Macrocyclic 'Dimer-of-dimers' Type Tetranuclear Copper(II) Complexes with Two Bridging Hydroxy Groups in a Face-to-face Manner†

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Macrocyclic tetranuclear copper(II) complexes of the general formula $[Cu_4L(OH)_2][X]_2[Y]_2$ ($L = L^1$, $X = Y = ClO_4^-$ or $X = MeCO_2$, $Y = PF_6$; $L = L^2$, $X = Y = ClO_4$ or $X = Y = PF_6^-$) have been obtained by template reactions, where L denotes the macrocycles formed by the [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 3,6-diazaoctane-1,8-diamine ($L = L^1$) or 3,6-dithiaoctane-1,8-diamine ($L = L^2$). The very efflorescent solvate complex $[Cu_4L^1(OH)_2][MeCO_2]_2[PF_6]_2{\cdot}4MeCN{\cdot}2Pr^iOH$ crystallizes in the monoclinic crystal system, space group $P2_1/a$, with $a = 13.038(5)$, $b = 21.251(5)$, $c = 12.757(3)$ Å, $\beta = 113.38(2)°$. The refinement converges with $R = 0.1215$ and $R' = 0.1187$. The tetranuclear cation $\{Cu_4L^1(OH)_2(Pr^iOH)_2(MeCN)_2\}^{4+}$ contains two dinuclear Cu^{II}_2 units in a 'dimer-of-dimers' arrangement. In each unit two copper(II) ions are bridged by an endogenous phenolic oxygen of $(L^1)^{2-}$ and an exogenous hydroxide oxygen with a Cu···Cu separation of 2.949(4) Å. A propan-2-ol molecule resides on the axial site of one copper ion and an acetonitrile molecule on the axial site of the other copper ion, affording a square-pyramidal geometry about both copper(II) ions. The two dinuclear skeletons assume a near coplane and the two bridging OH^- groups are facing each other with an O···O separation of 3.32(2) Å. The efflorescent solvate complex $[Cu_4L^2(OH)_2][PF_6]_4{\cdot}4MeCN{\cdot}4H_2O$ crystallizes in the triclinic crystal system, space group $P\bar{1}$, with $a = 12.576(9)$, $b = 13.082(6)$, $c = 11.682(6)$ Å, $\alpha = 109.54(4)$, $\beta = 106.99(5)$, $\gamma = 69.02(5)°$. The refinement converges with $R = 0.0835$ and $R' = 0.0812$. The centrosymmetric cation $\{Cu_4L^2(OH)_2(MeCN)_4\}^{4+}$ assumes a similar 'dimer-of-dimers' structure with two facing OH^- groups where an acetonitrile molecule co-ordinates at the axial site of each copper(II) ion. The Cu···Cu separation in the dinuclear unit is 2.976(2) Å and the O···O separation between the two facing OH^- groups is 3.80(1) Å. In all the tetranuclear complexes the two dinuclear units are magnetically isolated from each other and a significant antiferromagnetic interaction operates within each Cu^{II}_2 unit ($-J = 229$–357 cm^{-1} based on $\hat{H} = -2JS_1{\cdot}S_2$).

Polynuclear metal complexes have great value in studies which mimic the active sites of some multimetallobiosites,[1] in the search for appropriate systems for binding and activating simple molecules,[2–4] and in examining the mutual effects of neighbouring metal ions upon the physicochemical properties in such metal-condensed complexes.[5,6] Higher nuclearity of metal ions (> 2) has been found in biological systems such as the oxygen-evolving complex in photosystem II of green plants[7] and galactose oxidase.[8] A tetranuclear 'dimer-of-dimers' type Mn_4 core for this oxygen-evolving complex[9] and a mechanistic scheme that invokes the conversion of two water molecules (two OH^- or O^{2-} ions), in a face-to-face arrangement, into briding peroxide is proposed.[10] Apart from acting as models for oxygen-evolving complexes, such 'dimer-of-dimers' type complexes with two bridging groups in a face-to-face arrangement are of great interest for their incorporation of molecules among the four metal ions and unprecedented functions associated with the cooperative effects of the metal ions. Some tetranuclear metal complexes of the 'dimer-of-dimers' type have been reported[11,12] but the face-to-face arrangement of two bridging groups has rarely been achieved.[12]

The aim of this work was to synthesize such 'dimer-of-dimers' type complexes by a template procedure using two tetranucleating macrocyclic ligands, $(L^1)^{2-}$ and $(L^2)^{2-}$, formed by the [2 + 2] condensation of 2,6-diformyl-1-4-methylphenol with 3,6-diazaoctane-1,8-diamine or 3,6-dithiaoctane-1,8-diamine, respectively. The tetranuclear copper(II) complexes $[Cu_4L(OH)_2][X]_2[Y]_2$ ($L = L^1$, $X = Y = ClO_4$ or $X = MeCO_2$, $Y = PF_6$; $L = L^2$, $X = Y = ClO_4$ or $X = Y = PF_6$) exhibit the 'dimer-of-dimers' type structure with the two OH^- bridges in the face-to-face arrangement as confirmed by X-ray crystallography. Part of this work has been preliminarily reported.[13]

Experimental

Physical Measurements.—Elemental analyses (C, H and N) were obtained from the Elemental Analysis Service Center of Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption–flame emission spectrophotometer. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer using KBr discs, molar conductances in dimethylformamide (dmf) (*ca.* 1×10^{-3}, 1×10^{-4} or 1×10^{-5} mol dm^{-3}) on a DKK AOL-10 conductivity meter at 20 °C and electronic spectra in dmf (*ca.* 1×10^{-3} mol dm^{-3}) on a

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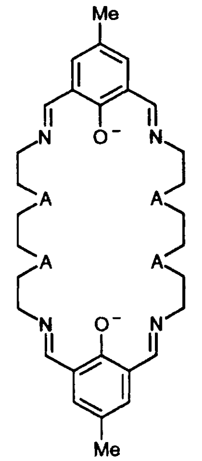
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.



$(L^1)^{2-}$ A = NH
$(L^2)^{2-}$ A = S

Shimadzu MPS-2000 spectrophotometer at room temperature. Magnetic susceptibilities were measured on a Faraday balance in the range 80–300 K. The apparatus was calibrated with $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine)[14] and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$ μ_B, where χ_A is the molar magnetic susceptibility per copper atom corrected for the diamagnetism of the constituent atoms using Pascal's constants.[15] Cyclic voltammograms were recorded on an apparatus comprising a HA-501 potentiostat–galvanostat, a HB-104 function generator, and a HF-201 coulomb–amperehour meter from Hokuto Denko Ltd. Measurements were carried out in dmf or acetonitrile solution (*ca.* 1 × 10^{-3} mol dm^{-3}) containing 0.1 mol dm^{-3} tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte, using a three-electrode cell equipped with a glassy-carbon working electrode, a platinum coil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Coulometry studies were performed on the same instrument using a platinum net as the working electrode.

Syntheses.—2,6-Diformyl-4-methylphenol was prepared by a modification[16] of the method of Denton and Suschitzky.[17] 3,6-Dithiaoctane-1,8-diamine was synthesized by the literature method.[18] Other chemicals were of reagent grade and used as purchased.

$[Cu_4L^1(OH)_2][ClO_4]_4$ **1**. A methanol solution (20 cm^3) of 2,6-diformyl-4-methylphenol (0.164 g, 1.0 mmol), copper(II) perchlorate hexahydrate (0.740 g, 2.0 mmol) and triethylamine (0.250 g, 2.5 mmol) was refluxed for 10 min. To the resulting deep green solution was added dropwise a methanolic solution (10 cm^3) of 3,6-diazaoctane-1,8-diamine (0.147 g, 1.0 mmol) and the mixture was refluxed for 2 h to give a deep green precipitate. It was separated by filtration, washed successively with methanol and diethyl ether and dried over P_2O_5 in a vacuum desiccator. Yield: 0.43 g (70%) (Found: C, 29.30; H, 3.65; Cu, 20.10; N, 8.85. Calc. for $C_{30}H_{44}Cl_4Cu_4N_8O_{20}$: C, 29.25; H, 3.60; Cu, 20.60; N, 9.10%). Selected IR data (KBr discs): 3640, 3240, 2940, 2875, 1650, 1140, 1115, 1090 and 625 cm^{-1}. Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 390. UV/VIS data [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 370 (13 300) and 616 (340).

$[Cu_4L^1(OH)_2][MeCO_2]_2[PF_6]_2$·MeOH **2**·MeOH. A methanol solution (20 cm^3) of 2,6-diformyl-4-methylphenol (0.164 g, 1.0 mmol), copper(II) acetate monohydrate (0.400 g, 2.0 mmol), and triethylamine (0.250 g, 2.5 mmol) was refluxed for 10 min. To the resulting green solution was added a methanol solution (10 cm^3) of 3,6-diazaoctane-1,8-diamine (0.147 g, 1.0 mmol), and the mixture was refluxed for 2 h. The addition of an aqueous solution of excess of ammonium hexafluorophosphate (NH_4PF_6) to the reaction mixture resulted in the precipitation of green microcrystals, which were separated by filtration, washed successively with methanol and diethyl ether, and dried over P_2O_5 in a vacuum desiccator. Yield: 0.29 g (44%) (Found: C, 32.40; H, 4.25; Cu, 19.45; N, 8.65. Calc. for $C_{35}H_{54}Cu_4F_{12}N_8O_9P_2$: C, 32.95; H, 4.25; Cu, 19.95; N, 8.80%). Selected IR data (KBr discs): 3620, 3200, 2925, 2875, 1650, 1560, 1400 and 840 cm^{-1}. Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 330. UV/VIS data [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 385 (10 800) and 634 (355).

A portion of **2** was dissolved in acetonitrile and the solution was layered with propan-2-ol to give single crystals of $[Cu_4L^1(OH)_2][MeCO_2]_2[PF_6]_2$·4MeCN·2$Pr^iOH$ **2**·4MeCN·2Pr^iOH (Found: C, 32.45; H, 4.45; Cu, 20.25; N, 8.85. Calc. for $C_{34}H_{50}Cu_4F_{12}N_8O_8P_2$: C, 32.85; H, 4.05; Cu, 20.45; N, 9.00%).

$[Cu_4L^2(OH)_2][ClO_4]_4$·H_2O **3**. This complex was obtained as deep green microcrystals by a method similar to that for complex **1** using 3,6-dithiaoctane-1,8-diamine (0.181 g, 1.0 mmol) instead of 3,6-diazaoctane-1,8-diamine. Yield: 0.36 g (55%) (Found: C, 27.20; H, 3.25; Cu, 19.75; N, 4.20. Calc. for $C_{30}H_{42}Cl_4Cu_4N_4O_{21}S_4$: C, 27.30; H, 3.20; Cu, 19.25; N, 4.25%). Selected IR data (KBr discs): 3600 (br), 2915, 2845, 1635, 1140, 1110, 1080 and 625 cm^{-1}. Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 360. UV/VIS data [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 374 (18 600) and 600 (880).

$[Cu_4L^2(OH)_2][PF_6]_4$·4MeCN·4H_2O **4**. Complex **3** (0.132 g, 1.0 mmol) was suspended in the minimum amount of acetonitrile and to this was added an aqueous solution of excess of NH_4PF_6 to result in the precipitation of efflorescent blue-green microcrystals. Yield: 0.12 g (73%) (Found: C, 24.75; H, 3.00; Cu, 15.90; N, 5.30. Calc. for $C_{34}H_{54}Cu_4F_{24}N_6O_8P_4S_4$: C, 24.95; H, 3.35; Cu, 15.55; N, 5.15%).

X-Ray Structural Analyses of Complexes **2**·4MeCN·2Pr^iOH *and* **4**.—A crystal of complex **2**·4MeCN·2Pr^iOH with approximate dimensions 0.35 × 0.30 × 0.20 mm and a crystal of complex **4** with approximate dimensions 0.45 × 0.38 × 0.25 mm, sealed in a glass tube, were used for the X-ray diffraction studies. Intensities and lattice parameters were obtained on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at 20 ± 1 °C. The lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 25 reflections in the 2θ range $27 \leqslant 2\theta \leqslant 30°$ for both complexes. For the intensity data collections the ω–2θ scan mode was used at a scan rate of 4° min^{-1}. For complex **2**·4MeCN·2Pr^iOH the octant measured was $(+h, +k, \pm l)$ and three standard reflections monitored every 100 reflections showed no systematic decrease in intensity. For complex **4** the octant measured was $(+h, \pm k, \pm l)$ and two standard reflections monitored every 150 reflections showed no systematic decrease in intensity. The intensity data were corrected for Lorentz and polarization factors but not for absorption. 3041 Independent reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2.5 \leqslant 2\theta \leqslant 48°$ for **2**·4MeCN·2Pr^iOH and 4763 reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2.5 \leqslant 2\theta \leqslant 52°$ for **4** were assumed to be observed. Crystal data for the two complexes are summarized in Table 1.

The structures were solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and equal weight (w = 1) was adopted for all reflections. Atomic scattering factors were taken from ref. 19. Hydrogen atoms were fixed at the calculated positions and were not refined. Reliability factors were defined as $R = \Sigma[||F_o| - |F_c||]/\Sigma|F_o|$ and $R' = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[w|F_o|^2]\}^{\frac{1}{2}}$, where the weights were taken as $w = 1/\sigma|F_o|$. All the calculations were made on a FACOM M-1800/20 computer in the Computer Center of Kyushu University by the use of local versions[20] of the UNICS III[21] and ORTEP[22] programs. The final positional

Table 1 Crystal data for complexes **2**·4MeCN·2Pr^{i}OH and **4**

Complex	**2**·4MeCN·2Pr^{i}OH	**4**
Formula	$C_{48}H_{78}Cu_4F_{12}N_{12}O_{10}P_2$	$C_{38}H_{60}Cu_4F_{24}N_8O_8P_4S_4$
M	1527.33	1719.22
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a/Å	13.038(5)	12.576(9)
b/Å	21.251(5)	13.082(6)
c/Å	12.757(3)	11.682(6)
α/°	90	109.54(4)
β/°	113.38(2)	106.99(5)
γ/°	90	69.02(5)
U/Å^3	3245(2)	1656(1)
Z	2	1
D_c/g cm^{-3}	1.563	1.723
D_m*/g cm^{-3}	1.593	1.702
μ(Mo-Kα)/cm^{-1}	14.37	16.02
Reflections measured	3694	5788
Observed reflections [$\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$]	3041	4763
F(000)	1568	914
R	0.1215	0.0835
R'	0.1187	0.0812

* Measured by flotation in CH_2Br_2–CH_2Cl_2 solution.

parameters of the non-hydrogen atoms with their estimated standard deviations for complexes **2**·4MeCN·2Pr^{i}OH and **4** are given in Tables 2 and 3, respectively. In the case of the former complex severe disorder is found for the acetate ion, the propan-2-ol molecule and the hexafluorophosphate ion. The relative occupancy factors used for the refinements are included in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Preparation and General Characterization.—Kahwa *et al.*[23] first reported dinuclear lanthanoid complexes of the macrocycle H_2L^1 but no X-ray crystallographic evidence was presented. In our related study using Pb^{II} as the template ion and 3,7-diazanonane-1,9-diamine as the tetraamine component, an unusual condensation occurs between the two secondary amino groups of the tetraamine and a C=O group of the 2,6-diformyl-4-methylphenol to give a macrocycle containing six-membered hexahydropyrimidine rings.[24] Similar condensations between dicarbonyl compounds and polyamines or hydroxylamines to form five-membered imidazolidine[25] or oxazolidine rings[26] are known. Based on our preliminary studies on the template synthesis of L^1 complexes, such an unusual condensation always occurs when Pb^{II}, Ba^{II}, Mn^{II} or Ni^{II} is used as the template ion; the desired tetranucleating macrocycles are available only when a linear tetraamine, alkylated at the secondary nitrogen atoms, is used.[27,28] In this study the macrocycle $(L^1)^{2-}$ and its analogue $(L^2)^{2-}$ were obtained as tetranuclear copper(II) complexes in good yields when Cu^{II} was used as the template ion.

The IR spectra of complexes **1**–**4** are similar to each other except for the bands due to the counter anions. All the complexes show the ν(OH) mode of the bridging OH$^-$ group at 3640–3600 cm^{-1} and the ν(C=N) mode at 1650–1635 cm^{-1}. For complexes **1** and **2** a weak band is seen at 3240–3200 cm^{-1} and is assigned to the ν(NH) mode of the secondary amine on the lateral chain. The asymmetric and symmetric acetate vibrations of **2** appear at 1560 and 1400 cm^{-1}, respectively The separation of the two vibrations is smaller than 200 cm^{-1}, suggesting bidentate co-ordination of the acetate group.[29] The perchlorate vibration of complexes **1** and **3** is seen as split bands at 1140, 1115–1110 and 1090–1080 cm^{-1}, implying co-ordinative interaction of the perchlorate ions.[30] A strong band at 845–835 cm^{-1} for complexes **2** and **4** is characteristic of the hexafluorophosphate ion. Molar conductances of complexes **1**–**4** in dmf are practically independent of concentration and fall in the range 330–400 S cm^2 mol^{-1} typical of 4 : 1 electrolytes in this solvent.[31]

Crystal Structures.—After many efforts single crystals of complex **2** were obtained as the solvate **2**·4MeCN·2Pr^{i}OH. The solvate was highly efflorescent and gave poor reliability factors R and R', but pertinent discussion of the complex structure is possible. An ORTEP view of the complex cation is shown in Fig. 1, together with the numbering scheme. Selected bond distances and angles together with their estimated standard deviations are listed in Table 4.

The complex molecule consists of the centrosymmetric tetranuclear complex cation $\{Cu_4L^1(OH)_2(Pr^iOH)_2(MeCN)_2\}^{4+}$, two acetate ions, two hexafluorophosphate ions and two acetonitrile molecules. The complex cation contains two dinuclear copper(II) units in a 'dimer-of-dimers' arrangement. In each dinuclear unit two copper(II) ions, Cu(1) and Cu(2), are bridged by an endogenous phenolic oxygen O(1) of $(L^1)^{2-}$ and an exogenous hydroxide oxygen O(2) with a Cu(1)···Cu(2) separation of 2.95(1) Å. The Cu(1)–O(1)–Cu(2) and Cu(1)–O(2)–Cu(2) angles are 97.6(6) and 100.2(7)°, respectively. The two copper ions in each 'dimer' are not equivalent. The geometry about Cu(1) is square pyramidal with the phenolic oxygen O(1), the imine nitrogen N(1), the amine nitrogen N(4′) and the bridging hydroxide oxygen O(2) at the basal plane and a propan-2-ol oxygen O(5) at the axial site. The geometry about Cu(2) is also square pyramidal but the axial site is occupied by an acetonitrile nitrogen N(5). The axial Cu(1)–O(5) and Cu(2)–N(5) distances are 2.46(1) and 2.61(2) Å, respectively, both of which are significantly elongated relative to the equatorial bond distances. The bond distances between the copper(II) and the nitrogen-donor atoms of $(L^1)^{2-}$ are common [1.99(1)–2.05(1) Å], whereas the Cu(1)–O(2) and Cu(2)–O(2) distances are significantly short [1.92(2) and 1.92(1) Å, respectively]. This relates to the large Cu(1)–O(1)–Cu(2) angle. The tetranuclear skeleton $\{Cu_4L^1(OH)_2\}$, except for the axial ligands, forms a near coplane with small deviations of the atoms from the least-squares plane. The two dinuclear units are in close proximity with two bridging hydroxide ions in a face-to-face mode [O(2)···O(2′) 3.32(2) Å]. The Cu(1)···Cu(1′), Cu(1)···Cu(2′) and Cu(2)···Cu(2′) interatomic separations are 6.510(5), 5.426(8) and 5.821(4) Å, respectively. The two acetate ions are free from co-ordination

Table 2 Final atomic coordinates (× 10^4) of non-hydrogen atoms in complex **2**·4MeCN·2Pr^{i}OH

Atom	*x*	*y*	*z*
Cu(1)	3137(2)	4798(1)	1072(2)
Cu(2)	2893(2)	5683(1)	−792(2)
O(1)	2109(10)	5453(6)	194(10)
O(2)	3697(11)	4932(5)	−94(10)
N(1)	2229(13)	4671(8)	2006(14)
N(2)	2100(12)	6504(6)	−1158(14)
N(3)	3702(12)	6013(6)	−1738(12)
N(4)	5986(12)	5982(6)	−1887(13)
C(1)	1331(15)	4929(10)	1829(17)
C(2)	828(14)	5485(8)	1099(17)
C(3)	−56(15)	5731(10)	1222(18)
C(4)	−515(15)	6345(9)	649(18)
C(5)	−1470(17)	6616(10)	860(22)
C(6)	−61(16)	6570(10)	−62(20)
C(7)	826(14)	6331(9)	−239(17)
C(8)	1296(14)	5712(8)	361(16)
C(9)	1285(14)	6654(8)	−932(17)
C(10)	2559(17)	6893(9)	−1808(20)
C(11)	2950(17)	6484(9)	−2566(18)
C(12)	4082(16)	5521(11)	−2378(18)
C(13)	4911(16)	5835(9)	−2805(17)
C(14)	6748(17)	6305(10)	−2354(19)
C(15)	7287(18)	5835(9)	−2905(21)
O(3)	4398(11)	3213(7)	293(12)
O(4)	4495(20)	3915(10)	−972(22)
O(4*)	5230(33)	3771(15)	−683(30)
C(16)	3765(20)	2934(10)	−1686(21)
C(17)	4340(18)	3365(11)	−704(20)
O(5)	4328(11)	5657(7)	2212(12)
C(18)	5301(30)	6074(14)	4029(31)
C(18*)	4671(66)	5956(24)	4097(59)
C(19)	3617(21)	6631(13)	2586(22)
C(20)	4200(21)	6032(9)	3083(20)
N(5)	1386(18)	5163(11)	−2601(19)
C(21)	1316(53)	4457(13)	−4183(41)
C(22)	1424(28)	4756(16)	−3242(25)
N(6)	2054(25)	5645(13)	−5513(23)
C(23)	1190(24)	6720(13)	−6077(24)
C(24)	1654(23)	6142(16)	−5806(22)
P(1)	4071(6)	7858(3)	−4185(7)
F(1)	3680(17)	7166(7)	−4574(15)
F(2)	4546(17)	8496(7)	−3750(17)
F(3)	3866(19)	7969(8)	−5482(14)
F(4)	5258(20)	7698(14)	−4099(24)
F(5)	4774(19)	7518(11)	−3008(19)
F(6)	2967(22)	8227(13)	−4718(25)
F(7)	2988(24)	7810(13)	−4014(31)
F(8)	3998(35)	7864(17)	−2914(24)

Occupancy factors: O(4) 0.6, O(4*) 0.4, C(18) 0.6, C(18*) 0.4, F(4) and F(5) 0.7, F(6) 0.6, F(7) and F(8) 0.5.

Table 3 Final atomic coordinates (× 10^4) of non-hydrogen atoms in complex **4**

Atom	*x*	*y*	*z*
Cu(1)	3 563(1)	2 909(1)	6 090(1)
Cu(2)	3 147(1)	1 827(1)	3 378(1)
S(1)	3 959(2)	2 327(2)	7 926(2)
S(2)	4 091(2)	226(2)	2 045(3)
O(1)	2 633(6)	3 278(5)	4 510(6)
O(2)	3 961(6)	1 457(5)	4 928(6)
N(1)	2 865(7)	4 418(6)	7 025(7)
N(2)	2 391(7)	2 460(7)	1 947(7)
N(3)	5 207(8)	3 293(7)	6 260(8)
N(4)	1 444(8)	1 194(8)	3 062(9)
C(1)	3 359(10)	3 738(9)	8 861(10)
C(2)	3 370(10)	4 637(9)	8 360(9)
C(3)	2 046(9)	5 209(8)	6 624(9)
C(4)	1 522(8)	5 164(8)	5 314(9)
C(5)	660(8)	6 162(8)	5 093(9)
C(6)	132(8)	6 244(8)	3 873(10)
C(7)	−774(9)	7 334(9)	3 670(11)
C(8)	465(8)	5 316(8)	2 918(9)
C(9)	1 304(8)	4 306(8)	3 088(9)
C(10)	1 813(8)	4 234(7)	4 331(9)
C(11)	1 605(8)	3 466(8)	1 997(9)
C(12)	2 678(10)	1 746(9)	758(9)
C(13)	2 965(11)	527(9)	699(10)
C(14)	3 821(9)	−971(9)	2 295(9)
C(15)	4 485(9)	−2 107(8)	1 537(9)
C(16)	6 689(11)	4 230(12)	6 250(12)
C(17)	5 852(9)	3 693(10)	6 256(9)
C(18)	−531(11)	784(12)	2 113(14)
C(19)	568(10)	1 025(9)	2 650(11)
P(1)	8 862(3)	2 828(4)	9 343(3)
F(1)	9 045(8)	3 334(10)	10 759(7)
F(2)	8 692(10)	2 397(13)	7 943(9)
F(3)	7 669(10)	3 617(11)	9 167(9)
F(4)	10 019(9)	1 942(10)	9 595(13)
F(5)	9 568(15)	3 447(15)	9 252(11)
F(6)	8 298(14)	2 051(16)	9 443(16)
P(2)	5 842(3)	2 694(3)	2 368(3)
F(7)	5 071(7)	2 632(7)	3 145(7)
F(8)	6 650(8)	2 698(9)	1 568(7)
F(9)	4 745(11)	3 365(11)	1 666(10)
F(10)	5 858(11)	3 869(10)	3 239(11)
F(11)	6 912(10)	2 287(14)	3 231(13)
F(12)	5 737(15)	1 641(10)	1 479(13)
O(3)	6 739(12)	416(9)	4 573(10)
O(4)	8 502(17)	675(14)	5 065(16)

in complex **2**·4MeCN·2Pr^{i}OH, in contrast to complex **2** where acetate co-ordination is suggested from the IR spectrum. Two hexafluorophosphate ions and two acetonitrile molecules are also captured in the crystal lattice.

The tetranuclear cation may have geometrical isomers with respect to the four secondary nitrogens on the lateral chains. X-Ray crystallography reveals that the central dimethylene groups in the lateral chains, combining the two dinuclear units, both assume a skew conformation, with one ethylene group above the least-squares plane of the macrocycle and the other group below it.

Single crystals of complex **4** were also efflorescent but gave better reliability factors. An ORTEP view of the complex cation with the atom-numbering scheme is given in Fig. 2. Selected bond distances and angles with their estimated standard deviations are listed in Table 5.

The crystal consists of the centrosymmetric complex cation $\{Cu_4L^2(OH)_2(MeCN)_4\}^{4+}$, four hexafluorophosphate ions and four water molecules. The complex has a 'dimer-of-dimers' structure similar to that of **2**·4MeCN·2Pr^{i}OH but both the Cu(1)–O(1)–Cu(2) and Cu(1)–O(2)–Cu(2) angles are enlarged [99.2(3) and 101.4(3)°, respectively] and the Cu(1)–N(1) and Cu(2)–N(2) distances shortened [1.934(7) and 1.952(9) Å, respectively]. This is evidently due to the long Cu(1)–S(1) and Cu(2)–S(2) bond lengths [2.369(4) and 2.309(3) Å, respectively] relative to the Cu(1)–N(1) and Cu(2)–N(2) bond distances [2.00(2) and 1.99(1) Å, respectively in **2**·4MeCN·2Pr^{i}OH. The Cu(1) ··· Cu(2) separation is also elongated [2.976(2) Å], but the elongation in the Cu(1)–O(2) and Cu(2)–O(2) bonds is small. Each copper atom assumes a square-pyramidal geometry with an acetonitrile nitrogen at the axial site with an average Cu–N bond distance of 2.345 Å. The two bridging OH$^-$ groups are facing, but the O(2) ··· O(2′) separation [3.80(1) Å] is much larger than the corresponding separation in **2**·4MeCN·2Pr^{i}OH. The interatomic Cu(1) ··· Cu(1′), Cu(1) ··· Cu(2′) and Cu(2) ··· Cu(2′) separations are 7.084(5), 6.212(4) and 6.687(5) Å, respectively.

Physicochemical Properties.—Each of the complexes **1**–**3** shows an intense absorption band at *ca.* 380 nm and a moderately intense band at 660–600 nm in dmf. They are

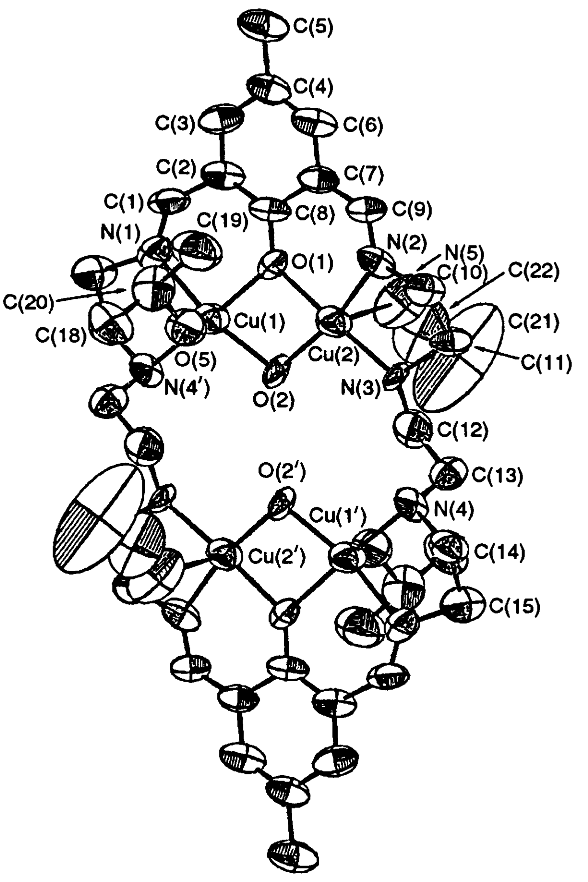


Fig. 1 An ORTEP view of the structure of the cation of complex **2**·4MeCN·2Pr^{i}OH

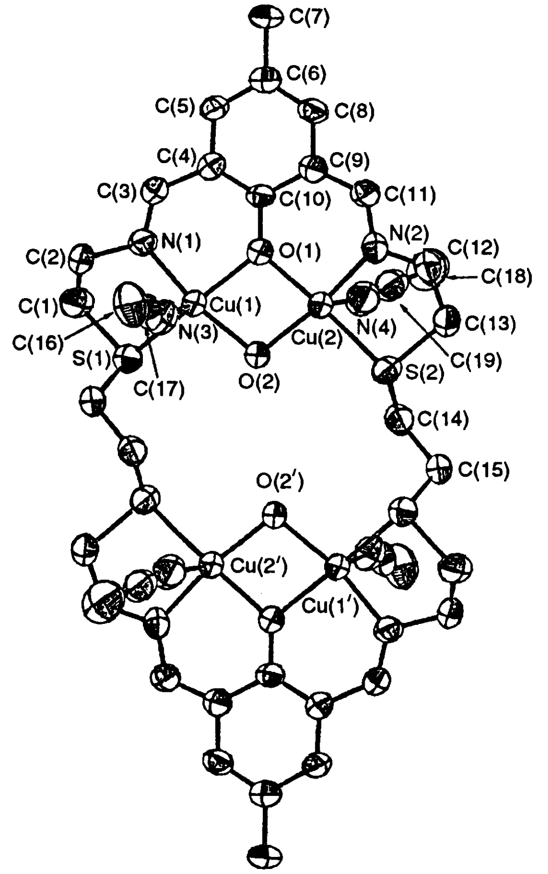


Fig. 2 An ORTEP view of the structure of the cation of complex **4**

Table 4 Selected bond distances (Å) and angles (°) of complex **2**·4MeCN·2Pr^{i}OH

Cu(1)–O(1)	1.949(12)	Cu(1)–O(2)	1.923(16)
Cu(1)–N(1)	2.003(21)	Cu(1)–N(4′)	2.048(13)
Cu(1)–O(5)	2.464(13)	Cu(2)–O(1)	1.970(16)
Cu(2)–O(2)	1.922(11)	Cu(2)–N(2)	1.987(13)
Cu(2)–N(3)	2.018(18)	Cu(2)–N(5)	2.610(20)
Cu(1) · · · Cu(2)	2.949(4)	Cu(1) · · · Cu(1′)	6.510(5)
Cu(1) · · · Cu(2′)	5.426(8)	Cu(2) · · · Cu(2′)	5.821(4)
O(2) · · · O(2′)	3.321(21)		
O(1)–Cu(1)–O(2)	80.4(6)	O(1)–Cu(1)–N(1)	90.3(6)
O(1)–Cu(1)–N(4′)	171.3(5)	O(1)–Cu(1)–O(5)	86.4(5)
O(2)–Cu(1)–N(1)	167.6(5)	O(2)–Cu(1)–N(4′)	101.9(7)
O(2)–Cu(1)–O(5)	90.1(5)	N(1)–Cu(1)–N(4′)	86.1(7)
N(1)–Cu(1)–O(5)	97.6(6)	N(4′)–Cu(1)–O(5)	101.9(7)
O(1)–Cu(2)–O(2)	79.9(6)	O(1)–Cu(2)–N(2)	90.8(7)
O(1)–Cu(2)–N(3)	173.9(6)	O(1)–Cu(2)–N(5)	93.5(7)
O(2)–Cu(2)–N(2)	167.1(7)	O(2)–Cu(2)–N(3)	104.3(6)
O(2)–Cu(2)–N(5)	98.0(6)	N(2)–Cu(2)–N(3)	84.3(7)
N(2)–Cu(2)–N(5)	91.4(6)	N(3)–Cu(2)–N(5)	90.4(7)
Cu(1)–O(1)–Cu(2)	97.6(6)	Cu(1)–O(2)–Cu(2)	100.2(7)

Primed atoms are related to the unprimed atoms by the symmetry operation: $1 - x, 1 - y, -z$.

Table 5 Selected bond distances (Å) and angles (°) of complex **4**

Cu(1)–O(1)	1.983(7)	Cu(1)–O(2)	1.921(6)
Cu(1)–S(1)	2.369(4)	Cu(1)–N(1)	1.934(7)
Cu(1)–N(3)	2.236(11)	Cu(2)–O(1)	1.926(6)
Cu(2)–O(2)	1.924(7)	Cu(2)–S(2)	2.309(3)
Cu(2)–N(2)	1.952(9)	Cu(2)–N(4)	2.453(12)
Cu(1) · · · Cu(2)	2.976(2)	Cu(1) · · · Cu(1′)	7.084(5)
Cu(1) · · · Cu(2′)	6.212(4)	Cu(2) · · · Cu(2′)	6.687(5)
O(2) · · · O(2′)	3.798(9)		
O(1)–Cu(1)–O(2)	78.9(3)	O(1)–Cu(1)–S(1)	156.5(3)
O(1)–Cu(1)–N(1)	91.0(3)	O(1)–Cu(1)–N(3)	102.2(4)
O(2)–Cu(1)–S(1)	99.9(2)	O(2)–Cu(1)–N(1)	168.3(3)
O(2)–Cu(1)–N(3)	94.9(3)	S(1)–Cu(1)–N(1)	87.0(3)
S(1)–Cu(1)–N(3)	101.3(3)	N(1)–Cu(1)–N(3)	93.0(4)
O(1)–Cu(2)–O(2)	80.2(3)	O(1)–Cu(2)–S(2)	167.7(3)
O(1)–Cu(2)–N(2)	91.7(3)	O(1)–Cu(2)–N(4)	97.0(3)
O(2)–Cu(2)–S(2)	99.2(2)	O(2)–Cu(2)–N(2)	169.6(3)
O(2)–Cu(2)–N(4)	98.6(4)	S(2)–Cu(2)–N(2)	87.4(2)
S(2)–Cu(2)–N(4)	95.2(2)	N(2)–Cu(2)–N(4)	88.7(4)
Cu(1)–O(1)–Cu(2)	99.2(3)	Cu(1)–O(2)–Cu(2)	101.4(3)

Primed atoms are related to the unprimed atoms by the symmetry operation: $1 - x, -y, 1 - z$.

assigned to the π–π* transition of the C=N linkage[32] and a d–d band of the copper(II) ion, respectively. It is to be noted that the absorption coefficients of the two bands are large in complex **3** relative to complexes **1** and **2**·MeOH, probably due to the co-ordination of the thioether sulfur.

The magnetic moments of complexes **1**–**3** are subnormal at room temperature (0.83–1.13 μ_B per copper), suggesting antiferromagnetic interactions within the complex molecules. As a first approximation the magnetic interaction between the two dinuclear units can be neglected due to the large separation between the two units. We have carried out magnetic analyses using the Bleaney–Bowers equations[33] for the $(S_1 = \frac{1}{2}) - (S_2 = \frac{1}{2})$ system, including the correction term, ρ, for paramagnetic impurity (all other symbols have their usual meanings) [equation (1)]. The cryomagnetic properties of

Table 6 Magnetic parameters and discrepancy factors [$R(\chi)$] for complexes **1–3**

Complex	J/cm^{-1}	g	$N\alpha$/cm^3 mol^{-1}	ρ	$10^{-2}R(\chi)$*
1	−259	2.10	100×10^{-6}	0.000	1.6
2·MeOH	−229	2.10	100×10^{-6}	0.027	2.9
3	−357	2.10	100×10^{-6}	0.017	2.1

* $R(\chi) = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2]^{\frac{1}{2}}$.

complexes **1–3** have been well simulated with this equation and the best-fit magnetic parameters are tabulated in Table 6.

$$\chi_A = [Ng^2\beta^2/kT]\{3 + \exp(-2J/kT)\}^{-1}(1 - \rho) + 0.45\rho/T + N\alpha \quad (1)$$

It is noted that the antiferromagnetic interaction of complex **3** (−357 cm^{-1}) is significantly stronger than those for complexes **1** and **2**·MeOH (−259 and −229 cm^{-1}). Magnetostructural correlations in di(μ-hydroxo)- and di(μ-alkoxo)-dicopper(II) complexes[34–36] have been extensively studied and it is known that the nature and the magnitude of the magnetic interaction are sensitive to the Cu–O–Cu bridge angle and thence the Cu ··· Cu separation; *i.e.*, the larger the Cu–O–Cu angle (or the Cu ··· Cu separation) the stronger the antiferromagnetic interaction. In complexes **2**·4MeCN·2Pr^{i}OH and **4** the average of the Cu–O(Ph)–Cu and Cu–O(H)–Cu angles is 98.9 and 100.3°, respectively, and the Cu ··· Cu separation is 2.95(1) and 2.977(3) Å, respectively. Unfortunately cryomagnetic investigations could not be made for complexes for **2**·4MeCN·2Pr^{i}OH and **4** because of their high efflorescence. However, it is naturally presumed that the skeletal structure of complexes **1** and **2**·MeOH is essentially the same as that of **2**·4MeCN·2Pr^{i}OH and the skeletal structure of complex **3** is the same as that of **4**. Based on this assumption, the magnetic interactions of complexes **1–3** are in line with the general magnetostructural correlation previously found for dinuclear copper(II) complexes.

In our previous study,[13] complex **1** showed four redox couples attributable to the stepwise reductions $Cu^{II}Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{I}Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{I}Cu^{I}$. In this work complex **2**·MeOH showed two irreversible couples near −0.45 V *vs.* SCE (E_{pc} −0.52, E_{pa} −0.38 V) and at −0.86 V *vs.* SCE (E_{pc} −0.93, E_{pa} −0.79 V), which are tentatively assigned to the two-electron processes $Cu^{II}Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{II}Cu^{II}$ and $Cu^{I}Cu^{I}Cu^{II}$-$Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{I}Cu^{I}$ respectively. Our attempts to prepare the mixed-complex by coulometry were in vain.

It is generally known[37] that the reduction potential of Cu^{II} shifts to positive potential by 0.2–0.3 V on substituting a nitrogen donor for a thioether sulfur. Thus, we expected that complex **3** would show reduction waves at a higher potential relative to complexes **1** and **2**·MeOH. However, **3** showed ill defined waves in spite of changes in solvent, electrode and supporting electrolyte.

The replacement of the two bridging OH$^-$ groups with other groups and the incorporation of simple molecules among the four copper ions present a very interesting challenge; studies along this line are under way.

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