Fluxionality in polynuclear copper(II) complexes containing aminoalcoholate ligands: syntheses, crystal structures, and ^{1}H nuclear magnetic resonance studies

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Three new polynuclear copper(II) complexes with aminoalcoholate and acetate as ligands, $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2]$ **1**, $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(H_2O)_2]$ **2** and $[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ **3** [Hbdmmp = 2,6-bis(dimethylaminomethyl)-4-methylphenol], have been synthesised and their structures were determined by X-ray diffraction analysis. In the solid state **1** has a one-dimensional structure linked by covalent bonds while **2** has an extended structure linked by both covalent and hydrogen bonds. The solution behaviour of compounds **1** and **3** has been examined by ^{1}H NMR spectroscopy. Compound **1** exists as a mixture of oligomers and undergoes a dynamic process in solution, which can be attributed to the formation of weak intermolecular Cu $\cdots$ O bonds through the acetate ligands. In contrast, no dynamic behaviour of **3** was observed. The magnetic properties of **1** and **3** were examined *via* magnetic susceptibility measurements which showed that both compounds are dominated by antiferromagnetism.

Polynuclear copper(II) complexes are of interest to chemists owing to their various applications in biochemistry, material chemistry and theoretical chemistry.[1] Our interest was prompted by their potential usefulness as precursors for copper-oxide-based superconductors.[2] One such class involves dialkylaminoalcoholate and acetate ligands. Those containing dialkylaminoethanolate ligands can be classified into two major types, type I, $[\{Cu_2(OCH_2CH_2NR_2)_2X_2\}_n]$ (X = halide or pseudo-halide) and type III, $Cu_n(O_2CR)_x(OCH_2CH_2NR_2)_{2n-x}L_y$ (L is a neutral donor such as H_2O or ROH). Many examples of type I compounds are known,[3] but only a few of type II.[4] During our investigation we have discovered two previously unknown dinuclear members of type II, $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2]$ **1** and $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(H_2O)_2]$ **2**. Since amino and carboxylate functional groups are common in copper complexes and copper proteins, we are interested not only in the solid-state structures but also in the solution behaviour of such complexes. Despite the enormous interest in copper chemistry, there is surprisingly little information on solution behaviour of copper(II) complexes obtained by NMR techniques. Previous studies have demonstrated [5] that when an even number of copper(II) ions are involved in a complex and these ions are magnetically coupled it is possible to study their solution behaviour by NMR spectroscopy. We therefore attempted a ^{1}H NMR study on the solution behaviour of **1**. For comparison, the structure and solution behaviour of $[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ **3** [Hbdmmp = 2,6-bis(dimethylaminomethyl)-4-methylphenol] has also been investigated.

Experimental

All reactions were performed under a nitrogen atmosphere using a dual-manifold Schlenk line and Schlenk flasks. Infrared spectra were recorded on a Nicolet FTIR-5DX spectrometer with samples prepared as KBr pellets, ^{1}H NMR on a Bruker AC300 spectrometer and EPR spectra on a Bruker ESP300E spectrometer. Elemental analyses were done at Canadian Microanalytical Service, Ltd., Delta, British Columbia. Solvents were distilled from appropriate drying agents prior to use. The Hbdmmp compound was synthesised *via* a procedure described in the literature.[6] The compounds $Cu(OMe)_2$ and 2-(dimethylamino)ethanol were obtained from Aldrich Chemical Co. A SQUID magnetometer (MPMS, Quantum Design) was used to measure the magnetic susceptibility of complex **1** in the temperature range 2–300 K and an applied magnetic field of 2000 G (0.2 T).

Syntheses

$[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2]$ 1. 2-(Dimethylamino)ethanol (142 mg, 1.592 mmol) and $Cu(OMe)_2$ (100 mg, 0.796 mmol) were mixed in tetrahydrofuran (thf, 15 cm^3) and stirred for 2 h whereupon $Cu(O_2CMe)_2 \cdot H_2O$ (158 mg, 0.796 mmol) was added. The solution was stirred for 3 h and filtered. The filtrate was concentrated *in vacuo* to approximately 7 cm^3 and cooled in a refrigerator to induce crystallisation. Dark blue crystals of $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(thf)]$ (155 mg, 0.314 mmol, yield 31%) were obtained, m.p. 162 °C (Found: C, 33.85; H, 6.00; N, 6.90. Calc. for the vacuum-dried sample, $C_{12}H_{26}Cu_2N_2O_6$: C, 34.20; H, 6.15; N, 6.65%). IR (KBr, cm^{-1}): 1582vs, 1462m, 1402s, 1338m and 1070m.

$[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(H_2O)_2]$ 2. Compound **2** was isolated initially as a minor product from the reaction of $Sr(OPr^i)_2$ and $Cu(O_2CMe)_2$ with $HOCH_2CH_2NMe_2$ intended to produce a Sr–Cu complex. It is also believed to form as a minor product from the reaction described above for **1**. We have not been able to obtain a sufficient amount of analytically pure **2** owing to its contamination by other products.

$[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ 3. Compound **3** was obtained by a similar procedure to that of Krebs and co-workers.[7] M.p. 215 °C (Found: C, 30.30; H, 3.90; N, 5.55. Calc. for the vacuum-dried sample: $C_{26}H_{42}Br_4Cu_4N_4O_3$: C, 30.25; H, 4.05; N, 5.40%).

X-Ray diffraction analysis

The blue single crystals of complexes **1** and **2** were obtained from a concentrated thf solution, dark green crystals of **3** from a CH_2Cl_2–methanol solution. They were mounted on a glass fibre and sealed with epoxy glue. Data were collected over the

Table 1 Crystallographic data for compounds **1–3***

	1	**2**	**3**
Formula	$C_{12}H_{26}Cu_2N_2O_6 \cdot C_4H_8O$	$C_{12}H_{30}Cu_2N_2O_8$	$C_{26}H_{42}Br_4Cu_4N_4O_3 \cdot CH_2Cl_2 \cdot CH_3OH$
M	493.5	457.5	1147.4
Space group	$I2/a$	$P2_1/c$	$P2_1/c$
a/Å	13.854(4)	8.94(1)	16.760(5)
b/Å	14.051(4)	11.64(2)	10.969(5)
c/Å	11.566(2)	18.45(3)	22.190(7)
β/°	91.028(8)	94.5(1)	96.85(3)
U/Å^3	2251.1(8)	1913(4)	4050(2)
D_c/g cm^{-3}	1.46	1.59	1.88
μ(Mo-Kα)/cm^{-1}	19.2	22.6	62.0
Transmission coefficient	0.82–1.00	0.68–1.00	0.34–1.00
Reflections measured ($+h$, $+k$, $\pm l$)	2082	3002	7530
Observed reflections	880 [$I > 3.00\sigma(I)$]	997 [$I > 2.00\sigma(I)$]	1767 [$I > 2.00\sigma(I)$]
No. of variables	116	152	270
Largest electron-density peak, e Å^{-3}	0.44	0.72	1.21
R	0.051	0.084	0.066
R'	0.046	0.073	0.061
Goodness of fit, S	1.72	2.29	1.95

* Details in common: monoclinic; $Z = 4$; 2θ range 3–50°; largest shift/e.s.d. in final cycle 0.0; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$; $S = [\Sigma(|F_o| - |F_c|)/\sigma(N_o - N_v)]^{\frac{1}{2}}$, N_o = number of observations, N_v = number of variables.

range $3 < 2\theta < 50°$ on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å), operated at 50 kV and 35 mA. Three standard reflections were measured every 150. At the end of data collection 13% decay in intensity was observed for **3**, no significant decay for **1** and **2**. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic software package[8] and corrected for decay and Lorentz-polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied to all compounds.

The crystal of complex **1** belongs to the monoclinic crystal system. Systematic absences (hkl, $h + k \neq 2n$, $h0l$, $l \neq 2n$) were consistent with both space groups Cc and $C2/c$. The latter was selected initially. The correctness of this choice was confirmed by the successful solution and refinement of the structure. To minimize correlation problems, the C-centred unit cell [a = 17.887(3), b = 14.051(4), c = 13.853(4) Å, β = 139.719(8)°, U = 2251.1(8) Å^3] was transformed to the body-centred cell, $I2/a$. The crystals of **2** and **3** belong to the monoclinic space group $P2_1/c$, uniquely determined by the systematic absences ($h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$). All structures were solved by direct methods and expanded using Fourier techniques. The positions of hydrogen atoms were calculated and included in structure-factor calculations. Full-matrix least-squares refinements minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o)]^{-1}$ were applied. Neutral atom scattering factors were taken from Cromer and Waber.[9] A thf solvent molecule displaying a C_2 rotation disorder was located in the crystal lattice of **1** (one per Cu_2 unit) and refined successfully. A CH_2Cl_2 and a disordered MeOH solvent molecule were found in the lattice of **3** (one of each per molecule). Crystallization of **3** from CH_2Cl_2–hexane yielded crystals containing one CH_2Cl_2 per molecule with the unit-cell parameters a = 19.87(1), b = 10.176(8), c = 20.55(2) Å, β = 110.25(5)°, U = 3898(4) Å^3, space group $P2_1/c$. The quality of the crystal and the data for the CH_2Cl_2- and methanol-solvated crystal are significantly better than that of the CH_2Cl_2-solvated crystal. Therefore, only the details of the former are described here. All non-hydrogen atoms in **1**, except those on the disordered thf molecule, were refined anisotropically. Only those atoms heavier than carbon in **2** and **3** were refined anisotropically except the oxygen atom of the disordered methanol in **3**. The crystals of **2** are very small and display significant twinning. The high R factors for **2** can be attributed to the poor quality of the crystal and insufficient data. The data for the X-ray diffraction analysis are summarised in Table 1.

Complete 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.*, 1996, Issue 1.

Results and Discussion

Syntheses and crystal structures of compounds 1–3

The new dinuclear complex $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2]$ **1** was obtained readily as the major product from the reaction of $Cu(OMe)_2$ and $Cu(O_2CMe)_2 \cdot H_2O$ with 2-(dimethylamino)ethanol (dmae) in a 1 : 1 : 2 ratio in thf. Its crystals contain one thf per molecule as established by single-crystal X-ray diffraction analysis. The composition and structure are closely related to those of the compound $[Cu_2(O_2CMe)_2(O_2CH_2CH_2NMe_2)_2(H_2O)_2]$ **2**, obtained initially as a trace product from a reaction intended to produce a Sr–Cu complex. Compound **2** is also believed to form as a trace product in the synthesis of **1**. To date we have not been able to obtain a sufficient amount of pure **2** *via* independent synthesis despite numerous attempts. Therefore, its full characterization has not been achieved.

Important positional parameters for compounds **1**–**3** are provided in Table 2, selected bond lengths and angles in Table 3. Both **1** and **2** contain a dinuclear Cu_2 unit which is shown in Figs. 1 and 2, respectively. The molecule of **1** has a C_2 axis. The two acetate ligands are oriented to each other in a *cis* fashion in **1** but in a *trans* fashion in **2**. In both compounds the copper atoms are bridged by the two oxygen atoms of the dmae ligands with a Cu···Cu separation of 2.891(2) Å in **1** and 2.880(4) Å in **2**. These distances are comparable with some of the short Cu···Cu distances reported previously for $[\{Cu(OCH_2CH_2NR_2)X\}_n]$ compounds. The Cu–O–Cu angles in both compounds [Cu–O(1)–Cu′ 96.3(3)° in **1**, Cu(1)–O(1)–Cu(2) 95.8(6), Cu(1)–O(2)–Cu(2) 94.7(7)° in **2**] are among the smallest observed for alkoxo-bridged dimers.[4] The geometries of the copper centres in both compounds are distorted from a square plane as indicated by the angles O(1)–Cu–O(2) 173.1(3) and O(1′)–Cu–N(1) 151.7(3)° in **1**, and O(1)–Cu(1)–N(2) 159.2(7), O(2)–Cu(1)–O(4) 173.2(8), O(1)–Cu(2)–O(5) 173.5(8) and O(2)–Cu(2)–N(1) 166.7(7)° in **2**. This distortion can be attributed to the presence of the fifth ligand at the axial position of the copper atom. As shown in Fig. 3, in compound **1** the O(2) atom of the acetate ligand co-ordinates to the fifth position of the neighbouring copper centre, Cu″–O(2) 2.519(7) Å, linking the

Table 2 Positional parameters

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1**							
Cu	0.766 67(9)	0.318 3(1)	0.123 7(1)	C(2)	0.962(1)	0.354(1)	0.106(1)
O(1)	0.837 8(4)	0.289 4(4)	−0.013 6(5)	C(3)	0.879(1)	0.491(1)	0.141(2)
O(2)	0.694 6(5)	0.331 1(5)	0.264 5(5)	C(4)	0.912(1)	0.390(1)	0.292(1)
O(3)	0.651 3(6)	0.476 9(5)	0.215 6(6)	C(5)	0.654 8(8)	0.410 9(9)	0.284 3(8)
N(1)	0.888 2(7)	0.392 6(7)	0.172 5(7)	C(6)	0.608 0(9)	0.421 8(9)	0.400(1)
C(1)	0.933 5(7)	0.326 7(9)	−0.012 4(8)				
Compound **2**							
Cu(1)	0.096 5(4)	0.259 7(2)	0.657 3(2)	C(1)	0.400(3)	0.131(2)	0.694(1)
Cu(2)	0.129 9(3)	0.014 3(2)	0.647 5(2)	C(2)	0.436(3)	0.039(2)	0.644(1)
O(1)	0.243(2)	0.142(1)	0.689 5(8)	C(3)	0.356(3)	−0.130(3)	0.581(2)
O(2)	−0.033(2)	0.122(1)	0.656 9(9)	C(4)	0.368(3)	−0.126(3)	0.715(2)
O(3)	0.328(2)	0.314(2)	0.551(1)	C(5)	−0.154(3)	0.134(3)	0.611(1)
O(4)	0.234(2)	0.385(1)	0.648 9(9)	C(6)	−0.213(2)	0.258(2)	0.605(1)
O(5)	−0.000(2)	−0.112(1)	0.613(1)	C(7)	−0.052(3)	0.340(2)	0.520(1)
O(6)	−0.021(2)	−0.150(1)	0.731 0(9)	C(8)	−0.107(3)	0.456(2)	0.622(1)
O(7)	0.173(2)	0.099(1)	0.524 3(9)	C(9)	0.320(3)	0.383(3)	0.600(2)
O(8)	−0.205(2)	0.099(1)	0.780(1)	C(10)	0.426(3)	0.486(2)	0.596(1)
N(1)	0.331(2)	−0.065(2)	0.645(1)	C(11)	−0.056(3)	−0.166(2)	0.670(1)
N(2)	−0.082(2)	0.336(2)	0.598(1)	C(12)	−0.185(3)	−0.246(2)	0.645(1)
Compound **3**							
Br(1)	0.603 0(2)	0.237 9(3)	0.162 3(2)	C(7)	1.117(2)	0.348(3)	0.051(2)
Br(2)	0.859 0(2)	0.312 6(4)	0.379 2(2)	C(8)	1.055(2)	0.255(3)	0.139(1)
Br(3)	0.742 5(2)	0.550 3(3)	0.229 7(2)	C(9)	0.993(2)	0.236(3)	0.173(1)
Br(4)	0.797 4(2)	−0.005 6(3)	0.267 2(2)	C(10)	0.915(2)	0.286(2)	0.155(1)
Cu(1)	0.742 0(2)	0.301 2(3)	0.172 4(2)	C(11)	1.003(2)	0.149(3)	0.226(1)
Cu(2)	0.865 8(2)	0.244 5(3)	0.276 9(2)	C(12)	1.037(2)	0.310(3)	0.296(1)
Cu(3)	0.714 2(2)	0.399 3(3)	0.304 3(2)	C(13)	1.006(2)	0.112(3)	0.333(1)
Cu(4)	0.691 4(2)	0.134 6(3)	0.281 0(2)	C(14)	0.731(2)	0.603(3)	0.384(1)
O(1)	0.754(1)	0.271(1)	0.258 7(8)	C(15)	0.598(2)	0.564(3)	0.343(1)
O(2)	0.860(1)	0.270(1)	0.190 3(8)	C(16)	0.666(2)	0.437(3)	0.424(1)
O(3)	0.643(1)	0.269(2)	0.323 7(8)	C(17)	0.604(2)	0.337(2)	0.416(1)
N(1)	0.754(1)	0.348(2)	0.086(1)	C(18)	0.552(2)	0.319(3)	0.461(1)
N(2)	0.984(1)	0.203(2)	0.285(1)	C(19)	0.500(2)	0.224(3)	0.461(1)
N(3)	0.675(1)	0.508(2)	0.368(1)	C(20)	0.449(2)	0.207(3)	0.514(1)
N(4)	0.610(1)	0.010(2)	0.303(1)	C(21)	0.494(2)	0.148(3)	0.413(2)
C(1)	0.686(2)	0.427(3)	0.060(1)	C(22)	0.540(2)	0.166(3)	0.368(1)
C(2)	0.756(2)	0.241(3)	0.048(1)	C(23)	0.594(2)	0.257(3)	0.367(1)
C(3)	0.827(2)	0.422(3)	0.086(1)	C(24)	0.532(2)	0.080(2)	0.312(1)
C(4)	0.906(2)	0.353(2)	0.103(1)	C(25)	0.637(2)	−0.060(3)	0.358(2)
C(5)	0.967(2)	0.371(2)	0.067(1)	C(26)	0.592(2)	−0.074(3)	0.252(1)
C(6)	1.041(2)	0.322(3)	0.088(1)				

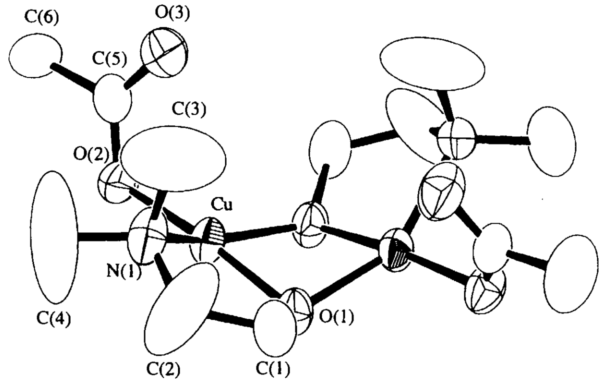


Fig. 1 An ORTEP diagram showing the structure of the dinuclear unit in compound **1** with the labelling scheme and 50% thermal ellipsoids

dinuclear units together and resulting in the formation of a one-dimensional zigzag-chain structure. The inter-dimer Cu ··· Cu′ distance in **1** is 3.533(2) Å. In compound **2** the fifth position of one of the Cu atoms is occupied by an H_2O ligand [Cu(2)–O(7) 2.54(2) Å] while the fifth position of the other copper centre is occupied by the acetate ligand [Cu(1)–O(6) 2.45(2) Å] (Fig. 4). In addition, there are extended hydrogen bonds in **2** (Figs. 4 and 5). The H_2O ligand [O(7)] forms an intramolecular hydrogen bond with the unco-ordinated O(3) atom of the acetate ligand and an intermolecular hydrogen bond with the O(5′) atom as evidenced by the distances O(7) ··· O(3) [2.88(2) Å] and O(7) ··· O(5′) [2.87(2) Å] (Fig. 5). The other H_2O molecule [O(8)] is hydrogen bonded to the alkoxo O(2) atom [O(2) ··· O(8) 2.85(3) Å] and the O(4′) atom of an acetate ligand in a neighbouring molecule [O(8) ··· O(4′) 2.84(2) Å] (Fig. 4). As a consequence, compound **2** has an extended network.

The structure of compound **3** (Fig. 6) is similar to that of [$Cu_4(\mu_4\text{-}O)(bmmp)_2Br_4$] [Hbmmp = 2,6-bis(morpholinomethyl)-4-methylphenolate] reported earlier by Krebs and co-workers.[7] The four copper atoms are bridged by an oxygen atom in a tetrahedral environment. Each bromide ligand is bound to a copper centre at the basal plane with a normal Cu–Br bond length [2.397(5)–2.427(5) Å] and to the second copper centre at the axial position with a long Cu–Br bond length [2.932(5)–3.080(5) Å]. As a consequence, the two methyl groups on the nitrogen atom have different environments, one on the same side as the axial bromide ligand

Table 3 Selected bond lengths (Å) and angles (°)

Compound **1**							
Cu · · · Cu′	2.891(2)	Cu–O(1)	1.927(6)	O(1)–C(1)	1.42(1)	C(1)–C(2)	1.47(1)
Cu–O(1′)	1.954(6)	N(1)–C(2)	1.40(1)	O(2)–C(5)	1.27(1)	C(5)–C(6)	1.51(1)
Cu–O(2)	1.934(6)	N(1)–C(3)	1.43(2)	O(3)–C(5)	1.22(1)		
Cu–N(1)	2.052(8)	N(1)–C(4)	1.41(1)				
Cu–N(1)–C(2)	104.5(7)	Cu–N(1)–C(3)	110.5(9)	O(1′)–Cu–N(1)	151.7(3)	O(2)–C(5)–O(3)	124(1)
Cu–N(1)–C(4)	115.4(8)	C(2)–N(1)–C(3)	107(1)	O(2)–Cu–N(1)	96.7(3)	O(2)–C(5)–C(6)	116(1)
O(1)–Cu–O(1′)	78.6(3)	C(2)–N(1)–C(4)	111(1)	Cu–O(1)–Cu′	96.3(3)	O(3)–C(5)–C(6)	119(1)
O(1)–Cu–O(2)	173.1(3)	C(3)–N(1)–C(4)	106(1)	Cu–O(1)–C(1)	113.8(5)	Cu–O(1′)–C(1′)	127.5(6)
O(1)–Cu–N(1)	84.5(3)	O(1)–C(1)–C(2)	109.6(8)	Cu–O(2)–C(5)	117.8(6)		
O(1′)–Cu–O(2)	100.4(3)	N(1)–C(2)–C(1)	115(1)				
Compound **2**							
Cu(1)–O(1)	1.96(2)	O(4)–C(9)	1.23(3)	Cu(2)–O(5)	1.95(2)	N(2)–C(7)	1.50(3)
Cu(1)–O(2)	1.98(1)	O(5)–C(11)	1.34(3)	Cu(2)–O(7)	2.54(2)	N(2)–C(8)	1.49(3)
Cu(1)–O(4)	1.92(2)	O(6)–C(11)	1.17(3)	Cu(2)–N(1)	2.02(2)	C(1)–C(2)	1.47(3)
Cu(1)–O(6)	2.45(2)	N(1)–C(2)	1.53(3)	O(1)–C(1)	1.40(3)	C(5)–C(6)	1.54(3)
Cu(1)–N(2)	2.06(2)	N(1)–C(3)	1.44(4)	O(2)–C(5)	1.33(3)	C(9)–C(10)	1.54(4)
Cu(2)–O(1)	1.92(2)	N(1)–C(4)	1.48(3)	O(3)–C(9)	1.22(3)	C(11)–C(12)	1.52(3)
Cu(2)–O(2)	1.94(2)	N(2)–C(6)	1.50(3)				
O(1)–Cu(1)–O(2)	78.9(6)	Cu(1)–O(4)–C(9)	119(1)	O(1)–Cu(2)–N(1)	85.6(7)	O(2)–Cu(2)–O(5)	94.8(7)
O(1)–Cu(1)–O(4)	98.1(7)	Cu(2)–O(5)–C(11)	110(1)	O(2)–Cu(2)–O(7)	89.6(6)	O(1)–C(1)–C(2)	108(2)
O(1)–Cu(1)–O(6)	105.4(6)	Cu(1)–O(6)–C(11)	132(1)	O(2)–Cu(2)–N(1)	166.3(7)	O(5)–Cu(2)–N(1)	98.9(8)
O(1)–Cu(1)–N(2)	159.2(7)	Cu(2)–N(1)–C(2)	100(1)	O(5)–Cu(2)–O(7)	97.9(7)	O(2)–C(5)–C(6)	113(2)
O(2)–Cu(1)–O(4)	173.1(8)	Cu(2)–N(1)–C(3)	117(1)	O(7)–Cu(2)–N(1)	87.8(7)	O(3)–C(9)–O(4)	129(3)
O(2)–Cu(1)–O(6)	98.8(7)	Cu(2)–N(1)–C(4)	109(1)	Cu(1)–O(1)–Cu(2)	95.8(6)	O(3)–C(9)–C(10)	113(2)
O(2)–Cu(1)–N(2)	85.3(7)	O(4)–Cu(1)–O(6)	87.8(6)	Cu(1)–O(1)–C(1)	136(1)	O(4)–C(9)–C(10)	116(2)
O(4)–Cu(1)–N(2)	96.0(7)	O(6)–Cu(1)–N(2)	90.3(6)	Cu(2)–O(1)–C(1)	116(2)	O(5)–C(11)–O(6)	126(2)
Cu(1)–N(2)–C(6)	106(1)	O(1)–Cu(2)–O(7)	87.0(6)	Cu(1)–O(2)–Cu(2)	94.7(7)	O(5)–C(11)–C(12)	112(2)
O(1)–Cu(2)–O(2)	80.8(6)	Cu(1)–N(2)–C(7)	105(1)	Cu(1)–O(2)–C(5)	111(1)	O(6)–C(11)–C(12)	121(2)
O(1)–Cu(2)–O(5)	173.5(8)	Cu(1)–N(2)–C(8)	112(1)	Cu(2)–O(2)–C(5)	126(1)		
Compound **3**							
Br(1)–Cu(1)	2.416(5)	N(1)–C(3)	1.49(3)	Cu(1)–O(2)	2.00(2)	N(4)–C(26)	1.47(3)
Br(1) · · · Cu(4)	3.080(5)	N(2)–C(11)	1.51(3)	Cu(1)–N(1)	2.01(2)	Cu(2)–O(1)	1.90(2)
Br(2)–Cu(2)	2.406(5)	N(2)–C(12)	1.48(3)	Cu(2)–O(2)	1.93(2)	Cu(2)–N(2)	2.02(2)
Br(2) · · · Cu(3)	2.932(5)	N(2)–C(13)	1.47(3)	Cu(3)–O(1)	1.90(2)	Cu(3)–O(3)	1.94(2)
Br(3) · · · Cu(1)	3.014(5)	N(3)–C(14)	1.42(3)	Cu(3)–N(3)	2.02(2)	Cu(4)–O(1)	1.92(2)
Br(3)–Cu(3)	2.427(5)	N(3)–C(15)	1.48(3)	Cu(4)–O(3)	1.98(2)	Cu(4)–N(4)	2.04(2)
Br(4) · · · Cu(2)	2.971(5)	N(3)–C(16)	1.49(3)	O(2)–C(10)	1.29(3)	O(3)–C(23)	1.34(3)
Br(4)–Cu(4)	2.397(5)	N(4)–C(24)	1.54(3)	N(1)–C(1)	1.49(3)	N(1)–C(2)	1.44(3)
Cu(1)–O(1)	1.93(2)	N(4)–C(25)	1.46(4)				
Br(3)–Cu(3)–O(3)	146.0(6)	O(1)–Cu(3)–N(3)	167.0(9)	O(1)–Cu(2)–N(2)	172(1)	Cu(2)–O(1)–Cu(4)	112.3(9)
O(1)–Cu(1)–N(1)	167.7(8)	Br(1)–Cu(1)–O(2)	152.7(5)	Cu(3)–O(1)–Cu(4)	101.8(9)	Cu(1)–O(1)–Cu(2)	102.7(9)
Br(4)–Cu(4)–O(3)	152.9(5)	Br(2)–Cu(2)–O(2)	153.0(5)	Cu(2)–O(1)–Cu(3)	113.6(8)	Cu(1)–O(1)–Cu(3)	113.7(9)
O(1)–Cu(4)–N(4)	170.3(9)	Cu(1)–O(1)–Cu(4)	113.2(8)				

while the other is on the opposite side. Similarly, the two protons of the methylene group also have different environments.

Magnetic properties of compounds 1 and 3

Magnetic susceptibilities of compounds **1** and **3** were measured at 2–300 K. The behaviour of **3** is very similar to that of $[Cu_4O(bmmp)_2Br_4]$, *i.e.* it is a strongly antiferromagnetically coupled system. The molar susceptibility (χ_m) and χ_m^{-1} for compound **1** are shown in Fig. 7. No maximum of χ_m was observed in the temperature range studied. Since the intramolecular Cu · · · Cu′ distance [2.891(2) Å] is much shorter than the intermolecular one [3.533(2) Å] one could assume that the magnetic exchange is dominated by the intramolecular interaction. We therefore attempted first to fit the susceptibility data by using the Bleaney–Bowers isolated-dimer model, but this was unsuccessful. A modified dimer equation (1) (ρ = fraction of paramagnetic impurity) was therefore used. A fitting obtained by using equation (1) yielded $J = -2.10$ cm^{-1}, $\theta = -29.4$ K, $\rho = 8.5\%$, $g = 2.258$, and $R = \Sigma[(\chi_{calc} - \chi_{exptl})/\chi_{exptl}]^2 = 1.30\%$. The g value is in good agreement with the value ($g_{av} = 2.17$) obtained from an EPR experiment performed at 110 K for a frozen solution ($CHCl_3$) of **1**. The large θ value suggests that compound **1** cannot be treated as an isolated dimer but instead as an extended magnetically coupled system. The negative θ value also indicates that the magnetic exchange in **1** is dominated by weak antiferromagnetism.[11]

$$\chi = (1 - \rho)\{2Ng^2\beta^2/[3k(T - \theta)][1 + \tfrac{1}{3}\exp(-2J/kT)]\} + \rho\chi_{mono} \quad (1)$$

^1H NMR studies of compounds 1 and 3

Since the intermolecular Cu · · · O bond in compound **1** is fairly weak [2.519(7) Å], it is possible that **1** may exist as a dinuclear species in solution. The complications owing to the interdimer interactions could then be minimized, thus making it possible to reveal the nature of the magnetic exchange within the dinuclear unit by ^1H NMR techniques. The solution behaviour of **1** was therefore examined by ^1H NMR methods at variable temperatures. A well resolved spectrum was obtained at 293 K. Based on the relative intensities of the signals and the crystal structural data, we assigned the resonance at δ 78.43 to NMe, those at δ 12.34 and 7.15 to OCH_2 and NCH_2, and that at δ 2.31 to O_2CMe. In order to assign the OCH_2 and NCH_2 resonances unambiguously two-dimensional ^1H NMR experiments were performed. However, owing to the broadness of the signal at δ 12.34, no definite correlation was observed. As the temperature decreases, the signals at δ 78.43 and 12.34 experience a downfield shift, while that at δ 7.15 has a slight upfield shift and that at δ 2.31 experiences no shift (Fig. 8). An important feature is the change of the NMe resonance pattern with temperature. At 293 K only one broad signal was observed which coalesces at approximately 253 K and becomes two resonances at about 233 K. Further decrease in temperature causes these two resonances to broaden, which is apparently owing to the increase in susceptibility. We believe that this phenomenon is caused by a dynamic process. If the copper(II) ion in the dinuclear unit is four-co-ordinate and has a square-planar geometry in solution, only one NMe signal should be observed even at low temperature because the activation energy for the conformational change of a five-membered ring is usually too small to cause two different methyl environments in the temperature range investigated. Hence, we postulate that the copper(II) ion of **1** may have a five-co-ordinate geometry such as a square pyramid at low temperature. The occupation of the axial position by a fifth co-ordinating atom can result in two different NMe environments. In fact the crystal structure of **1** shows two distinct NMe environments, one on the same side of the weakly bonded acetate oxygen atom and the other on the opposite side. The five-co-ordinate geometry of the copper(II) ion in the solid state can be attributed to the formation of the weak intermolecular Cu • • • O bond. In solution there are two possible mechanisms for the formation of the five-co-ordinate copper centres in **1**. The first is an intramolecular process involving chelation of the acetate ligand (Scheme 1). The second mechanism is an intermolecular process involving the formation of acetate bridges as depicted in Scheme 1, where either the unco-ordinated oxygen atom of the acetate forms an intermolecular Cu • • • O bond or the co-ordinated oxygen atom is bound to the second copper centre in the same manner as in the solid state. In order to differentiate these two processes we conducted a concentration-dependent ^1H NMR experiment. The ^1H NMR spectra of compound **1** in $CDCl_3$ at five different concentrations (0.0045–0.072 mol dm^{-3}) were recorded at 293 K. The results showed unambiguously that the chemical shifts of **1** are concentration-dependent. The isotropic shifts of the NMe and the CH_2 signals increase with increasing concentration (Fig. 9). At temperatures below 230 K, however, the chemical shifts of **1** are independent of concentration, suggesting that at low temperature the structure of **1** in solution may be the same as in the solid state regardless of the concentration. We therefore conclude that compound **1** exists in solution as a mixture of oligomers and its dynamic behaviour must be caused by a rapid intermolecular dissociation and association process *via* the oxygen atom of the acetate ligand. By using the chemical

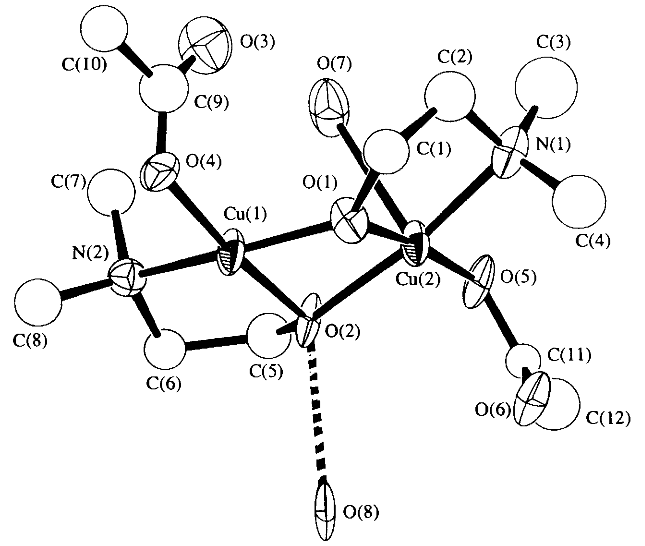


Fig. 2 An ORTEP diagram showing the structure of the dinuclear unit in compound **2** with the labelling scheme and 50% thermal ellipsoids

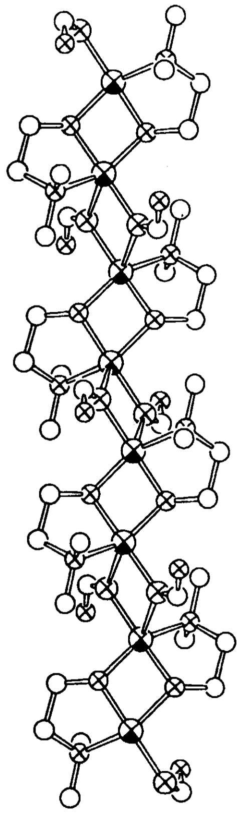


Fig. 3 The polymeric structure of compound **1**. The methyl group of the acetate ligand is omitted for clarity

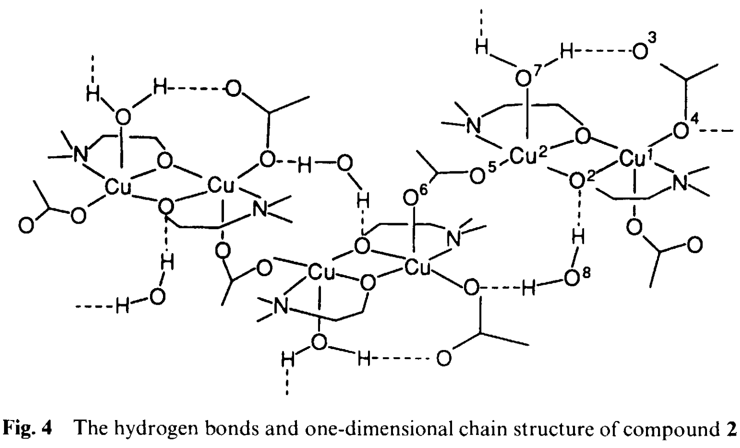


Fig. 4 The hydrogen bonds and one-dimensional chain structure of compound **2**

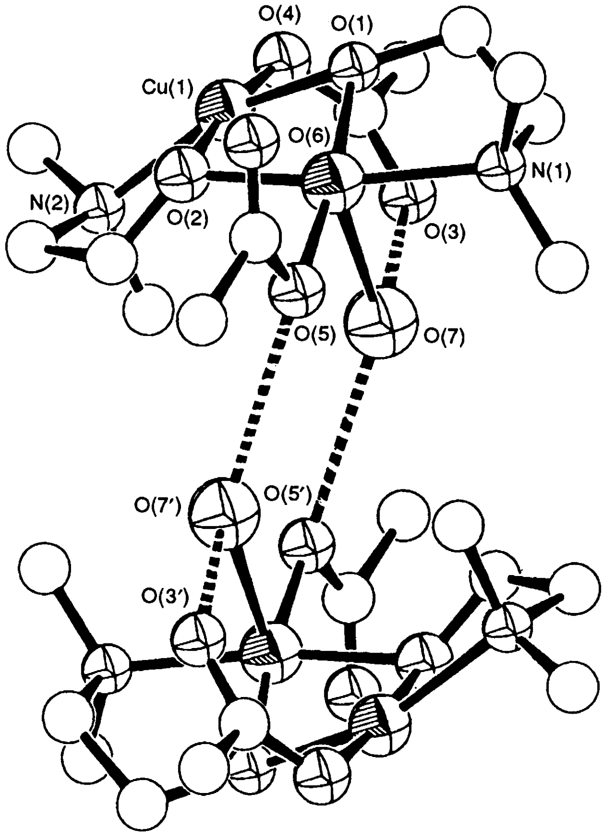


Fig. 5 An ORTEP diagram showing the hydrogen bonds between the chains of compound **2**

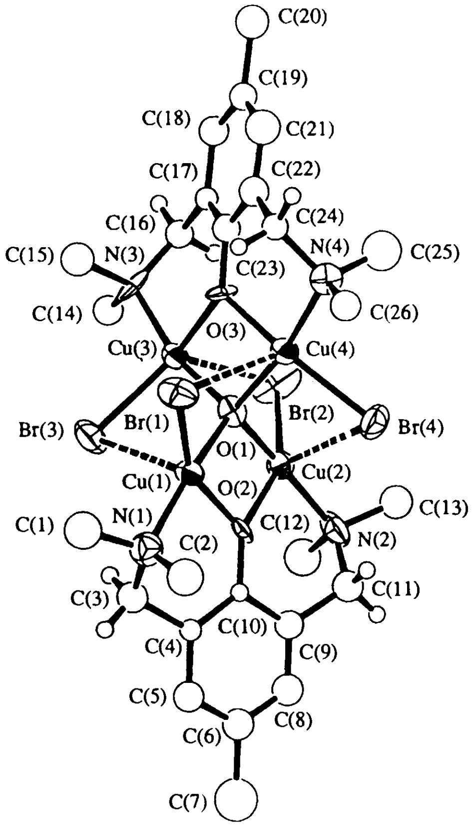


Fig. 6 An ORTEP diagram showing the structure of compound **3** with the labelling scheme

shifts of the two NMe signals at 233 K and the coalescence temperature of 253 K, the activation energy for this process is estimated to be 11 kcal mol^{-1} (*ca.* 46 kJ mol^{-1}). The formation

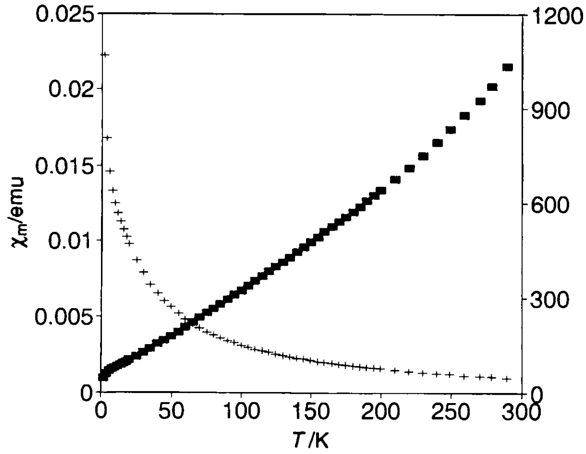


Fig. 7 Plots showing the temperature dependence of the magnetic susceptibility (χ_m) (+) and its reciprocal (■) for compound **1**

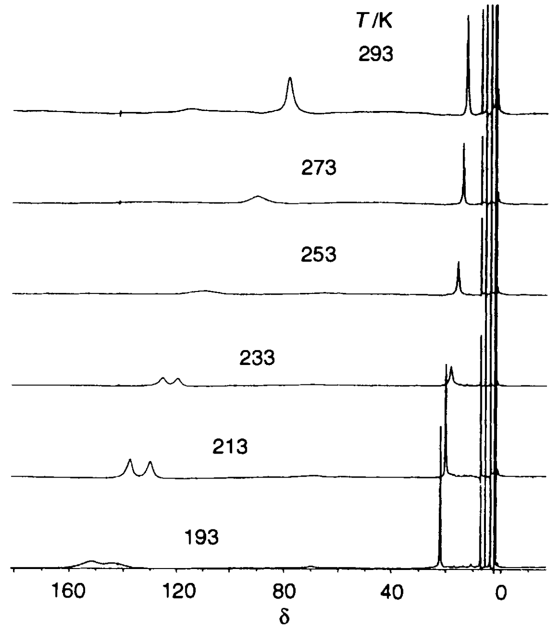
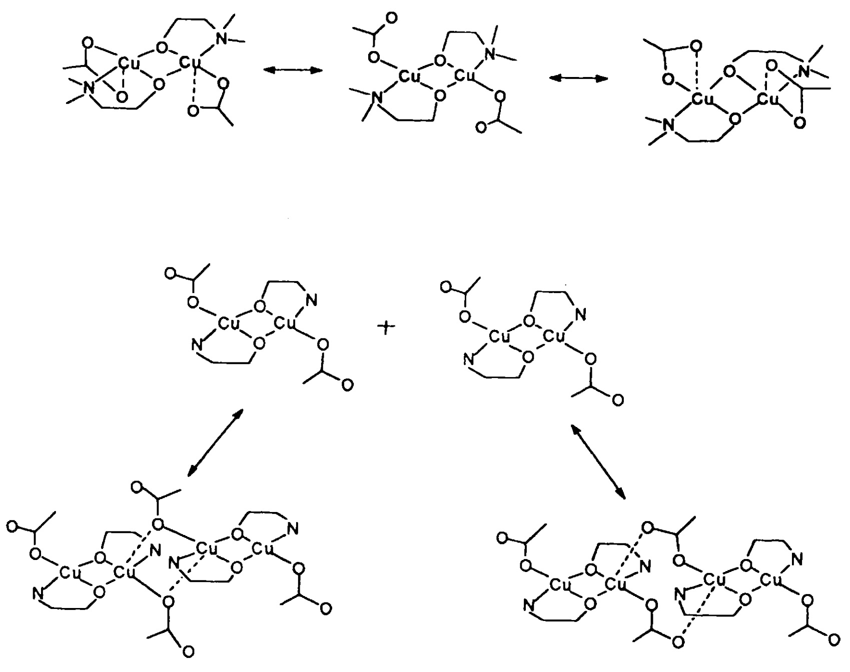


Fig. 8 Variable-temperature ^{1}H NMR spectra of compound **1** in CD_2Cl_2

of oligomers of **1** in solution makes the magnetic exchanges at least as complicated as in the solid state. Therefore, quantitative analysis of the ^{1}H NMR data for **1** has not been achieved.

We have recently reported a similar intramolecular dynamic process caused by the position switching of weakly bound acetate ligands between two copper(II) centres in a tetranuclear copper(II) complex[5c] $[Cu_4(\mu_4\text{-}O)(bdmmp)_2(O_2CCF_3)_4]$ **4** (Scheme 2 and Fig. 10). The activation energy for this dynamic process is similar to that observed in **1**. We believe that these dynamic processes are not only associated with the Jahn–Teller distortion of the copper(II) ion, but more importantly with the ease of the swinging motion of the acetate ligand which apparently requires little energy. It is possible that such dynamic processes may be quite common among polynuclear copper(II) complexes with acetate ligands. As a comparative study we examined the solution behaviour of the tetranuclear complex $[Cu^{II}_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ **3** which has a similar structure to that of **4**. The variable-temperature ^{1}H NMR spectra of **3** are shown in Fig. 11. In the 293 K spectrum, the resonances at δ 3.45 and 12.77 are assigned to the methyl protons on the phenyl ring and phenyl protons, respectively, those at δ 17.79 and 79.81 to the two methylene protons H_a and H_b, while the two at δ 23.97 and 29.57 are assigned to the protons of the two methyl groups (H_c and H_d) on the nitrogen



Scheme 1

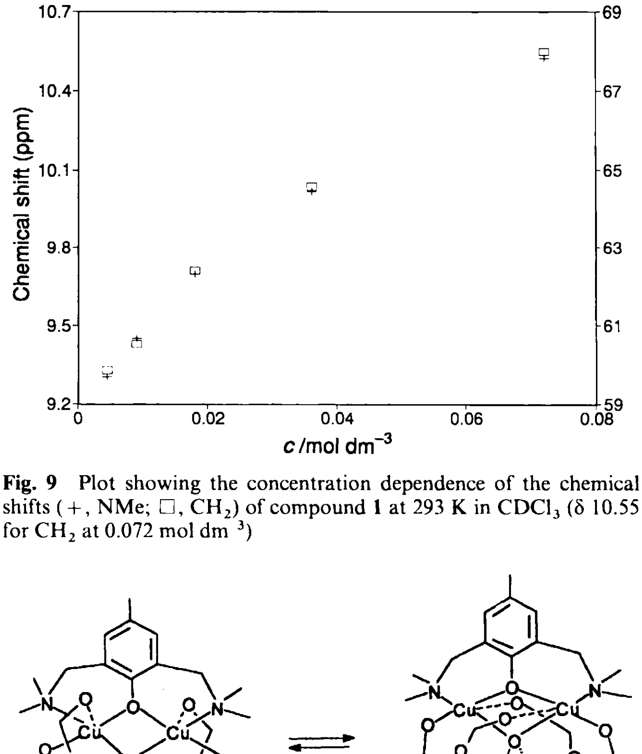
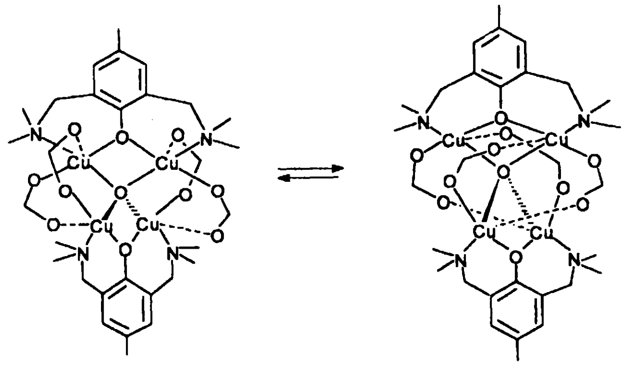


Fig. 9 Plot showing the concentration dependence of the chemical shifts (+, NMe; □, CH_2) of compound **1** at 293 K in $CDCl_3$ (δ 10.55 for CH_2 at 0.072 mol dm^{-3})



Scheme 2

atom. All resonances experienced upfield shifts with decreasing temperature. However, in contrast to the behaviour of **4**, no dynamic process was observed in the ^1H NMR spectra of **3**. The lack of dynamic behaviour in **3** reflects the relative rigidity of the weak Cu–Br bond. Unlike in compound **4** where the position switching of the axial ligand can be accomplished by rotation of the acetate ligand around the C–O bond, in **3** the position switching has to involve a significant movement of the

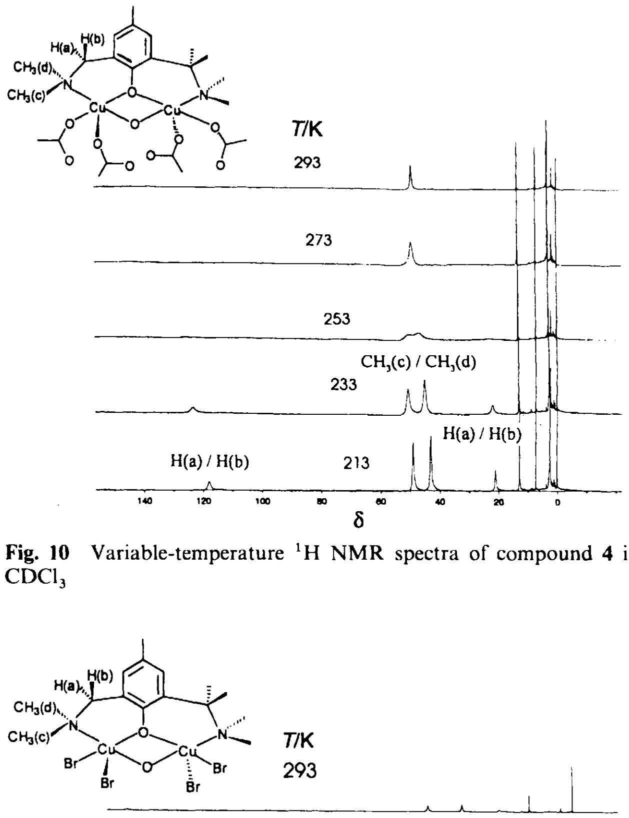


Fig. 10 Variable-temperature ^1H NMR spectra of compound **4** in $CDCl_3$

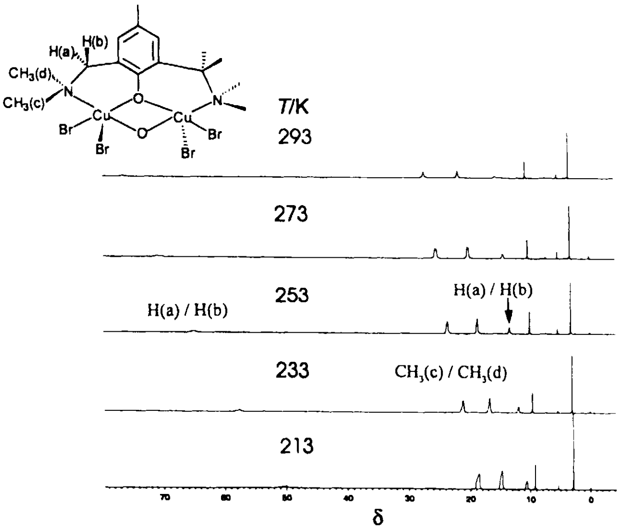


Fig. 11 Variable-temperature ^1H NMR spectra of compound **3** in $CDCl_3$

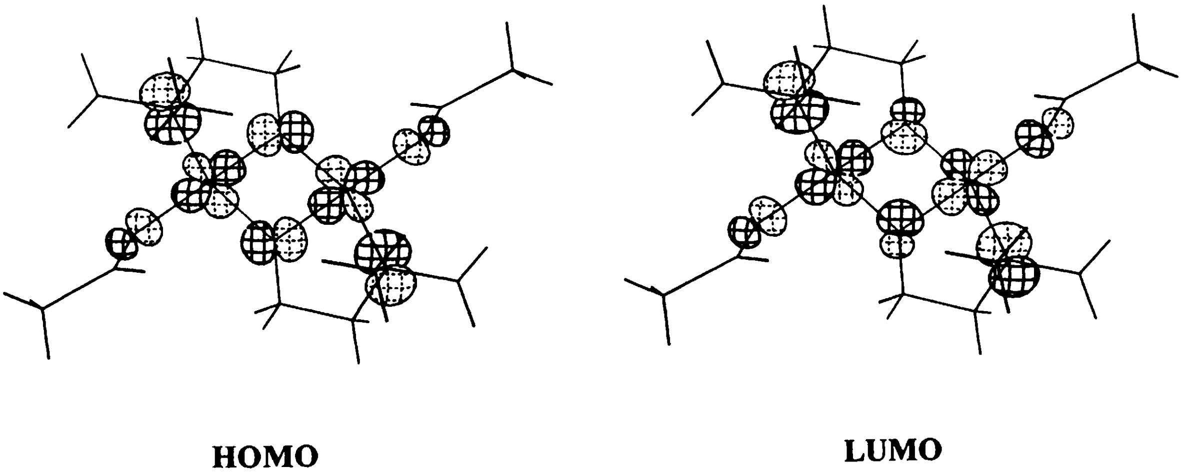
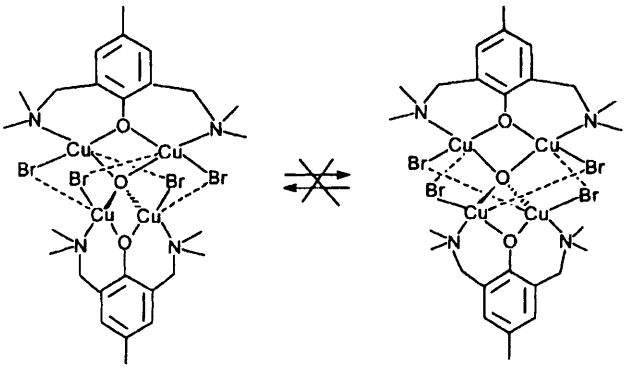


Fig. 12 Molecular orbital diagrams showing the HOMO and LUMO orbitals of compound **1** obtained from the EHMO calculation. The compositions of these two orbitals are essentially the same as those obtained from ZINDO calculations except that the relative energy levels of these two orbitals in the ZINDO calculation are reversed



Scheme 3

$CuBrNO_2$ plane which apparently requires too much energy to occur (Scheme 3). Similar locking effects by the weakly bound axial halide ligand have been observed in $[Cu_6O(OH)(bdmap)_3Cl_6]$ [bdmap = 1,3-bis(dimethylamino)propan-2-olate] reported earlier by our group.[5b]

Molecular orbital calculations on the electronic structure of compound 1

Molecular orbital calculations were performed for the dinuclear unit of compound **1** using the extended-Hückel molecular orbital (EHMO) method[12] and the Zerner's Intermediate Neglect of Differential Overlap (ZINDO) method.[13] The molecular geometry was established by using the crystallographic coordinates of the dinuclear unit. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) from both calculations consist mostly of the symmetric and antisymmetric combinations of the two $d_{x^2-y^2}$ orbitals from the two copper centres. There are also substantial contributions from the co-ordinating atoms to these two orbitals (Fig. 12). The results of both calculations indicate that there is a considerable energy gap between the HOMO and the LUMO orbitals. Although the energy value obtained has no practical meaning owing to the limitation of these calculation methods, the results do imply that the ground state of **1** is $S = 0$, that is it is antiferromagnetically coupled. The EHMO calculation results suggest that the HOMO is the antisymmetric combination (*anti*) of the $d_{x^2-y^2}$ orbitals and the LUMO is the symmetric combination (*sym*). However, the relative energy levels of the *sym* and *anti* orbitals are reversed in the ZINDO calculation. Previous theoretical calculations and experimental results on dinuclear copper complexes with double hydroxo bridges suggested that a doubly bridged dinuclear copper(II) complex with a Cu–X–Cu angle greater than 97° typically has an antiferromagnetically coupled ground state with the symmetric combination being HOMO.[4,12] Although the ZINDO result seems in agreement with the structure and susceptibility data for compound **1**, conclusions regarding the nature of the magnetic exchange of **1** cannot be reached owing to the existence of extended magnetic couplings in this system. The increase of the 2s orbital exponent of the bridging oxygen atom can have a significant impact on the relative energy levels of the symmetric and antisymmetric $d_{x^2-y^2}$ orbital combinations.[13] We have attempted a calculation by increasing the 2s exponent of the bridging oxygen atom from 2.275 to 2.70 in the EHMO calculation, but the order of the *sym* and *anti* orbitals did not change. Nevertheless, the conflicting results from the EHMO and ZINDO calculation methods appear to imply that the real energy gap between the HOMO and the LUMO orbitals of the dinuclear unit may be quite small so that it is not distinguishable by these low-level MO calculations.

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