]$	3.100(3)	105.7(6)	n.a.	70.8	5
4 $[Cu_2L^2(O_2CMe)]\cdot H_2O$[d]	3.502(2)	133.3(3)	5.4	165.0	6*a*, *b*
5 $[Cu_2L^2(O_2CMe)]$[d]	3.237(1)	114.3(2)	70.8	−37.8	7
6 $[Cu_2L^3(O_2CMe)][ClO_4]_2$[d]	3.459(2)	130.6(5)	n.a.	−24.0	8
7 $[Cu_2L^4(O_2CMe)][ClO_4]_2$[d]	3.562(3)	133.2(7)	n.a.	0	9
8 $[Cu_2L^5(O_2CMe)]$[d]	3.495(3)	134.5(5)	18.7	170	6*b*
$[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core					
1 $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$	3.339(2)	120.1(2)	32.2	55.6	This work
2[e] $[Cu_2(OH)(O_2CMe)(dmen)_2][ClO_4]_2$–	3.368(3)	116.4(1)	18.1	20.2[f]	This work
$[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen)_2][ClO_4]_2\cdot 2NaClO_4$	3.395(7)	123.6(2)	45.5		
$[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(\mu\text{-}OH_2/MeOH)]^{2+}$ core					
9 $[Cu_2(OH)(O_2CMe)(MeOH)L^6][ClO_4]_2\cdot 1.5thf$[g]	3.156(3)	109.3(4)	62.5	−2.6	12
10 $[Cu_2(OH)(O_2CMe)(H_2O)(bipy)_2][ClO_4]_2$[h]	3.035(2)	103.8(2)	61.9	−38.6	13
11 $[Cu_2(OH)(O_2CMe)(H_2O)(phen)_2][NO_3]_2$[i]	3.017(2)	103.4(2)	122.8	−111.0	14

[a] thf = Tetrahydrofuran; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline. [b] Cu–OH/OR–Cu angle. [c] δ = Dihedral angle between two copper planes; n.a. = not available. [d] The bridging alkoxo-oxygen is provided by the multidentate ligand. [e] The product has two complexes in a 1 : 1 ratio. [f] Corresponds to the bulk material. [g] Cu–μ-MeOH 2.59(1) Å. [h] Average Cu–μ-OH_2 2.392(4) Å. [i] Average Cu–μ-OH_2 2.349(4) Å.

ferromagnetically coupled dicopper(II) unit.[12–14] The magnitude of J depends on the Cu···Cu separation and the Cu–O–Cu angle. The weakly bridging ligand X has a profound effect on the dimeric core structure. The complex showing the shortest Cu–X distance has the shortest Cu···Cu separation, the smallest Cu–O–Cu angle and the highest positive J value. The extent of ferromagnetic interaction also depends on the loss of coplanarity of the two copper planes.

The asymmetrically dibridged complexes with a $[Cu_2(\mu\text{-}OR)(\mu\text{-}O_2CMe)]^{2+}$ core, however, do not show any apparent magnetostructural correlations. The metal co-ordination geometry plays a vital role in dictating the superexchange pathway. The trigonal-bipyramidal complex $[Cu_2L^3(O_2CMe)][ClO_4]_2$[8] with a $(d_{z^2})^1$ ground state is ferromagnetic. The complex has a comparable Cu···Cu distance and a Cu–O–Cu angle to those in the antiferromagnetic $[Cu_2L^2(O_2CMe)]\cdot H_2O$.[6] Similarly, the tropocoronand complex $[Cu_2(OMe)(O_2CMe)L^1]$[5] has the shortest Cu···Cu distance and the smallest Cu–O–Cu angle but is antiferromagnetic. The co-ordination geometry of the metal is pseudo-tetrahedral. Again the negligible magnetic interaction in $[Cu_2L^4(O_2CMe)][ClO_4]_2$ has been ascribed[9] to the difference in metal co-ordination geometries, *viz.* tetragonal and trigonal bipyramidal with $(d_{x^2-y^2})^1$ and $(d_{z^2})^1$ ground states. The geometrical differences make the half-filled orbitals unable to interact through the phenolato bridge.

A meaningful comparison of the magnetostructural data can only be made among complexes having an essentially same co-ordination geometry at the metal centres. Hence, four structurally similar complexes, $[Cu_2L^2(O_2CMe)]\cdot H_2O$, $[Cu_2L^2(O_2CMe)]$, $[Cu_2L^5(O_2CMe)]$ and $[Cu_2(OH)(O_2CMe)(tmen)_2][ClO_4]_2$, having square-planar copper(II) centres with a $(d_{x^2-y^2})^1$ ground state, were chosen for magnetostructural correlations. The dmen product is excluded from the correlation since its crystal structure shows the presence of two different dicopper(II) complexes, and significant interactions between the lattice sodium ions and the μ-hydroxo ligands. The nature of superexchange phenomena and the magnitude and sign of J are found to vary with the Cu···Cu distance which primarily depends on the Cu–O–Cu angle (φ) and on the extent of deviation (δ) from coplanarity of the copper(II)-containing square planes. Plots of $-2J$ *versus* Cu···Cu distance, the dihedral angle (δ) between the two copper planes and the Cu–O–Cu bridge angle (φ) are shown in Fig. 5. An excellent linear fit of $-2J$ (singlet–triplet separation) with the Cu···Cu distance is observed. The empirical relationships obtained from the least-squares fit are $d(\text{Cu}\cdots\text{Cu/Å}) = 0.002\,58(J/\text{cm}^{-1}) + 3.28$ and $-2J/\text{cm}^{-1} = 769.6\,d(\text{Cu}\cdots\text{Cu/Å}) - 2523$.

The spin–spin coupling in the asymmetrically dibridged dicopper(II) cores is intrinsically weak. A Cu–O–Cu angle of 120° is expected to make the complexes **1** and **2** strongly antiferromagnetic according to theoretical predictions made by Hoffmann and co-workers[4a] and the magnetostructural correlations proposed by Hatfield and Hodgson and co-

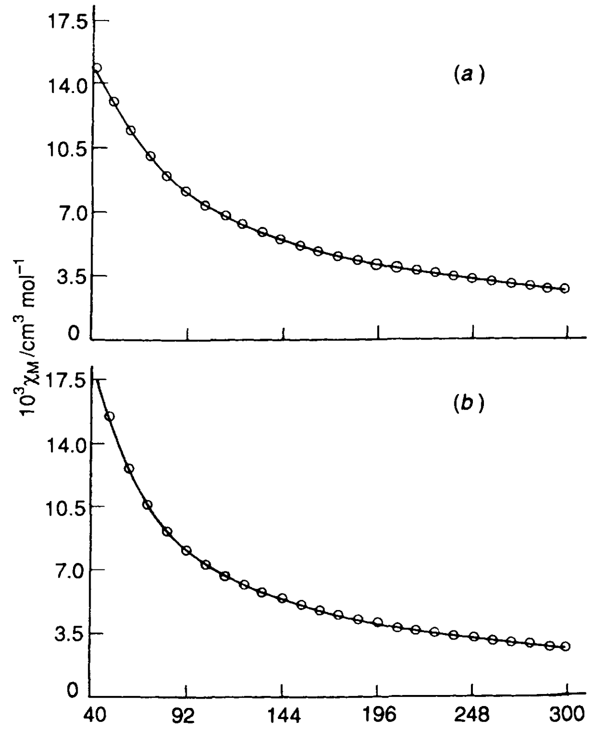
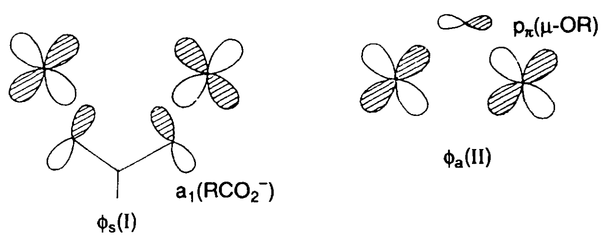


Fig. 4 Plots of molar susceptibility *vs.* temperature for complexes **1** (*a*) and **2** (*b*). The circles are the experimental points and the solid lines are the least-squares fits to the experimental data (fitting parameters are given in the text)



workers[3] on complexes having a $[Cu_2(\mu\text{-}OH)_2]^{2+}$ core. The replacement of a monoatomic bridging hydroxide by a three-atom bridging acetate has a dramatic effect on the superexchange pathways. In the $[Cu_2(\mu\text{-}OH)_2]^{2+}$ core the magnitude of antiferromagnetic interactions has been shown to be proportional to the energy separation between the two highest d-like molecular orbitals, *viz.* symmetric (φ_{sym}) and antisymmetric (φ_{asym}) combinations of magnetic orbitals, irrespective of their energy order. Nishida and co-workers[6] and Reed and co-workers[8] have indicated that in the asymmetrically dibridged core the interactions of RO^- and RCO_2^- with the magnetic orbitals of the metal are 'countercomplementary'. While the φ_{sym} orbital (I) is destabilized by the a_1 orbital of the acetate, the oxygen p_π orbital of the alkoxo bridge destabilizes the φ_{asym} orbital (II). The extent of destabilization is similar in both cases and a net reduction in the magnitude of the antiferromagnetic interaction is observed in these asymmetrically dibridged complexes. Any change in δ and φ angles leading to an increase in the Cu ··· Cu separation is expected to enhance an antiferromagnetic interaction in the dicopper core as evidenced from the linear correlation shown in Fig. 5.

In summary, new asymmetrically dibridged dicopper(II) complexes containing the hitherto unknown $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)]^{2+}$ core have been prepared and structurally characterized. The complexes are weakly antiferromagnetic.

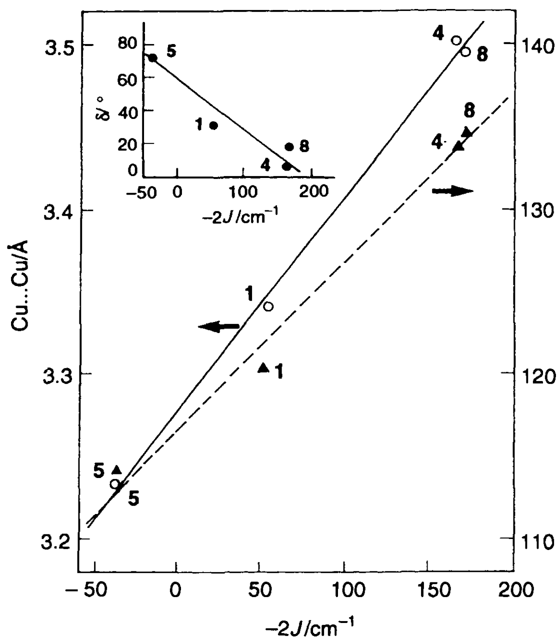


Fig. 5 Linear plots of the $-2J$ value of four structurally similar complexes listed in Table 5 *versus* the Cu ··· Cu distance (solid line) and the Cu–O–Cu angle (dashed line); the inset shows a plot of $-2J$ *versus* the dihedral angle (δ) between two copper-containing square planes

The $-2J$ values of complex **1** and its structural analogues show an excellent linear fit when plotted against the Cu ··· Cu distances. The results are of significance for understanding the magnetostructural relationships in this emerging class of complexes of chemical and biological importance.

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