Unsymmetric Dicopper(II) Complexes of Dinucleating Ligands bearing Chemically Distinct Co-ordination Environments

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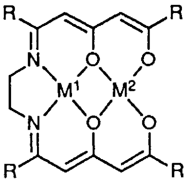
Dicopper(II) complexes of unsymmetrical dinucleating Schiff-base ligands bearing chemically distinct co-ordination sites have been prepared and their properties studied. The ligands were derived from the condensation of 4-bromo-2-formyl-6-(4-methylpiperazin-1-ylmethyl)phenol and 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol with 2-(aminomethyl)pyridine, 2-(2-aminoethyl)pyridine, and 2-(aminomethyl)-4-nitrophenol.

The evolution of dinucleating ligands has stimulated much interest in their potential application as models for dinuclear metallo-biosites.[1,2] Such ligands have been classified as compartmental ligands, isolated donor sets, extendable macrotricycles, and separated donor sets and each of these has been further sub-divided. With the exception of a few 'side-off' compartmental ligands,[1,3,4] the donor sets that these systems present to each metal ion are identical. However, in dinuclear transition-metal bio-sites the metal ions are often found in chemically or geometrically distinct environments. For example the unsymmetrical nature of the dicopper site in haemocyanin is demonstrated in the X-ray crystal structure of deoxyhaemocyanin[5] and sequence homology studies on tyrosinases have shown that whilst one of the copper sites has been highly conserved throughout evolution the structure of the second copper site has been quite variable.[6] For most of the tyrosinases three histidines are suitably positioned to co-ordinate each of the coppers, but for a few cases Cu_B is apparently only co-ordinated to two histidines and this latter observation led to the suggestion that for modelling studies unsymmetrical dinucleating ligands should be viewed as desirable targets.[2]

The non-equivalent nature of the metal co-ordination sites in 'side-off' compartmental ligands allows the preparation of hetero- and homo-dinuclear transition-metal complexes **1**.[7]



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Unfortunately these are of limited use as model compounds for the copper biosites as they are inflexible systems with restricted co-ordination geometries and they contain incorrect terminal and endogenous bridging ligand types. The Cu–Cu separation is *ca.* 3.0 Å, compared with those of *ca.* 3.5 Å at the biosites, and they are unable to support relevant exogenous bridging groups.

'End-off' compartmental ligands are better candidates for the provision of distinct co-ordination environments. Many of this sub-group of dinucleating ligands are derived from a 2,6-disubstituted phenol (Fig. 1). Ligands of this type readily form dinuclear transition-metal complexes that can co-ordinate either one or two exogenous bridging groups.[8–11] They strongly favour the formation of dimetallic species because of the enforced ideal distance between the donor sets, and the presence of the endogenously bridging phenolate group. Functionalised dialkylaminomethyl sidearms can be introduced at the activated 2, 4 and 6 positions of phenol by condensation with an appropriate secondary amine and formaldehyde[12] and this variation on the Mannich reaction has been used successfully with a 4-substituted phenol to prepare the symmetric dinucleating ligand **2**.[13,14]

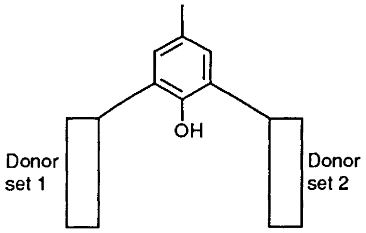
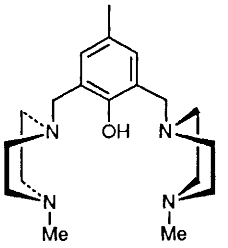


Fig. 1 Schematic representation of 'end-off' compartmental ligands



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In the present work the Mannich reaction has been used to introduce a single pendant arm into a 2,4-disubstituted phenol. Subsequent reaction of the aldehyde group provided a route into asymmetric dinucleating ligands as condensation of 5-bromosalicylaldehyde with formaldehyde and a secondary amine yielded versatile aldehydes which by condensation with primary amines then gave 'side-off' dinucleating Schiff-base ligands. The preparation and properties of dinuclear copper(II) complexes of these ligands are herein reported.

Experimental

Elemental analyses were carried out by the Sheffield University microanalytical service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrophotometer (4000–600 cm^{-1}) or 1710 Fourier-transform spectrophotometer (4000–400 cm^{-1}), electronic absorption spectra using a Philips PU8720 UV–visible scanning spectrophotometer operating in the range

280–900 nm, ^1H NMR spectra at 220 MHz on a Perkin-Elmer R34 spectrometer, and ^{13}C NMR spectra (62.9 MHz) using a Bruker AM-250 spectrometer. Electron impact (EI) and chemical impact (CI, ammonia) spectra were recorded on a Kratos MS25 instrument operating at low resolution and positive-ion fast atom bombardment (FAB) mass spectra on a Kratos MS80 spectrometer. The matrix solvent used was 3-nitrobenzyl alcohol unless otherwise stated.

Magnetic susceptibility experiments were performed with a variable-temperature superconducting SHE900 magnetometer operating at 5 kG (0.5 T) in the range 5–300 K. Diamagnetic corrections were evaluated by using Pascal's constants. The samples were placed in KELF buckets which were calibrated independently. The data were least-squares fitted to the Bleaney–Bowers equation. The quantity minimised in the fitting process was $[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2$. The quality of the fit was estimated through the statistical indicator $R = [(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/N(\chi_M T)_{obs}^2$ where N is the number of measurements; R amounted to 4.7×10^{-7}.

CAUTION: Although no problems were encountered during the preparation of the perchlorate salts described below, suitable care and precautions should be taken when handling such potentially hazardous compounds.

4-Bromo-2-formyl-6-(4-methylpiperazin-1-ylmethyl)phenol **3**.—(*a*) *As the hydrobromide salt* **3**·2HBr. *N*-Methylpiperazine (4.5 g, 45 mmol), paraformaldehyde (2.2 g, 73 mmol), and 5-bromosalicylaldehyde (11.0 g, 55 mmol) were refluxed in ethanol (150 cm^3) for 18 h. The initial deep orange solution slowly became paler over this period. The yellow solution was cooled to room temperature and aqueous hydrobromic acid (48%, 15 cm^3) added with stirring. The hydrobromide salt of **3** precipitated as a pale yellow powder. Recrystallisation from ethanol–48% HBr gave yellow needles of **3**·2HBr (13.3 g, 62%) (Found: C, 32.80; H, 4.10; Br, 50.10; N, 5.80. $C_{13}H_{19}Br_3N_2O_2$ requires C, 32.90; H, 4.00; Br, 50.50; N, 5.90%), ν(C=O) 1650 cm^{-1}.

(*b*) *As the neutral species* **3**. The salt **3**·2HBr (4.00 g, 8.4 mmol) was taken up in water (100 cm^3) and neutralised with excess of potassium carbonate (2.5 g, 18 mmol). The intense yellow, cloudy solution was extracted with CH_2Cl_2 (2 × 50 cm^3), the extracts were combined and the solvent removed under reduced pressure without drying. The resulting sticky yellow oil was taken up in diethyl ether (100 cm^3), dried over $MgSO_4$, filtered, and the solvent removed to give a pale yellow solid. Recrystallisation from diethyl ether gave yellow crystals of compound **3** (2.13 g, 81%), m.p. 83–84 °C (Found: C, 50.00; H, 5.50; Br, 25.40; N, 8.80. $C_{13}H_{17}BrN_2O_2$ requires C, 49.90; H, 5.50; Br, 25.50; N, 8.90%); *m/z* (EI) 312 (M^+, 19%), (CI) 313 ($M + H^+$, 100%), for ^{79}Br, ν(C=O) 1780 cm^{-1}.

4-Bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol **4**.—(*a*) *As the hydrobromide salt* **4**·2HBr·2H_2O. *N,N,N'*-Triethyl-1,2-diaminoethane (6.0 g, 42 mmol), 5-bromosalicylaldehyde (10.0 g, 50 mmol), and paraformaldehyde (2.0 g, 67 mmol) were refluxed in ethanol (150 cm^3) for 4 h. The solution was cooled to room temperature, hydrobromic acid (48%, 15 cm^3) added, and the solvent removed under reduced pressure. Ethanol (100 cm^3) was added and distilled off under reduced pressure. This operation was performed three more times, after which the resulting brown glassy solid had begun to crystallise. Trituration with ethanol eventually gave a light brown powder. Recrystallisation from ethanol–48% HBr gave **4**·2HBr·2H_2O as a white powder (12.6 g, 54%) (Found: C, 34.50; H, 5.60; Br, 43.40; N, 4.90. $C_{16}H_{31}Br_3N_2O_4$ requires C, 34.60; H, 5.60; Br, 43.20; N, 5.05%), ν(C=O) 1660 cm^{-1}.

(*b*) *As the neutral species* **4**.—The same procedure was used as for the preparation of compound **3**. Recrystallisation from diethyl ether gave yellow crystals (79%), m.p. 81–82 °C (Found: C, 54.00; H, 7.10; Br, 22.30; N, 7.60. $C_{16}H_{25}BrN_2O_2$ requires C, 53.80; H, 7.05; Br, 22.40; N, 7.80%); *m/z* (CI) 357 ($M + H^+$, 42%), for ^{79}Br, ν(C=O) 1645 cm^{-1}.

N-Hydroxymethylbenzamide and *N*-benzoyl-2-hydroxy-5-nitrobenzylamine were prepared by the literature method.[15]

2-Hydroxy-5-nitrobenzylamine Hydrobromide.—*N*-Benzoyl-2-hydroxy-5-nitrobenzylamine (5.45 g, 20 mmol) was suspended in a mixture of hydrobromic acid (48%, 100 cm^3) and water (100 cm^3), and refluxed until the solution became clear (*ca.* 24 h). Care was taken during the first few hours as the reaction mixture tended to froth and climb up the condenser. The clear light green solution was cooled in ice and the majority of the benzoic acid crystallised out. The solution was filtered (sinter) and the filtrate washed with diethyl ether to extract any remaining benzoic acid. The resulting aqueous solution was reduced to near dryness under reduced pressure, ethanol (100 cm^3) added and removed. This procedure was repeated until a yellow powder only slightly soluble in ethanol was obtained. Recrystallisation from propan-1-ol–diethyl ether gave 2-hydroxy-5-nitrobenzylamine hydrobromide as a yellow powder (3.79 g, 76%) (Found: C, 33.90; H, 3.90; Br, 31.80; N, 11.10. $C_7H_9BrN_2O_3$ requires C, 33.80; H, 3.60; Br, 32.10; N, 11.25%). IR 1490 and 1350 cm^{-1} (arylNO_2); $\delta_H(D_2O)$ 8.21 (1 H, d), 8.09 (1 H, double doublet), 7.02 (1 H, d), and 4.28 (2 H, s).

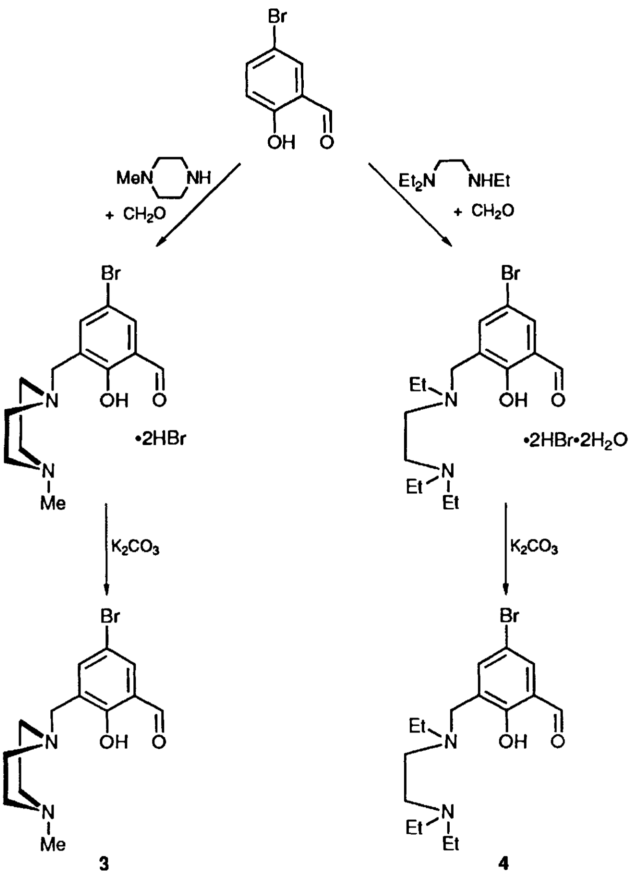
$[Cu_2Br(HCO_2)(H_2O)L^1][ClO_4]$.—The salt **3**·2HBr (0.48 g, 1 mmol), 2-aminomethylpyridine (0.11 g, 1 mmol), and triethyl orthoformate (0.5 cm^3) were refluxed in methanol (50 cm^3) for 1.5 h to give a clear, golden-yellow solution. Sodium hydroxide (pellets, 0.16 g, 4 mmol) was added and the mixture refluxed for 10 min. The solution was allowed to cool (*ca.* 10 min) and copper(II) perchlorate hexahydrate (0.75 g, 2 mmol) added with stirring. The clear, intense green solution was filtered and clusters of dark green microcrystals were deposited upon standing (*ca.* 3 d). The crystalline product was filtered off, washed with methanol then diethyl ether and air dried, whereupon the crystals lost solvent and turned to a green powder (0.32 g, 41%) (Found: C, 31.50; H, 3.25; Br, 20.60; Cl, 4.60; N, 7.10. $C_{20}H_{25}Br_2ClCu_2N_4O_8$ requires C, 31.10; H, 3.30; Br, 20.70; Cl, 4.60; N, 7.30%).

$[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$.—This was prepared as above but using **4**·2HBr·2H_2O (0.55 g, 1 mmol). Dark brown microcrystals (0.21 g, 26%) (Found: C, 33.80; H, 4.35; Br, 19.30; Cl, 4.30; N, 6.70. $C_{23}H_{33}Br_2ClCu_2N_4O_8$ requires C, 33.90; H, 4.10; Br, 19.60; Cl, 4.35; N, 6.90%).

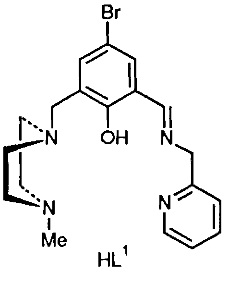
$[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$.—The salt **4**·2HBr·2$H_2O$ (0.55 g, 1 mmol), 2-aminomethylpyridine (0.11 g, 1 mmol), and triethyl orthoformate (0.5 cm^3) were refluxed in methanol (80 cm^3) for 2 h. Sodium hydroxide (0.16 g, 4 mmol) was added and the mixture refluxed for 1 h. The yellow solution was cooled slightly and copper(II) bromide (0.68 g, 3 mmol) added. Once all the solid had dissolved the dark brown solution was filtered and brown rhombohedral crystals were deposited upon standing (*ca.* 24 h) (0.35 g, 38%) (Found: C, 29.80; H, 3.50; Br, 34.30; N, 6.00. $C_{46}H_{62}Br_8Cu_6N_8O_6$ requires C, 30.00; H, 3.40; Br, 34.70; N, 6.10%).

$[Cu_2Br(HCO_2)(H_2O)_2L^3][ClO_4]$.—This was prepared as for $[Cu_2Br(HCO_2)(H_2O)L^1][ClO_4]$ but using 2-aminoethylpyridine (0.12 g, 1 mmol). Thin green plates (0.44 g, 55%) (Found: C, 31.60; H, 3.70; Br, 19.80; Cl, 4.40; N, 6.60. $C_{21}H_{29}Br_2ClCu_2N_4O_9$ requires C, 31.40; H, 3.60; Br, 19.90; Cl, 4.40; N, 7.00%).

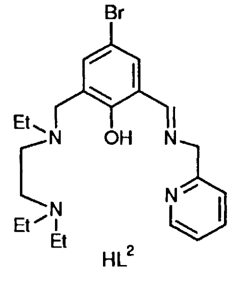
$[Cu_2Br(HCO_2)(MeOH)L^4][ClO_4]$.—This was prepared as for $[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$ but using 2-aminoethylpyridine (0.12 g, 1 mmol). Dark green rhombohedral plates (0.40 g, 47%) (Found: C, 35.40; H, 4.30; Br, 18.60; Cl, 4.10; N, 6.40. $C_{25}H_{37}Br_2ClCu_2N_4O_8$ requires C, 35.60; H, 4.40; Br, 18.90; Cl, 4.20; N, 6.60%).



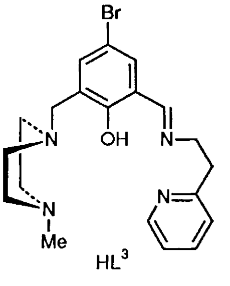
Scheme 1



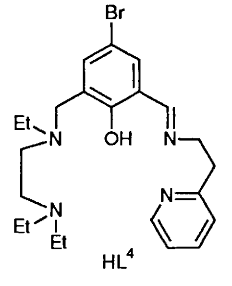
HL^1



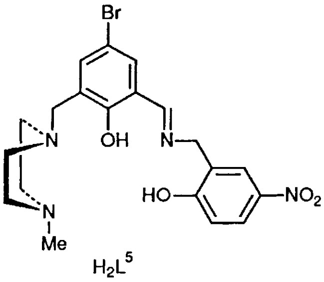
HL^2



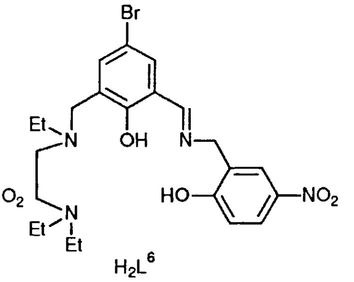
HL^3



HL^4



H$_2$L^5



H$_2$L^6

[$Cu_2(OMe)Br(MeOH)_2L^5$].—The salt **3**·2HBr (0.24 g, 0.5 mmol), 2-hydroxy-5-nitrobenzylamine hydrobromide (0.13 g, 0.5 mmol), and triethylamine (0.15 g, 1.5 mmol) were refluxed in methanol (20 cm^3) for 30 min. Addition of copper(II) perchlorate (0.37 g, 1 mmol) resulted in the immediate formation of a green precipitate which mostly redissolved upon addition of more triethylamine (0.15 g, 1.5 mmol) and refluxing. The dark green solution was cooled and trace amounts of a white powder precipitated upon standing (*ca.* 4 h). The solution was filtered and the residue discarded. Clean, dark green microcrystals were deposited after *ca.* 2 d (0.28 g, 37%) (Found: C, 36.10; H, 3.90; Br, 20.60, 20.70; N, 7.70. $C_{23}H_{32}Br_2Cu_2N_4O_7$ requires C, 36.20; H, 4.20; Br, 20.90; N, 7.30%).

[$Cu_2(OH)(MeOH)L^6$][ClO_4].—This was prepared as above but using the salt **4**·2HBr·2H$_2$O (0.28 g, 0.5 mmol). The product was isolated as an emerald-green powder (0.13 g, 17%) (Found: C, 36.60; H, 4.20; Br, 10.15; Cl, 4.50; N, 7.10. $C_{24}H_{34}BrClCu_2N_4O_{10}$ requires C, 36.90; H, 4.40; Br, 10.20; Cl, 4.50; N, 7.20%).

Results and Discussion

Ligand Synthesis.—Condensation of 5-bromosalicylaldehyde with formaldehyde and the appropriate secondary amine gave the versatile aldehydes **3** and **4** which were initially isolated and purified as dihydrobromide salts (Scheme 1). The free aldehydes may be liberated upon neutralisation with a mild base such as potassium carbonate.

In the IR spectra of compounds **3** and **4** the position of the aldehyde band ν(CO) is variable occurring at 1625 and 1680 cm^{-1} for **3**·2HBr and **3**, and at 1660 and 1645 cm^{-1} for **4**·2HBr·2H$_2$O and **4** respectively. This range of values indicates the presence of free and hydrogen-bonded aldehyde functions. The CI (NH_3) mass spectra of the free aldehydes **3** and **4** give $M + H^+$ peaks (^{79}Br isotope) at 313 (100%) and 357 (42%) respectively. The ^{1}H and ^{13}C NMR spectra of both aldehydes and their salts are assigned as in Tables 1 and 2.

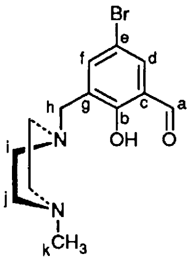
Condensation of the aldehydes **3** and **4** with primary amines gave Schiff bases that are potentially unsymmetric dinucleating ligands. In order to introduce a flexible phenolic sidearm into these systems 2-(aminomethyl)-4-nitrophenol was prepared; reaction of *N*-hydroxymethylbenzamide[15] with 4-nitrophenol gave exclusively the monosubstituted product 2-(benzoylaminomethyl)-4-nitrophenol. Hydrolysis of the amide group gave 2-(aminomethyl)-4-nitrophenol which was isolated as the hydrobromide salt.

The aldehydes **3** and **4** were condensed with 2-(aminomethyl)pyridine, 2-(2-aminoethyl)pyridine, and 2-(aminomethyl)-4-nitrophenol to give the Schiff base ligands HL^1–HL^4, H$_2$L^5 and H$_2$L^6 which were not isolated but used *in situ*.

Dinuclear Copper(II) *Complexes of the Unsymmetric Schiff Bases.*—Symmetric dinucleating ligands can only lead to minor differences in metal environment upon complexation, and this is always due to steric constraints imposed by other ligands or by the metals themselves. Therefore a necessary step towards the synthesis of appropriate models for dinuclear metallo-proteins and -enzymes is the preparation of dinucleating ligands that can provide chemically distinct donor sets.

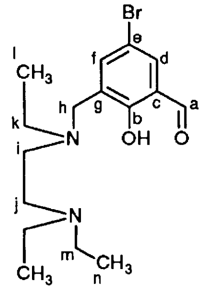
Many dinuclear copper(II) complexes of 'end-off' compartmental ligands incorporating an endogenous phenolate bridging group have been reported.[2] Although the crystal structure of deoxyhaemocyanin excludes the presence of a protein-based endogenous bridge it has been stated that a structure having much better resolution is required to settle the question of whether there might be a hydroxide acting as a bridging ligand.[5,16] Consequently it is not unreasonable to view dinuclear copper(II) complexes of 'end-off' compartmental ligands incorporating an endogenous phenolate bridging group as suppositional models for the dicopper(II) site.[17] These

Table 1 Proton and ^{13}C NMR assignments for compounds **3** and **3**·2HBr



	3·2HBr				**3**		
	$\delta_H(D_2O)$	$\delta_C(D_2O)$			$\delta_H(CDCl_3)$	$\delta_C(CDCl_3)$	
H_a	10.00 (1 H, s)	C_a	197.2	H_a	10.27 (1 H, s)	C_a	189.5
H_d	8.15 (1 H, d)	C_b	158.3	H_d	7.77 (1 H, d)	C_b	160.4
H_f	8.06 (1 H, d)	C_f	142.4	H_f	7.39 (1 H, d)	C_f	137.1
H_h	4.65 (2 H, s)	C_d	139.1	H_h	3.73 (2 H, s)	C_d	130.3
H_i/H_j	3.80 (8 H, br s)	C_g	122.2	H_i	2.65 (4 H, br s)	C_g	125.5
		C_c	118.4	H_j	2.53 (4 H, br s)	C_c	124.1
H_k	3.12 (3 H, s)	C_e	111.5	H_k	2.31 (3 H, s)	C_e	111.1
		C_h	53.5			C_h	59.3
		C_i	50.1			C_i	54.6
		C_j	48.5			C_j	52.4
		C_k	43.0			C_k	45.7

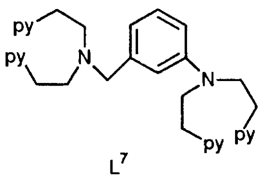
Table 2 Proton and ^{13}C NMR assignments for compounds **4** and **4**·2HBr·2H_2O



	4·2HBr·2H_2O				**4**		
	$\delta_H(CDCl_3)$	$\delta_C(CDCl_3)$			$\delta_H(CDCl_3)$	$\delta_C(CDCl_3)$	
H_a	9.90 (1 H, s)	C_a	197.9	H_a	10.40 (1 H, s)	C_a	189.5
H_d	8.11 (1 H, d)	C_b	159.1	H_d	7.75 (1 H, d)	C_b	161.9
H_f	8.03 (1 H, d)	C_f	142.9	H_f	7.29 (1 H, d)	C_f	137.2
H_h	4.54 (2 H, s)	C_d	139.8	H_h	3.64 (2 H, s)	C_d	129.4
H_i/H_j	3.73 (4 H, s)	C_g	123.3	H_i/H_j	2.67 (4 H, m)	C_g	127.7
H_k	3.40 (2 H, q)	C_c	120.4	H_m	2.59 (4 H, q)	C_c	124.9
H_m	3.35 (4 H, q)	C_e	112.7	H_k	2.57 (2 H, q)	C_e	109.9
H_l	1.46 (3 H, t)	C_h	52.1	H_n	1.06 (6 H, t)	C_h	54.4
H_n	1.37 (6 H, t)	C_i	49.7	H_l	1.05 (3 H, t)	C_i	49.6
		C_j	49.4			C_j	49.5
		C_k	47.6			C_k	47.2
		C_m	46.8			C_m	46.1
		C_l	9.2			C_l	10.7
		C_n				C_n	10.6

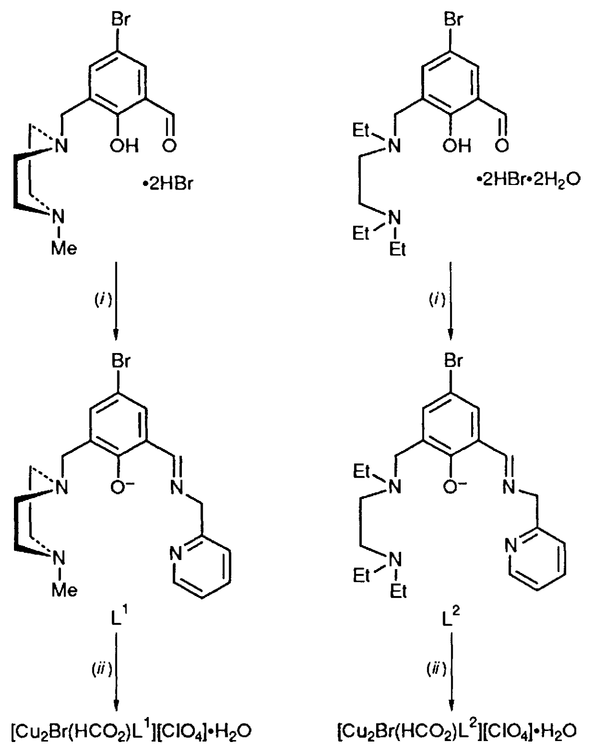
systems have proved useful in understanding aspects of the type III copper proteins such as the magnetic interactions between the coppers as mediated by a variety of bridging groups,[18] and the activation and subsequent reaction of co-ordinated dioxygen.[19]

To date all 'end-off' compartmental ligands used to prepare potential model compounds for type III copper proteins have been symmetrical with two formally equivalent copper co-ordination environments. Although small departures from total symmetry are usually present in the corresponding dinuclear copper complex they are not large and may often only exist in the solid state. A recent communication has reported a ligand L^7 which can be regarded as spatially unsymmetrical but in which the two pendant arms bear identical donor atoms.[20] In contrast condensation of the functionalised salicylaldehydes **3** and **4** with primary amines gives the present dinucleating Schiff-base ligands which are spatially and co-ordinatively unsymmetric. These 'end-off' compartmental ligands contain two metal co-ordination sites, the non-equivalence of which depends upon the nature of the primary amine used and so will give dinuclear copper(II) complexes in which the copper ions are in chemically distinct environments.



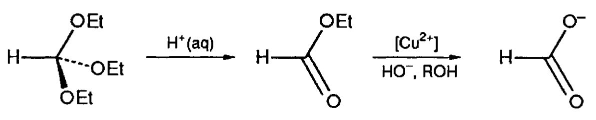
L^7

Reaction of 3•2HBr with 2-aminomethylpyridine in the presence of triethyl orthoformate in methanol (*ca.* 2 h reflux) gave a golden-yellow solution containing the dinucleating Schiff-base ligand HL^1. The triethyl orthoformate acts as a water scavenger, the removal of which helps drive the condensation to completion. Addition of 4 equivalents of sodium hydroxide neutralises the acid present and deprotonates the phenol. The remaining equivalent was added to deprotonate any exogenous bridging group incorporated in the final dinuclear copper(II) complex. Addition of 2 equivalents of copper(II) perchlorate hexahydrate to the above solution resulted in an immediate colour change to intense green. After standing (*ca.* 3 d), dark green microcrystals were deposited which upon drying turned to a green powder that analysed as the dinuclear complex $[Cu_2Br(HCO_2)(H_2O)L^1][ClO_4]$. The analogous reaction with HL^2 gave a green-brown solution from which brown crystals of $[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$ were isolated (Scheme 2).



Scheme 2 (*i*) 2-Aminomethylpyridine; (*ii*) $Cu(ClO_4)_2{\cdot}6H_2O$

Both compounds are found to have incorporated a formate anion which originates from the triethyl orthoformate used in the reaction (Scheme 3). The initial hydrolysis product of triethyl orthoformate under acidic conditions is ethyl formate.[21] Subsequent reaction to give the formate anion may have occurred upon addition of the slight excess of sodium hydroxide, or more likely as a result of metal-catalysed hydrolysis of the ester.[22] Unfortunately symmetric and antisymmetric stretching modes of the formate group could not be identified in the IR spectra of these compounds and therefore could not be used to confirm the above formulations. The crystals obtained were of suitable size for a X-ray diffraction structure determination but decomposed upon irradiation.



Scheme 3

Repetition of the preparation of $[Cu_2Br(HCO_2)(H_2O)L^2]$-$[ClO_4]$ with copper(II) nitrate trihydrate gave similar brown crystals which were more robust and suitable for crystallographic study, the preliminary results of which have been reported.[23] The compound obtained had the apparent formulation $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2]_2[Cu_2Br_4]$ but the population density of the dinuclear copper(I) anion $[Cu_2Br_4]^{2-}$ was less than expected. This was consistent with the elemental analysis of a sample of the crystals, which suggested the presence of a proportion of a non-bromide-containing anion. This was assumed to be nitrate although due to the small amount present and possible disorder this could not be confirmed by either infrared spectroscopy or crystallography. The occupancy of $[Cu_2Br_4]^{2-}$ was calculated to be approximately 60%.[23]

In an attempt to prepare pure the major component of this complex, a solution of HL^2 was treated with 3 equivalents of copper(II) bromide, the theoretical stoichiometry required to maximise the yield of $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2]_2[Cu_2Br_4]$. Crystals were best obtained by using more dilute reaction conditions to slow down the crystallisation process. Both elemental analysis and a second crystal structure determination were consistent with the presence of the $[Cu_2Br_4]^{2-}$ anion in 100% occupancy. Within error the unit-cell dimensions were identical for the two complexes and the two structures were very similar.

The molecular structure of the dinuclear copper(II) cation in $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2]_2[Cu_2Br_4]$ is shown in Fig. 2 and the co-ordination geometry of each copper(II) is summarised in Table 3.[23] The constitution of the deprotonated Schiff-base ligand L^2 is as expected with the phenolate group acting as an endogenous bridge. This bridge is markedly asymmetric with Cu–O distances of 1.91 and 2.22 Å. In addition there are two exogenous bridges: a bromide and a formate. The bromide bridge is also asymmetric with Cu–Br distances of 2.75 and 2.48 Å. This difference is not peculiar to this complex and has been reported for one other bromide-bridged dinuclear copper(II) complex.[24] Interestingly the longer Cu–Br bond is associated with the shorter Cu–O(phenolate) bond and *vice versa*. The formate is bound almost symmetrically with Cu–O distances of

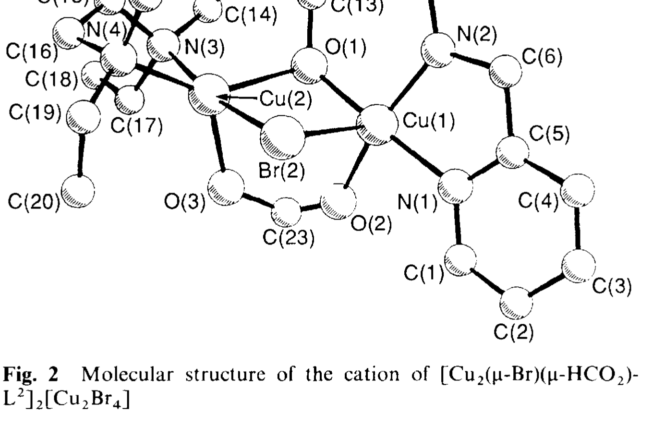


Fig. 2 Molecular structure of the cation of $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)\text{-}L^2]_2[Cu_2Br_4]$

Table 3 Co-ordination environments (bond lengths in Å, angles in °) of Cu(1) and Cu(2) in $[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$

Cu(1)-O(1)	1.908(26)	85.6(5)			
Cu(1)-O(2)	2.006(21)	96.9(6)	89.6(11)		
Cu(1)-N(1)	1.982(32)	96.2(6)	177.5(8)	91.9(11)	
Cu(1)-N(2)	1.886(23)	102.9(7)	94.3(12)	160.1(9)	83.6(12)
		Br(2)	O(1)	O(2)	N(1)
Cu(2)-Br(2)	2.477(6)				
Cu(2)-O(1)	2.217(16)	86.7(6)			
Cu(2)-O(3)	2.128(25)	92.5(7)	83.4(7)		
Cu(2)-N(3)	2.068(29)	169.3(7)	87.8(8)	95.9(9)	
Cu(2)-N(4)	2.094(23)	94.1(8)	145.4(9)	131.0(8)	85.3(10)
		Br(2)	O(1)	O(3)	N(3)

Cu(1)-Cu(2) 3.244(9) Cu(1)-O(1)-Cu(2) 103.4(10) Cu(1)-Br(2)-Cu(2) 76.5(2)

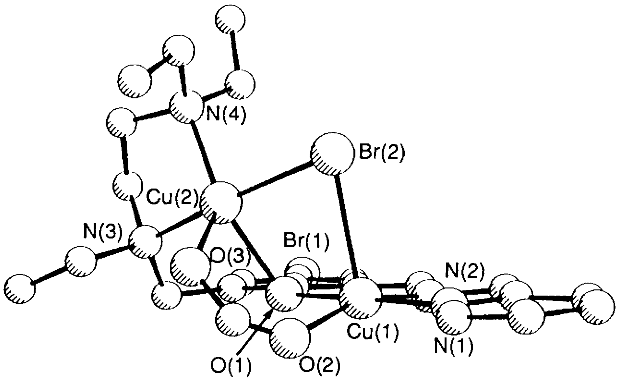
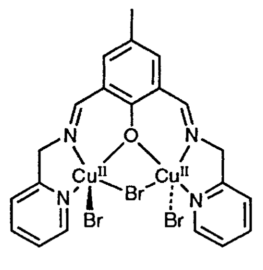
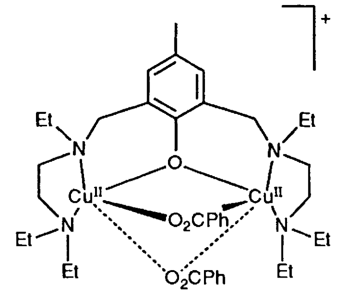


Fig. 3 View of the cation showing the 'buckling' allowed because of the flexibility of the aliphatic sidearm



I



II

2.01 and 2.13 Å. The Cu(1)–Cu(2) distance is 3.24 Å which is typical for this type of complex. Each copper ion is five-co-ordinate and the donor sets are completed by two nitrogen atoms from the sidearms of the ligand. Although both sidearms are N_2 chelates, the chemical environments they provide are different. Atoms N(1) and N(2) are both from unsaturated amines (a pyridine and an imine) whereas N(3) and N(4) are both from tertiary aliphatic amines.

The geometry of Cu(1) is distorted square pyramidal with the bridging bromide as the apical ligand. This is a result of the near-coplanar orientation of the phenol with the imine and pyridine of the sidearm. The fourth donor atom of the square base is O(2) and lies 0.59 Å below the least-squares plane of the planar ligand fragment. Within error Cu(1) lies in this plane, the deviation being only 0.02 Å above it. The aliphatic sidearm contains no rigid groups or conjugation and therefore is flexible enough to come out of the plane of the rest of the ligand. A consequence of this 'buckling' is that Cu(2) is 1.85 Å above the plane of the phenol/pyridine fragment (Fig. 3), and its geometry is significantly distorted from both square-based pyramidal and trigonal bipyramidal. A full crystallographic discussion is in preparation.[25]

The symmetric parents of the hybrid ligand HL^2 are 4-methyl-2,6-bis[*N*-(2-pyridylmethyl)formimidoyl)]phenol HL^8 and 2,6-bis[(2-diethylaminoethyl)ethylaminomethyl]-4-methylphenol HL^9. Both of these ligands have been structurally characterised as dinuclear copper(II) complexes, for example $[Cu_2(\mu\text{-}Br)Br_2L^8]I$[24] and $[Cu_2(\mu\text{-}PhCO_2)_2L^9][PF_6]II$.[26] Only a single exogenous bridge is present in the former with each copper also co-ordinated to a terminal bromide. The ligand dictates that the metal geometries are distorted square pyramidal, similar to that observed for Cu(1) in $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2]_2[Cu_2Br_4]$. In contrast the latter incorporates two exogenous bridges (both benzoates), but the copper atoms are again in square-pyramidal geometries and not in the distorted environment found for Cu(2) in $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2]_2[Cu_2Br_4]$.

The dinuclear copper(I) anion $[Cu_2Br_4]^{2-}$ is a planar species in which the metal geometry is trigonal planar with two of the bromides acting as asymmetric bridges.[23] The shortest Cu–Br distance is to the terminal bromide and the molecular dimensions are similar to those found in other crystallographically characterised cases of this anion.[27,28]

The copper(I) ions of the anion must be formed in solution from the copper(II) bromide. Bromide ion itself is capable of this reduction and a similar reaction has been reported in the presence of chloride ions.[29] The initial copper(I) species formed is the linear anion $[CuBr_2]^-$ which can reversibly dimerise to give $[Cu_2Br_4]^{2-}$. Both anions can be isolated from solutions of copper(I) bromide depending on the nature of the cation present.[27,30] It is interesting that in $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L^2][Cu_2Br_4]$ the dimeric form of the copper(I) anion is favoured in the solid state, furthermore under conditions of competiton with the nitrate ion the $[Cu_2Br_4]^{2-}$ moiety is predominantly incorporated into the lattice. The small fraction of nitrate inferred in the crystals of the same formula implies similar spatial requirements for the anion sets, but probably only occurs because of the low concentration of bromide, and hence $[CuBr_2]^-$, in the mother-liquor. In contrast in the presence of perchlorate, $[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$ crystallises exclusively with the $[(H_2O)_2{\cdot}(ClO_4)_2]^{2-}$ anion set, and the $[Cu_2Br_4]^{2-}$ species is not observed. This is probably due to crystal packing with perchlorate anions being energetically favoured and/or a lower solubility of the perchlorate in methanol.

Using the same procedure as for HL^1 and HL^2, solutions of the homologous ligands with the more flexible 2-aminoethylpyridine moiety as the imine-based sidearm were prepared, HL^3 and HL^4. Complexation with copper(II) perchlorate hexahydrate gave dark green crystals, the elemental analyses of which were consistent with the formulations $[Cu_2Br(HCO_2)(H_2O)_2L^3][ClO_4]$ and $[Cu_2Br(HCO_2)(MeOH)L^4][ClO_4]$.

The positive ion FAB mass spectra of these complexes are similar to those of $[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$ and $[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$ and confirm the presence of the $[Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)L]^+$ triply bridged core. Peaks at +2

Table 4 Positive-ion FAB mass spectra of the dinuclear complexes $[CuBr(HCO_2)(H_2O)L^1][ClO_4]$ **i**, $[Cu_2Br(HCO_2)(H_2O)L^2][ClO_4]$ **ii**, $[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$ **iii**, $[Cu_2Br(HCO_2)(H_2O)_2L^3][ClO_4]$ **iv** and $[Cu_2Br(HCO_2)(MeOH)L^4][ClO_4]$ **v**

	m/z[a] (% intensity)				
$[fragment]^+$	**i**	**ii**	**iii**	**iv**	**v**
$[Cu_2Br(HCO_2)L]$	653 (100)	697 (20)	—[b]	667 (51)	711 (26)
$[Cu_2BrL]$	608 (40)	652 (29)	652 (17)	622 (18)	666 (11)

[a] 3-Nitrobenzyl alcohol matrix. [b] Not observed.

Table 5 Electronic absorption spectra of the dinuclear complexes; key as in Table 4

i	**ii**	**iv**	**v**
345 (2370)[a]	355 (5870)	340 (2895)	355 (6350)
405[b] (1030)	—[c]	405[b] (820)	—[c]
450[b] (485)	—[c]	450[b] (415)	—[c]
480[b] (315)	485[b] (190)	485[b] (315)	475[b] (200)
685 (201)	700 (125)	690 (185)	710 (115)

[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1} per Cu). [b] Shoulders. [c] Not observed.

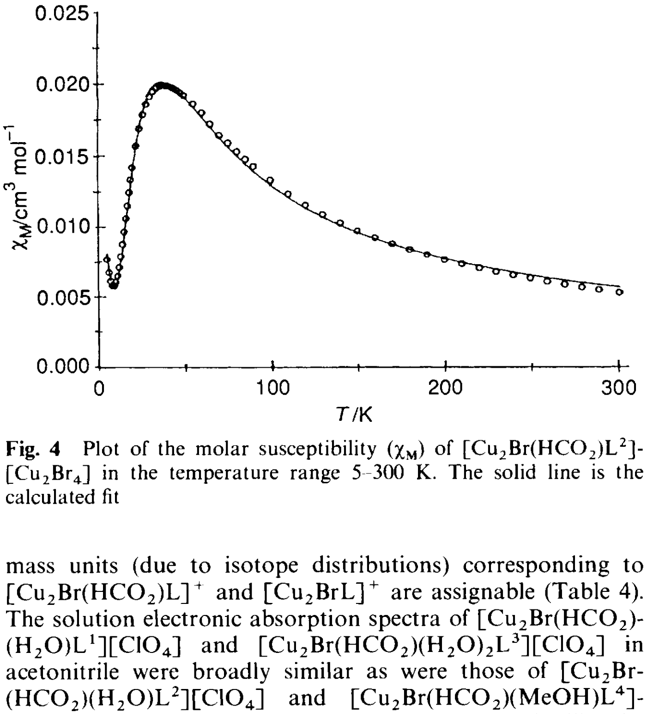


Fig. 4 Plot of the molar susceptibility (χ_M) of $[Cu_2Br(HCO_2)L^2]$-$[Cu_2Br_4]$ in the temperature range 5–300 K. The solid line is the calculated fit

mass units (due to isotope distributions) corresponding to $[Cu_2Br(HCO_2)L]^+$ and $[Cu_2BrL]^+$ are assignable (Table 4). The solution electronic absorption spectra of $[Cu_2Br(HCO_2)$-$(H_2O)L^1][ClO_4]$ and $[Cu_2Br(HCO_2)(H_2O)_2L^3][ClO_4]$ in acetonitrile were broadly similar as were those of $[Cu_2Br$-$(HCO_2)(H_2O)L^2][ClO_4]$ and $[Cu_2Br(HCO_2)(MeOH)L^4]$-$[ClO_4]$ (Table 5), but unfortunately due to poor solubility the spectrum of the structurally characterised $[Cu_2Br(HCO_2)L^2]_2$-$[Cu_2Br_4]$ could not be recorded. The *N*-methylpiperazine sidearm complexes display a more intense charge-transfer band at *ca.* 355 nm and only the single shoulder is apparent. These features indicate structural differences between the two types of complex. This is not surprising as the rigidity of the piperazine ring restricts the 'buckling' of the ligand observed for $[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$. The spectrum of $[Cu_2Br(HCO_2)$-$(H_2O)_2L^3][ClO_4]$ in the range 300–800 nm is the best resolved of the four, especially in the 400–500 nm region where the weak shoulders are observed. The intense absorptions at *ca.* 350 nm are assigned as the π–π^* transition of the co-ordinated imine.[31] The shoulders in the 400–500 nm region are probably charge-transfer bands associated with the triply bridged dinuclear copper(II) core and the broad bands at 700 nm are d–d in character.

The magnetic data for $[Cu_2Br(HCO_2)L^2]_2[Cu_2Br_4]$ are illustrated in Fig. 4 as the temperature dependence of the molar susceptibility; the susceptibility curve presents a maximum at T = 39 K. This behaviour is characteristic of a pair of copper atoms interacting antiferromagnetically. The slight increase at low temperatures reveals the presence of a small amount of an uncoupled species. This behaviour can be accounted for by the usual Bleaney–Bowers equation (1) modified to include a

$$\chi = \frac{2Ng^2\beta^2}{kT}\left[3 + \exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1 - P) + \frac{Ng^2\beta^2P}{2kT} + \text{t.i.p.} \quad (1)$$

monomeric impurity. All the symbols have the usual meanings and P is the proportion of monomeric impurity. Least-squares fitting of the data produces the following 'best-fit' parameters: g = 2.072, $2J$ = -42 cm^{-1}, P = 0.035 and temperature-independent paramagnetism (t.i.p.) = 204 × 10^{-6} cm^3 mol^{-1}.

The magnetic properties of copper pairs are satisfactorily accounted for by considering the symmetry of the magnetic orbitals of the two interacting metallic fragments.[18,32] Direct electronic communication is necessary for antiferromagnetic interaction and so the overlap between metal magnetic orbitals and the highest occupied orbital(s) of the intervening atom(s) is the major determining factor for antiferromagnetic coupling. Ample theoretical and experimental evidence has been provided that antiferromagnetic interactions are mediated by bridging ligands which occupy equatorial positions in tetragonal environments of the metal or axial positions in trigonal-bipyramidal ones.

In the 'parent' benzoate-bridged complex $[Cu_2(\mu\text{-}PhCO_2)_2L^9][PF_6]$ the copper atoms are square pyramidal and the apices are occupied by one oxygen from each benzoate anion; the basal planes are close to orthogonal. The value of $-2J$ is 126.4 cm^{-1} and it is concluded that there is negligible contribution to the antiferromagnetic interaction from the benzoate because the apical co-ordination of one of its two oxygen atoms inhibits the required direct communication.[26] For the 'parent' bromide-bridged complex $[Cu_2(\mu\text{-}Br)Br_2L^8]$ which has a $-2J$ value of 68 cm^{-1} the situation is less obvious as the geometry at each copper is intermediate between a trigonal bipyramid and a square pyramid.[24]

In the present complex the situation is quite clear for Cu(1) which is in a square-pyramidal environment; the $d_{x^2-y^2}$ magnetic orbital (containing the unpaired electron) points toward the endogenous phenolate oxygen and the exogenous formate but does not interact strongly with the apical bromide ion. The situation is more complicated for Cu(2) the geometry at which is intermediate between a square pyramid and a trigonal pyramid. In the latter situation the d_{z^2} magnetic orbital (containing the unpaired electron) points toward the exogenous bromide ion and does not interact strongly with the bridging phenolate and formate ligands which occupy equatorial positions. This situation is not favourable to a strong interaction since the most significant exchange pathway involves the phenolate oxygen which is equatorial to both copper atoms and thus has poor overlap with the core of the d_{z^2} orbital on Cu(2). In the alternate limiting case where the co-ordination around Cu(2) is best described as square pyramidal the $d_{x^2-y^2}$ magnetic orbital points toward the phenolate oxygen and the bromide, the formate being apical. This situation is

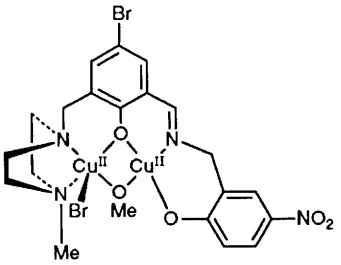


Fig. 5 Proposed structure of [$Cu_2(OMe)Br(MeOH)_2L^5$]

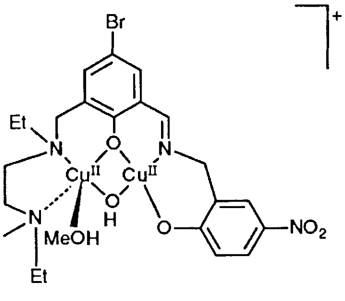


Fig. 6 The proposed structure of [$Cu_2(OH)(MeOH)L^6$][ClO_4]

more likely to give significant exchange as the phenolate oxygen is now equatorial to the two copper atoms and can overlap with both $d_{x^2-y^2}$ magnetic orbitals. The moderate interaction which is revealed by the magnetic susceptibility measurements can be explained by the distortion of the co-ordination sphere of Cu(2); the strain introduced by the saturated ethylenediaminomethylene chain causes a significant deviation of the co-ordination sphere of Cu(2) from the tetragonal symmetry usually encountered in complexes involving an endogenous phenoxo-bridge. It is the tetragonal geometries in which two copper atoms share two corners that are ideally suited to maximising the overlap of the metal and bridging ligand orbitals thus leading to significant antiferromagnetic interactions. The presence of bulky peripheral ligands or large exogenous bridging atoms induces distortions or even ruptures of the tetragonal geometries which eventually result in a lowering if not a cancellation of the singlet stabilisation in such highly distorted systems.[24,26,33,34]

Condensation of both aldehydes with 2-aminomethyl-4-nitrophenol gave yellow methanolic solutions of the dinucleating ligands H_2L^5 and H_2L^6. Characterisable dinuclear copper(II) complexes could only be isolated from these solutions in the absence of triethyl orthoformate.

Complexation of H_2L^5 with copper(II) perchlorate hexahydrate in the presence of base (triethylamine) gave dark green microcrystals of [$Cu_2(OMe)Br(MeOH)_2L^5$]. As for the previous complexes the bromide ion originates from the hydrobromide salts of the aldehyde used in the *in situ* preparation of H_2L^5. The infrared spectrum shows no bands characteristic of the perchlorate anion. The elemental analysis indicates the presence of only a single bromide and is consistent with the second anion being methoxide. The incorporaion of the basic methoxide group under the relatively mild reaction conditions is plausible only if it is co-ordinated as an exogenous bridge.

A sharp band at 2805 cm^{-1} in the infrared spectrum is assigned as the symmetric C–H stretching mode of the methoxide, and is similar in position and intensity to that observed for other μ-OMe dinuclear copper(II) complexes.[35] Unfortunately the nature of this band could not be confirmed by exchange with CD_3OD as [$Cu_2(OMe)Br(MeOH)_2L^5$] was only soluble in solvents that irreversibly altered the complex. It should be noted that this band is not assignable to the *N*-methyl group of the piperazine ring as it is not apparent in the spectra of either [$Cu_2Br(HCO_2)(H_2O)L^1$][ClO_4] or [$Cu_2Br(HCO_2)(H_2O)_2L^3$][ClO_4]. Moreover a sharp band at 2870m cm^{-1} is present for all the *N*-methylpiperazine sidearm complexes but not for the (*N*-2-diethylaminoethyl)ethylaminomethyl sidearm complexes.

The location of the bromide is unknown but the failure to form an ionic perchlorate salt and the poor solubility of the complex suggest that it may be co-ordinated to one of the copper ions. Symmetric 'end-off' compartmental ligands with anionic sidearms (phenolate or carboxylate) give complexes in which the coppers are approximately square planar with no (or only weakly bound) axial ligands,[36] whereas for piperazine or other N_2 aliphatic based sidearms five-co-ordinate copper is observed.[14,26] In addition it is highly unlikely that Cu(1) is co-ordinated by four anionic ligands so the bromide is assumed to be bound to Cu(2), giving a square-pyramidal geometry with the bromide as the apical ligand (Fig. 5). Also present are two methanol molecules of solvation.

The positive-ion FAB mass spectrum shows peaks at *m/z* 588 (80%) [Cu_2L^5]$^+$ and 667 (72%) [Cu_2BrL^5]$^+$. A methoxide-bridged species is not apparent in the mass spectrum but the incorporation of a molecule of the matrix, 3-nitrobenzyl alcohol (HX), is observed at *m/z* 740 (80%) [$Cu_2L^5(X)$]$^+$. The room-temperature magnetic moment is 1.04 μ_{BM} per Cu atom indicating appreciable antiferromagnetic coupling (spin-only value = 1.73 μ_{BM}) which is as expected for dinuclear copper complexes of ligands of this type.[2]

Application of the above synthetic procedure to the complexation of H_2L^6 gave [$Cu_2(OH)(MeOH)L^6$][ClO_4] as an emerald-green powder. The structure of this complex differs from that of L^5 in several respects. The infrared spectrum shows that it is a salt with bands characteristic of non-co-ordinated perchlorate at 1100 and 625 cm^{-1}. The elemental analysis indicates that the other anion is not bromide and there is no band at *ca.* 2800 cm^{-1} characteristic of a bridging methoxide, therefore suggesting the presence of a bridging hydroxide. Although this interpretation is consistent with the elemental analysis the O–H stretch of the hydroxide cannot be identified in the infrared spectrum and only a broad featureless band at 3300–3650 cm^{-1} is apparent. The methanol molecule of solvation may possibly be weakly bound to one of the coppers as a fifth ligand (Fig. 6).

In the above work we have reported the systematic design, synthesis and characterisation of unsymmetrical dinuclear copper(II) complexes. Such complexes can be viewed as first-generation models for the dinuclear copper-centres in metalloproteins and -enzymes.

Acknowledgements

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