Synthesis, electrochemical and magnetic properties of Cu_3 complexes of a series of new compartmental trinucleating ligands H_4L †

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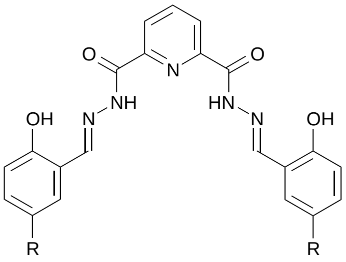
A series of linear trinuclear copper(II) complexes $[Cu_3L(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$ {H_4L = 2,6-bis[(5-substituted salicylidene)hydrazinocarbonyl]pyridine; $L = L^1$, R = H; $L = L^2$, R = Me_3; $L = L^3$, R = Bu^t; $L = L^4$, R = OMe_3; $L = L^5$, R = Cl; $L = L^6$, R = Br; dmso = dimethyl sulfoxide} have been synthesized and characterized on the basis of infrared and electronic spectra, electrochemical and variable-temperature (80–300 K) magnetic measurements. The crystal and molecular structure of $[Cu_3L^1(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$ has been established by X-ray diffraction. The structure consists of a $Cu^{II}Cu^{II}Cu^{II}$ trinuclear cation, unco-ordinated perchlorate anions, and a water molecule of crystallization. Each copper ion is in a square-pyramidal environment. The compartmental ligand L^1 co-ordinates in two different modes: (*i*) as tridentate in the terminal compartment defined by the hydrazonic carbonyl, hydrazonic nitrogen and phenolic oxygen; (*ii*) tridentate in the central chamber defined by the pyridyl nitrogen and two hydrazonic nitrogens. Cryomagnetic investigations reveal a moderately strong antiferromagnetic spin exchange among adjacent copper(II) ions in each complex ($J = -40$ to -65 cm^{-1}), showing that the compartmental ligands of the $Cu^{II}Cu^{II}Cu^{II}$ are good mediators for spin-exchange interactions. Cyclic voltammetry of complex **1** showed one oxidation wave attributed to $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{-e^-} Cu^{II}Cu^{III}Cu^{II}$, a one-electron transfer reduction peak due to $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{+e^-} Cu^{II}Cu^{I}Cu^{II}$ and a two-electron transfer wave established as $Cu^{II}Cu^{I}Cu^{II} \xrightarrow{+2e^-} Cu^{I}Cu^{I}Cu^{I}$.

Intensive investigations of bimetallic molecules have focused attention on various synergistic interactions in these systems. This fundamental question has broad implications for metallobiomolecules,[1–6] the search for appropriate systems for binding and activating simple molecules,[7,8] catalysis,[9] electron-transfer processes [10] and magnetic interactions.[11] The study of compartmental ligands and their complexes has been a very active area of research, and will continue to expand.[12–15] Although the greatest effort and success have been in the study of dinuclear copper(II) complexes, there has been little work on oligomeric copper(II) complexes with more than two copper ions, particularly linear trinuclear complexes,[16–23] due to a lack of suitably characterized compounds.

A trinuclear copper cluster may be of importance in a number of the multicopper blue oxidases [24] such as ascorbate oxidase and laccase. These multicopper blue oxidases catalyse the four-electron reduction of oxygen to water with concomitant one-electron oxidation of a variety of substrates such as ascorbate, polyphenols and polyamines.[25] The expectation that the unique behaviour may similarly be shown by complexes in which a single ligand organizes more than two metal centres into some predetermined arrangement has prompted us to study the synthesis and properties of complexes of compartmental ligands such as 2,6-bis[(5-substituted salicylidine)hydrazinocarbonyl]pyridine potentially capable of binding up to three metal centres in close proximity.

In 1985, G. Paolucci *et al.*[26] first reported the 5-H derivative as a potential mono-, bi- and tri-nucleating ligand towards uranyl ions. Unfortunately, the co-ordination modes they suggested were wrong. In this study, we report the synthesis, structure, spectral, electrochemical and magnetic properties of Cu_3 complexes of the compartmental ligands H_4L^{1-6}.[27]



	R
H_4L^1	H
H_4L^2	Me
H_4L^3	Bu^t
H_4L^4	OMe
H_4L^5	Cl
H_4L^6	Br

Experimental

Materials

2,6-Bis(hydrazinocarbonyl)pyridine was prepared by reaction of diethyl 2,6-pyridinecarboxylate ester with hydrazine hydrate in ethanol and recrystallized from a large amount of water as colourless needles.[27] The potentially trinucleating ligands H_4L^{1-6} were synthesized by the following published methods.[26,27] 5-Chloro and 5-bromo-salicylaldehyde were obtained from Aldrich (USA) and the corresponding 5-methyl, 5-*tert*-butyl, and 5-methoxy derivatives were prepared in good yields by employing the Duff [28] reaction. All the other chemicals were commercially available and used without further purification. Dimethyl sulfoxide (dmso) for electrochemical experiments was purified before using the standard method. **CAUTION:** owing to the hazardous nature of metal perchlorates containing organic ligands, the drying temperature was kept below 50 °C. Only small amounts were prepared at a time and handled with extreme care.

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† *Non-SI units employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Physical measurements

Elemental analyses of C, H and N were determined with a Perkin-Elmer model 240C automatic instrument, metal analysis on a Shimadzu AA-680 atomic absorption flame emission spectrophotometer. Infrared spectra were recorded as Nujol mulls (KBr pellets) on a Nicolet 5-DX spectrophotometer in the range 4000–400 cm^{-1}, electronic spectra on a Shimadzu UV-3100 spectrophotometer in the 300–900 nm region in dmso solutions. Cyclic voltammograms were performed with a Princeton Applied Research model 273 potentiostat-galvanostat (EG&G Ltd.) at room temperature in dmso solution by using a three-electrode system consisting of a platinum-disc working electrode, a platinum-wire auxiliary electrode and a silver–silver chloride (saturated LiCl in ethanol) reference electrode with 0.1 mol dm^{-3} tetraethylammonium perchlorate as the supporting electrolyte. Solutions were deoxygenated with ultrahigh-purity N_2 that had been passed through a pair of chromium(II) perchloric acid columns and a $CaSO_4$ drying column. Blanks indicated that no electroactive impurities were present in the scan range from 1.0 to −1.5 V. The potential of the reference electrode was determined to be ≈−0.06 V *vs.* normal hydrogen electrode (NHE) by using the ferrocenium–ferrocene couple as the internal standard. X-Band ESR spectra of complexes were obtained on a Bruker ESR 3000 instrument. Magnetic susceptibilities were measured on a CAHN-200 Faraday-type magnetometer operating at 50 kG (5 T) in the range 80–300 K. Calibrations were made with $[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine) for the Faraday balance.[29] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}}$, where χ_A is the atomic magnetic susceptibility corrected for diamagnetism of the constituting atoms using Pascal's constants.[30,31]

Syntheses

Dinuclear complex $H_2[Cu_2(H_2L^1)(O_2CMe)_4]$1′. This complex was synthesized for the electrochemical experiment to assign all the electrochemical behaviour. To a solution of H_4L^1 (0.403 g, 1 mmol) dissolved in dmso (10 cm^3) was added solid $Cu(O_2CMe)_2\cdot H_2O$ (0.20 g, 1 mmol). The resulting mixture was stirred at room temperature for 1 h until a clear brown solution formed. Another portion of $Cu(O_2CMe)_2\cdot H_2O$ (0.20 g, 1 mmol) in dmso (10 cm^3) was added, and heated at 80 °C for 5 h. The green precipitate formed was filtered off, washed with ethanol and dried *in vacuo*. Yield: 0.72 g (94%) (Found: C, 45.45; H, 3.25; Cu, 16.5; N, 9.25. Calc. for $C_{29}H_{25}Cu_2N_5O_{12}$: C, 45.45; H, 3.80; Cu, 16.60; N, 9.15%).

Trinuclear complexes. All complexes were synthesized in a similar manner. A typical preparation is as follows: H_4L^1 (0.403 g, 1 mmol) suspended in ethanol (40 cm^3) was treated with $Cu(ClO_4)_2\cdot 6H_2O$ (1.48 g, 4 mmol) in ethanol (10 cm^3). The resulting mixture was refluxed for 5 h. The green precipitate formed was filtered off, washed freely with portions of hot ethanol and dried *in vacuo*. This grass-green precipitate in dmso (10 cm^3) was heated at 80 °C for 2 h, and the resultant orange-red solution was cooled. Ethanol (50 cm^3) was added and a red-brown crystalline precipitate **1** appeared. Yield: 0.91 g (75%) (Found: C, 25.5; H, 3.85; Cu, 15.65; N, 5.75. Calc. for $C_{31}H_{47}Cl_2Cu_3N_5O_{19}S_5$: C, 25.5; H, 3.85; Cu, 15.65; N, 5.75%). The complexes $[Cu_3L(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$ ($L = L^2$–L^6) were obtained similarly: **2**, yield 0.97 g (78%) (Found: C, 31.85; H, 4.10; Cu, 15.35; N, 5.60. Calc. for $C_{33}H_{51}Cl_2Cu_3N_5O_{19}S_5$: C, 31.85; H, 4.10; Cu, 15.3; N, 5.65%); **3**, yield 0.97 g (73%) (Found: C, 35.25; H, 4.75; Cu, 14.3; N, 5.25. Calc. for $C_{39}H_{63}Cl_2Cu_3N_5O_{19}S_5$: C, 35.25; H, 4.75; Cu, 14.35; N, 5.25%); **4**, yield 1.01 g (79%) (Found: C, 31.05; H, 4.00; Cu, 14.9; N, 5.45. Calc. for $C_{33}H_{51}Cl_2Cu_3N_5O_{19}S_5$: C, 31.05; H, 4.00; Cu, 14.95; N, 5.50%); **5**, yield: 0.90 g (70%) (Found: C, 28.9; H, 3.50; Cu, 14.8; N, 5.50. Calc. for $C_{31}H_{45}Cl_4Cu_3N_5O_{19}S_5$: C, 28.95; H, 3.50; Cu, 14.85; N, 5.45%); **6**, yield 1.13 g (82%) (Found: C, 27.05; H, 3.25; Cu, 13.85; N, 5.15. Calc. for $C_{31}H_{45}Br_2Cl_2Cu_3N_5O_{19}S_5$: C, 27.1; H, 3.30; Cu, 13.85; N, 5.10%).

Crystallography

Crystal data. $C_{31}H_{47}Cl_2Cu_3N_5O_{19}S_5$ **1**, $M = 1215.64$, monoclinic, space group $P2_1/n$, $a = 15.672(8)$, $b = 19.809(2)$, $c = 15.442(3)$ Å, $\beta = 94.73(3)°$, $U = 4777.6(7)$ Å^3, μ(Mo-Kα) = 8.54 cm^{-1}.

Data collection and reduction. Single crystals of complex **1** were obtained by slow vapour diffusion of ethanol into a dmso solution of the complex. A crystal with approximate dimensions 0.20 × 0.30 × 0.35 mm sealed in a glass tube was used for the X-ray diffraction study. Intensities and lattice parameters were obtained on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 20 ± 1 °C. The diffraction range was $0 < \theta < 25°$. For the intensity data collection the θ–2θ scan mode was used. The octant measured was $\pm h$, $\pm k$, $\pm l$. The intensity data were corrected for Lorentz-polarization factors, and absorption effects.[32] 9018 Unique reflections were collected, 3494 of which with $I > 3\sigma(I)$ were assumed to be observed.

The structure was solved by direct methods and Fourier synthesis. Refinement was carried out by full-matrix least-squares, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ with equal weights ($w = 1$) for all reflections. Atomic scattering factors were taken from ref. 33. All non-hydrogen atoms were found from the *E* map; hydrogen atoms were located geometrically but not refined. The final values of *R* and *R′* were 0.0646 and 0.0694, respectively. All the calculations were carried out on a P2P11/44 computer using the SDP program. [34]

Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/276.

Results and Discussion

Synthesis and general properties

The trinuclear copper complexes $[Cu_3L(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$ **1** ($L = L^1$, R = H), **2** ($L = L^2$, R = Me), **3** ($L = L^3$, R = Bu^t), **4** ($L = L^4$, R = OMe), **5** ($L = L^5$, R = Cl) and **6** ($L = L^6$, R = Br) are air stable both in the solid state and in solution. In the absence of dmso, some complexes were isolated, which have similar properties, suggesting a similar structure to that of **1**. Relevant IR spectral data are summarized in Table 1.

The infrared spectra (KBr pellets) of free H_4L show the presence, in the ν(C=O) stretching region, of an intense absorption band at *ca.* 1685 cm^{-1}. For the trinuclear complexes the absorption bands due to ν(NH) stretching and the amide I band ν(C=O) were absent, but a new strong band centred at *ca.* 1600 cm^{-1}, the C=N−N=C stretching vibration, can be observed, in good agreement with data obtained for analogous trinuclear uranyl complexes,[26,27] indicating that the ligands are coordinated in the enolic form. The phenolic ν(C−O) stretching and bending vibrations observed at *ca.* 1530 and 1270 cm^{-1} for the free H_4L are displaced to the higher frequency by *ca.* 20 cm^{-1} for the trinuclear copper(II) complexes. This is probably consistent with an increase in C−O bond length and extended delocalization of the π system of the azine moiety.[35,36] For the complexes a medium strong peak at *ca.* 1020 cm^{-1} is ascribed to the S=O stretching mode of dmso.[37,38] This shift to lower frequency of the S=O stretching band compared with free

Table 1 Selected IR spectral, molar conductance and visible spectral data for complexes **1**–**6**

	IR			λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
Complex	ν(C=N)	ν(C–O)	Λ_M/ohm^{-1} cm^2 mol^{-1}	c.t.	d–d
1	1605	1550, 1290	240	315 (20 042)	425 (20 855), 730 (451)
2	1615	1548, 1287	235	310 (20 100)	420 (21 020), 728 (438)
3	1600	1552, 1292	242	318 (20 080)	428 (20 785), 725 (446)
4	1610	1553, 1295	241	313 (19 970)	423 (20 975), 723 (453)
5	1612	1545, 1285	238	317 (19 982)	427 (21 005), 726 (417)
6	1608	1550, 1293	245	315 (20 017)	423 (20 820), 728 (465)

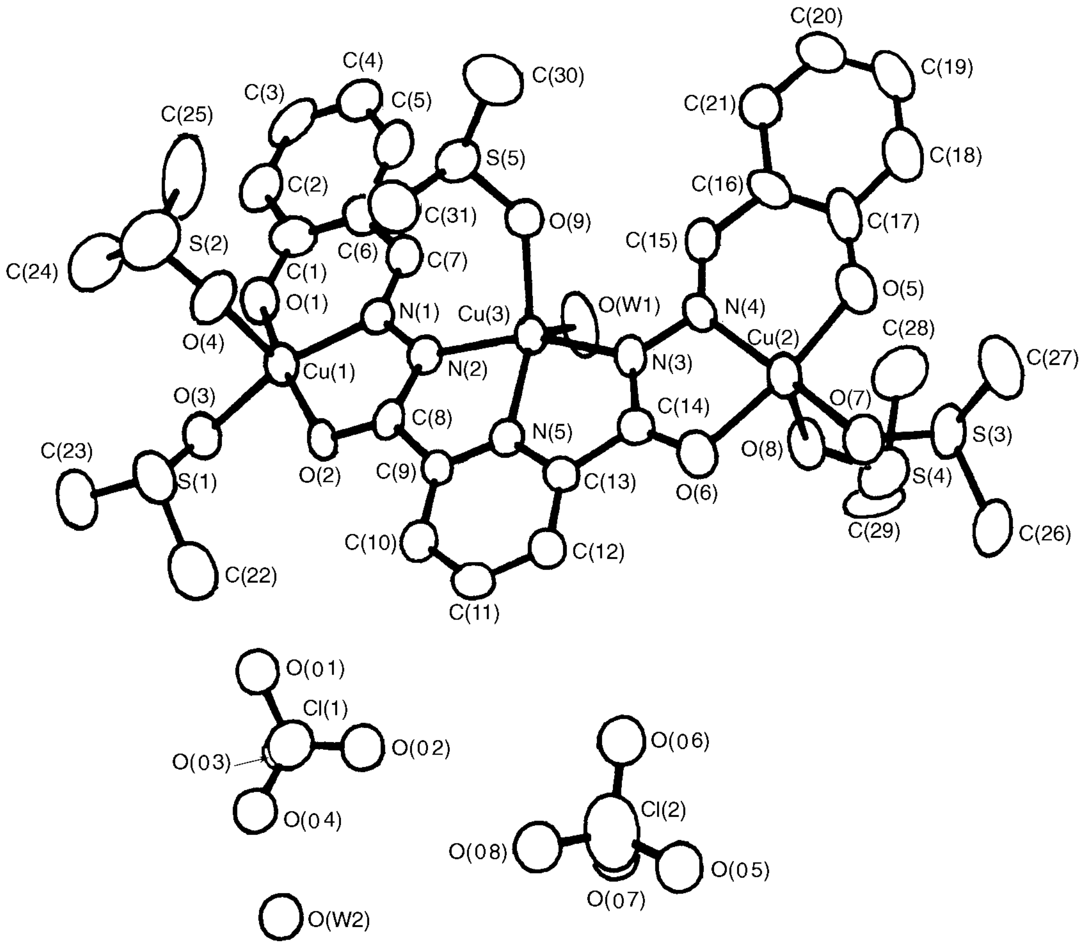


Fig. 1 An ORTEP[43] view of complex **1** with the atom numbering scheme

gaseous dmso (1102 cm^{-1}) is consistent with O-co-ordinated dmso.[39] All of the perchlorate salts show strong bands near 1090–1100 (antisymmetric stretch) and sharp bands at 620–625 cm^{-1} (antisymmetric bend), indicative of unco-ordinated perchlorate anions.

The molar conductance of complex **1**′ in dmso is nearly zero, indicating that the complex behaves as a non-electrolyte. Conductance data for the trinuclear complexes in dmso at *ca.* 10^{-3} mol dm^{-3} at 25 °C are in the range 230–250 ohm^{-1} cm^2 mol^{-1}, indicating that all the complexes **1**–**6** are 1:2 electrolytes in solution,[40] and non-co-ordination of ClO_4^-, is in accord with the IR spectra.

The UV/VIS spectroscopic data for the copper(II) trinuclear complexes have been measured in the range 300–900 nm. The absorption maxima with the corresponding absorption coefficients in dmso solutions are given in Table 1. The compounds have similar spectra, showing two intense bands at *ca.* 31 750 ($\varepsilon \approx 20\,000$) and 23 530 cm^{-1} (21 000 dm^3 mol^{-1} cm^{-1}) which are assigned to the $\pi \longrightarrow \pi^*$ transition associated with the azomethine group and a $d \longrightarrow \pi^*$ transition, respectively. A broad d–d band of Cu^{II} is seen at *ca.* 13 700 cm^{-1}. It has been shown by Hathaway and co-workers[41] that it is possible to predict the stereochemistry of the local copper(II) environment in complexes of unknown crystal structure from the positions and intensities of d–d transitions of CuX_5 chromophores. In general, trigonal-bipyramidal complexes with $^2A_1'$ ground states exhibit a single, relatively intense band at 12 500 ± 1500 cm^{-1}; on the other hand, the electronic spectra of square-based pyramidal complexes consist of two clearly resolved bands in the range 15 000 ± 2000 cm^{-1}. On the basis of the above arguments and the actual crystal structure of complex **1**, a strongly distorted square-pyramidal geometry is assigned to the trinuclear copper(II) centres in complexes **1**–**6** rather than a trigonal-bipyramidal geometry. The splitting of d orbitals in square-planar complexes has been discussed by Nishida and Kida[42] in terms of the effect of π bonding with ligands. The large splitting of the d–d bands in the present complexes indicates the strong π-basic character of the ligands, which can stabilize the higher oxidation state of the metal ion.

Structure of complex 1

The crystal structure of $[Cu_3L^1(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$ with the atom numbering scheme is depicted in Fig. 1. Selected bond distances and angles with their estimated standard deviations are listed in Table 2. Each copper ion is in a distorted square pyramidal environment.

The complex molecule consists of the trinucleating ligand L^1, three Cu ions, five dmso molecules, two water molecules, and two perchlorate ions. Two perchlorate ions and one water molecule involved are free from co-ordination and captured in the lattice. The ligand L^1 co-ordinates with copper(II) ions in two different modes as : (*i*) tridentate in the terminal compartment defined by the hydrazonic nitrogen and phenolic oxygen; (*ii*) in the central chamber defined by the pyridyl nitrogen and two hydrazonic nitrogens. The terminal Cu(1) and Cu(2) have almost the same environments, distorted square pyramidal, with a strongly distorted basal plane made up of NO_2 defined by mode (*i*), the fourth site being occupied by an oxygen of dmso while the oxygen of the other dmso molecule is in the apical site. The bond lengths between Cu and the phenolic oxygen [Cu(1)−O(1) 1.910(9), Cu(2)−O(5) 1.885(10) Å] and the imine nitrogen [Cu(1)−N(1) 1.930(10), Cu(2)−N(4) 1.941(10) Å] are similar to those found in related salicylaldiminato complexes.[44]

Table 2 Selected bond distances (Å) and angles (°) for $[Cu_3L^1(dmso)_5(H_2O)][ClO_4]_2\cdot H_2O$

Cu(1)−O(1)	1.910(9)	O(2)−C(8)	1.264(14)
Cu(1)−O(2)	1.997(8)	O(5)−C(17)	1.30(2)
Cu(1)−O(3)	1.972(9)	O(6)−C(14)	1.279(5)
Cu(1)−O(4)	2.246(10)	N(1)−N(2)	1.399(13)
Cu(1)−N(1)	1.930(10)	N(1)−C(7)	1.30(2)
Cu(2)−O(5)	1.885(10)	N(2)−C(8)	1.34(2)
Cu(2)−O(6)	1.996(9)	N(3)−N(4)	1.396(14)
Cu(2)−O(7)	1.952(9)	N(3)−C(14)	1.32(2)
Cu(2)−O(8)	2.347(11)	N(4)−C(15)	1.28(2)
Cu(2)−N(4)	1.941(10)	N(5)−C(9)	1.321(15)
Cu(3)−O(W1)	2.095(11)	N(5)−C(13)	1.326(14)
Cu(3)−O(9)	2.026(10)	C(1)−C(6)	1.41(2)
Cu(3)−N(2)	2.009(10)	C(6)−C(7)	1.43(2)
Cu(3)−N(3)	2.013(10)	C(15)−C(16)	1.44(2)
Cu(3)−N(5)	1.950(10)	C(16)−C(17)	1.43(2)
O(1)−C(1)	1.33(2)		
O(1)−Cu(1)−O(2)	169.5(4)	Cu(1)−N(1)−N(2)	114.6(8)
O(1)−Cu(1)−O(3)	89.2(4)	Cu(1)−N(1)−C(7)	127.9(8)
O(1)−Cu(1)−O(4)	97.5(4)	Cu(1)−O(1)−C(1)	126.0(8)
O(1)−Cu(1)−N(1)	93.3(4)	Cu(1)−O(2)−C(8)	109.7(8)
O(2)−Cu(1)−O(3)	93.7(4)	Cu(2)−N(4)−N(3)	112.6(7)
O(2)−Cu(1)−O(4)	92.3(4)	Cu(2)−N(4)−C(15)	127.7(9)
O(2)−Cu(1)−N(1)	81.1(4)	Cu(2)−O(5)−C(17)	129.1(9)
O(3)−Cu(1)−O(4)	95.4(4)	Cu(2)−O(6)−C(14)	108.0(8)
O(3)−Cu(1)−N(1)	163.6(4)	Cu(3)−N(2)−C(8)	115.9(7)
O(4)−Cu(1)−N(1)	100.3(4)	Cu(3)−N(3)−C(14)	116.0(8)
O(5)−Cu(2)−O(6)	169.4(4)	Cu(3)−N(5)−C(9)	118.6(8)
O(5)−Cu(2)−O(7)	90.5(4)	Cu(3)−N(5)−C(13)	118.7(8)
O(5)−Cu(2)−O(8)	98.2(5)	O(1)−C(1)−C(6)	122.1(1)
O(5)−Cu(2)−N(4)	92.5(4)	C(1)−C(6)−C(7)	127.0(1)
O(6)−Cu(2)−O(7)	93.7(4)	N(1)−C(7)−N(6)	121.0(1)
O(6)−Cu(2)−O(8)	91.2(4)	N(1)−N(2)−C(8)	109.7(8)
O(6)−Cu(2)−N(4)	82.0(4)	O(2)−C(8)−N(2)	125.0(1)
O(7)−Cu(2)−O(8)	94.9(4)	O(5)−C(17)−C(16)	123.0(1)
O(7)−Cu(2)−N(4)	171.2(5)	C(15)−C(16)−C(17)	124.0(1)
O(8)−Cu(2)−N(4)	92.9(4)	N(4)−C(15)−C(16)	124.0(1)
O(W1)−Cu(3)−O(9)	102.1(4)	O(6)−C(14)−N(3)	126.0(1)
O(W1)−Cu(3)−N(2)	97.6(4)	N(4)−N(3)−C(14)	111.1(9)
O(W1)−Cu(3)−N(3)	94.5(4)	N(2)−C(8)−C(9)	113.0(1)
O(W1)−Cu(3)−N(5)	125.7(4)	N(5)−C(9)−C(8)	114.0(1)
O(9)−Cu(3)−N(2)	101.3(4)	N(5)−C(13)−C(14)	112.0(1)
O(9)−Cu(3)−N(3)	94.0(4)	N(3)−C(14)−C(13)	113.0(1)
O(9)−Cu(3)−N(5)	132.0(4)	N(2)−Cu(3)−N(5)	78.7(4)
N(2)−Cu(3)−N(3)	158.1(4)	N(3)−Cu(3)−N(5)	79.4(4)

Magnetic properties

Magnetic susceptibility measurements were made on powdered samples in the temperature range 80–300 K. The temperature dependences of the magnetic susceptibility (χ_A) and effective magnetic moments (μ_{eff}) per Cu for **1** are shown in Fig. 2. Corresponding data for complexes **2**–**6** are in Table 3.

For a linear copper(II) trinuclear oligomer the magnetic interaction can be modelled quite well by the spin Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$ where $S_1 = S_2 = S_3 = \frac{1}{2}$, which assumes an isotropic exchange interaction and neglects next-nearest-neighbour intratrimer coupling between the end atoms, *e.g.* $J_{13} = 0$. The energy levels of this Hamiltonian can easily be shown to be $E_1 = 0$ $(S = \frac{1}{2})$, $E_2 = J$ $(S = \frac{1}{2})$, $E_3 = -\frac{3}{2}J$ $(S = \frac{3}{2})$. Thus, the magnetic susceptibility obtained from the Van Vleck equation is given by[20] expression (1) where $x = \exp(J/kT)$ and

$$\chi_A = \frac{Ng^2\beta^2}{4k(T-\theta)}\frac{1 + x + 10x^3}{1 + x + 2x^3} + N_\alpha \qquad (1)$$

other symbols have their usual meanings. The cryomagnetic properties of complex **1** are well simulated by this equation, using the magnetic parameters $g = 2.10$, $J = -50$ cm^{-1}, $\theta = -0.65$ K, and $N_\alpha = -270 \times 10^{-6}$ cm^3 mol^{-1}. Similarly good magnetic simulations have been obtained for **2**–**6**. The best-fitting parameters obtained are summarized in Table 3.

The environment around the terminal copper(II) ions is square pyramidal with $(d_{x^2-y^2})^1$ ground states. The moderately strong antiferromagnetic interactions in complexes **1**–**6** can be interpreted by considering two contrasting effects: (*i*) the magnetic orbitals of terminal copper(II) ions, $d_{x^2-y^2}$, point from the metal toward the four nearest neighbours and overlap on either side of the intraligand bridge, which favours strong ferromagnetic interactions; (*ii*) the geometry around the central copper ion strongly deviates from a square pyramid toward a trigonal bipyramid, but is still far from a purely trigonal-bipyramidal chromophore as evidenced by the d–d transitions in the UV/VIS spectra and the crystal structure. The increase in d_{z^2} character of the magnetic orbital of Cu(3) in the structure reduces the magnetic exchange interaction. The resulting general effect led to $J = -40$ to -65 cm^{-1}.

The Cu···Cu separations in complexes **1**–**6** are so large that the exchange integral cannot originate from direct interaction, and the observed spin coupling is likely to arise through a superexchange mechanism operating *via* Cu−N−N−Cu−N−N−Cu linkages. Scheme 1 shows the orientation of the relevant orbitals.

Of the two possible orbital-exchange pathways, σ and π, the σ pathway is considered to provide the dominant antiferromagnetic interaction. Owing to the symmetry properties of the σ interaction, $d_{x^2-y^2}$ orbitals on the copper(II) ions and σ

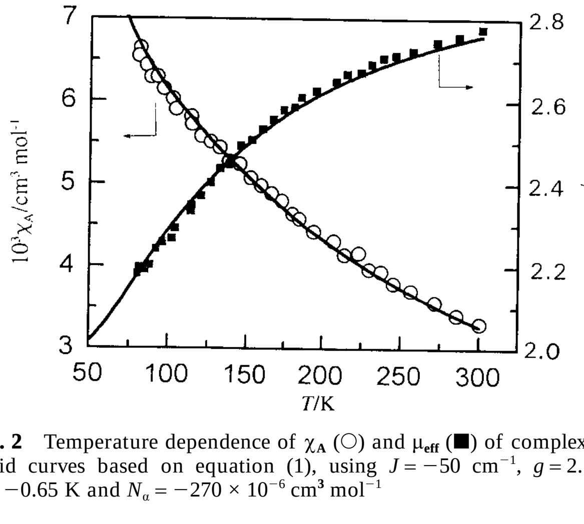
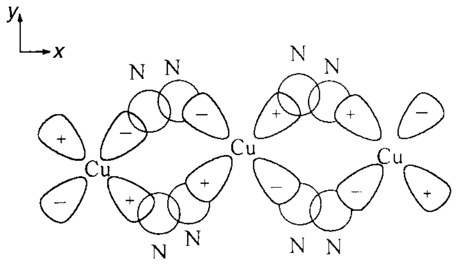


Fig. 2 Temperature dependence of χ_A (○) and μ_{eff} (■) of complex **1**. Solid curves based on equation (1), using $J = -50$ cm^{-1}, $g = 2.10$, $\theta = -0.65$ K and $N_\alpha = -270 \times 10^{-6}$ cm^3 mol^{-1}

Table 3 Magnetic data for complexes **1**–**6**

Complex	μ_{eff}/μ_B 300 K	80 K	*g*	*J*/cm^{-1}	θ	10^6*N*$_\alpha$/cm^3 mol^{-1}
1	2.824	2.099	2.10	−50	−0.65	−270
2	2.860	2.236	2.10	−45	−0.80	−240
3	2.837	2.377	2.10	−48	−0.47	−200
4	2.874	2.217	2.10	−42	−0.53	−250
5	2.774	2.025	2.10	−57	−0.76	−230
6	2.654	1.976	2.10	−63	−0.71	−240



Scheme 1

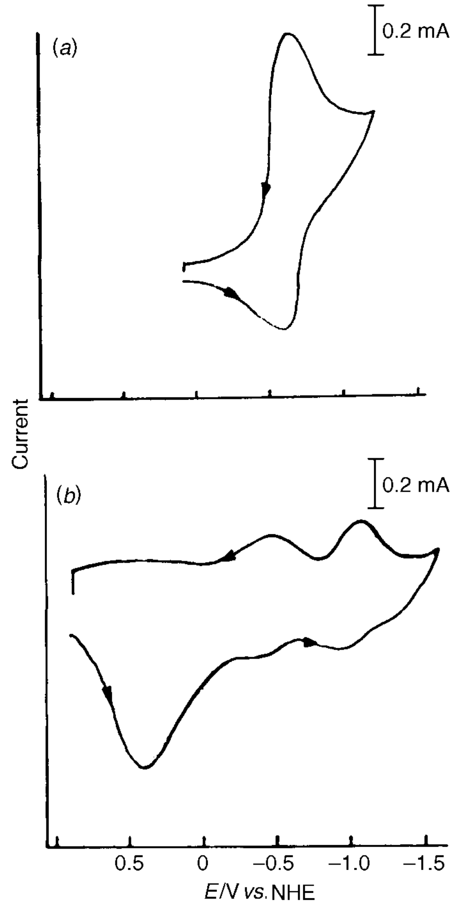


Fig. 3 Cyclic voltammograms of complexes **1**′(*a*) and **1**(*b*) in dmso at a scan rate of 0.2 V s^{-1}

orbitals on the two bridging nitrogen atoms are involved in the exchange pathway for unpaired spin density. This is in accord with the rational description of the antiferromagnetic exchange mechanism by Okawa *et al.*[45] using dimethylglyoximate dianion as bridging ligand.

Electrochemical properties

The general behaviour of the complexes was investigated (in dmso) by cyclic voltammetry. The cyclic voltammogram of complexes **1** and **1**′ is given in Fig. 3. In the potential range +1 to −1.5 V *vs.* NHE, **1**′ shows a reduction wave at −0.70 V. This step is only partially reversible ($I_{p(red)}/I_{p(ox)} \approx 0.95$) even at a scan rate of 5 V s^{-1}. A coulometric experiment indicated that two electrons are involved in this step. The redox scheme $Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{I}$ has been established for the electrochemical behaviour of **1**′. The cyclic voltammetric behaviour of **1** at 0.2 V s^{-1} in the potential range +1.0 to −1.5 V *vs.* NHE shown in Fig. 3 reveals a one-electron oxidation at $E_{pa} = 0.43$ V. When this complex is cathodically scanned (0.0 to −1.5 V) two reduction peaks at $E_{pc}{}^1 = -0.35$ and $E_{pc}{}^2 = -1.03$ V are observed. When the sweep is reversed at −1.5 V toward the anodic direction, a small oxidation wave is observed at ⩾ 0.05 V s^{-1}. By comparing the electrochemical behaviour of **1** with **1**′, the behaviour of the trinuclear copper(II) complexes can be interpreted according to the following scheme: positive potential, $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{-e^-} Cu^{II}Cu^{III}Cu^{II}$; negative potential, $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{+e^-} Cu^{II}Cu^{I}Cu^{II} \xrightarrow{+2e^-} Cu^{I}Cu^{I}Cu^{I}$. The other trinuclear copper(II) complexes exhibit similar electrochemical behaviour.

ESR spectra

The X-band powder ESR spectra at room temperature exhibit a broad and almost symmetrical feature centred at $g = 2.10$. The solution ESR spectrum at room temperature for one-electron oxidation (dmso) of complex **1** exhibits four hyperfine lines, consistent with the interaction of the electron with only copper centres ($I = \frac{3}{2}$), indicating the redox chemistry is metal rather than ligand based.[46]

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