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The Crystal Structure of a μ-Phenolato Copper(II) Dinuclear Complex containing Two Chemically Distinct Metal Co-ordination Environments

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The crystal structure of $[L^1Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)]_2[Cu_2Br_4]$ (**3**) is reported, where HL^1 is the Schiff base derived from the condensation of 2-aminomethylpyridine and 2-[(*N*-diethylaminoethyl-*N*-ethyl)aminomethyl]-4-bromo-6-formylphenol (**1**); the structure comprises a copper(II) dinuclear cation with phenolate, bromide, and formate bridges in which the metals have different co-ordination environments, and a copper(I) dinuclear dianion with bromide bridges.

Copper(II) binuclear complexes of ligands that provide an endogenous μ-phenolato bridge served as useful models for the type 3 Cu–Cu site in copper proteins and enzymes such as haemocyanin and tyrosinase[1] until the revelation, through the crystal structure,[2] that deoxyhaemocyanin does not contain such a bridge. If the phenolato bridge is regarded strictly as a device to provide a suppositional model for a one-atom endogeneous bridge,[3] as indicated to be present in oxyhaemocyanin from EXAFS studies,[4] it can still be used to study the constraints imposed on the Cu · · · Cu separation in the bimetallobiomolecule and also the requirements for the incorporation of the exogenous bridge. To date, all ligands prepared for this purpose have provided identical co-ordination environments for the two metals, but the need for model compounds in which the copper ions are co-ordinated in different environments is now recognised, particularly with regard to modelling studies on tyrosinase.[5] The preparation of the salicylaldehyde derivative (**1**) allows the synthesis of dinuclear complexes in which the metal environments are chemically different. The condensation of (**1**) with a functionalised primary amine produces an asymmetric Schiff base capable of forming such dinuclear complexes. This approach adds a new and desirable degree of flexibility to the synthesis of bimetallic complexes.

Condensation of (**1**) with 2-aminomethylpyridine gives the dinucleating ligand HL^1. The parents of this hybrid ligand are 2,6-bis[*N*-(2-pyridylmethyl)-formimidoyl]-4-methylphenol (HL^2) and 2,6-bis[*N*-(2-diethylaminoethyl)-*N*-ethylaminomethyl]-4-methylphenol (HL^3), both of which have been structurally characterised as dinuclear copper(II) complexes; $[L^2Cu_2(\mu\text{-}Br)Br_2]$ and $[L^3Cu_2(\mu\text{-}PhCO_2)_2][PF_6]$, respectively.[6,7] In each of these complexes the copper ions are five co-ordinate and have distorted square based pyramid geometries.

Table 1. The co-ordination environments of the two copper(II) ions in the cation of (**3**).

	Bond length/Å	Bond angles/°			
		Br(2)	O(1)	O(2)	N(1)
Cu(1)–Br(2)	2.752(4)				
Cu(1)–O(1)	1.91(3)	85.6(5)			
Cu(1)–O(2)	2.01(2)	96.9(6)	89.6(11)		
Cu(1)–N(1)	1.98(3)	96.2(6)	177.5(8)	91.9(11)	
Cu(1)–N(2)	1.89(2)	102.9(7)	94.3(12)	160.1(9)	83.6(12)
		Br(2)	O(1)	O(3)	N(3)
Cu(2)–Br(2)	2.477(6)				
Cu(2)–O(1)	2.22(2)	86.7(6)			
Cu(2)–O(3)	2.13(3)	92.5(7)	83.4(7)		
Cu(2)–N(3)	2.07(3)	169.3(6)	87.8(8)	95.9(9)	
Cu(2)–N(4)	2.09(2)	94.1(8)	145.4(9)	131.0(8)	85.3(10)
Cu(1)–Cu(2)	3.244(6)		Cu(1)–Br(2)–Cu(2)		76.5(2)
			Cu(1)–O(1)–Cu(2)		103.4(10)

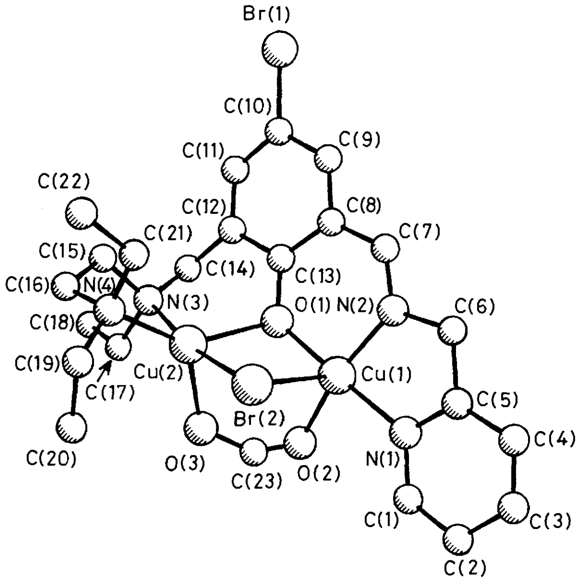


Figure 1. The molecular structure of the dinuclear copper(II) cation. See Table 1 for the co-ordination environments of Cu(1) and Cu(2).

The ligand HL^1 was prepared *in situ* as follows: (**1**)·2HBr (0.001 mol), 2-aminomethylpyridine (0.001 mol), and triethylorthoformate (0.5 cm^3) were refluxed in methanol for 2 h. Potassium hydroxide (0.004 mol) was added and the solution refluxed for a further hour. To this solution containing the deprotonated ligand $(L^1)^-$ was added either copper(II) nitrate trihydrate (0.002 mol) or copper(II) bromide (0.003 mol). The resulting dark brown solutions were filtered, and (**2**) and (**3**), respectively, were deposited as brown rhombohedral plates after allowing to cool overnight.

The crystal structures† of both (**2**) and (**3**) consist of a dinuclear copper(II) cation (Figure 1) and a dinuclear copper(I) dianion (Figure 2). The crystal of (**2**) examined was of good quality, a data set was collected, and the structure was solved. It was found that about 40% of the anions were replaced by nitrate. The microanalysis indicated this and the refinement agreed well with a 60% population of the $[Cu_2Br_4]^{2-}$ anion. The best refinement model we have yet been able to find has a number of partially occupied O sites rather than well defined nitrate groups; it is likely that the nitrate positions are disordered and overlap with the much heavier Cu and Br atoms which complicates matters. The preparation was subsequently repeated in the absence of nitrate to yield crystals of (**3**) in which the anions were 100% $[Cu_2Br_4]^{2-}$ and a new data set was collected. The current results of both refinements are presented here. It is intended to publish full structural results for both crystals at a later date.

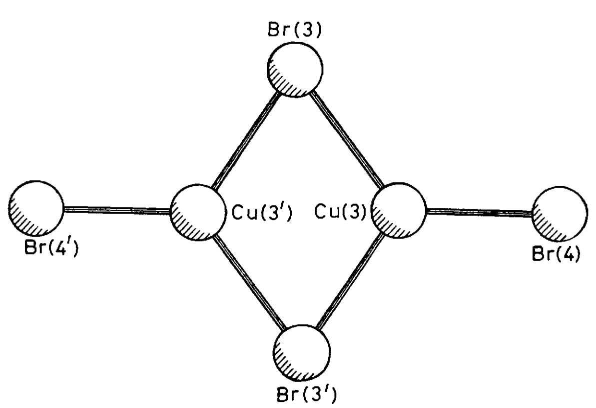
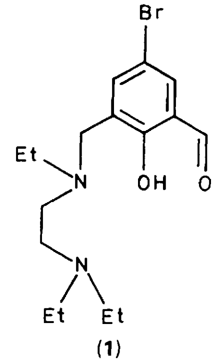
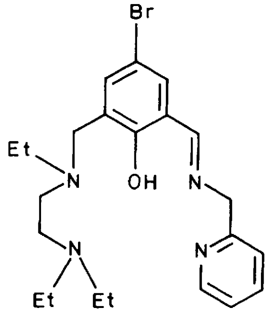


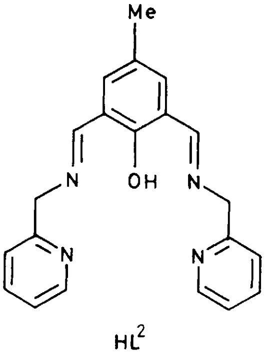
Figure 2. The molecular structure of the dinuclear copper(I) dianion. Bond lengths and angles for (**3**): Cu(3)–Cu(3′) 2.881(12), Cu(3)–Br(3) 2.50(1), Cu(3)–Br(4) 2.33(1), Cu(3)–Br(3′) 2.48(1) Å; Br(3)–Cu(3)–Br(3′) 109.3(3), Br(3)–Cu(3)–Br(4) 127.7(3), and Br(3′)–Cu(3)–Br(4) 123.0(4)°.



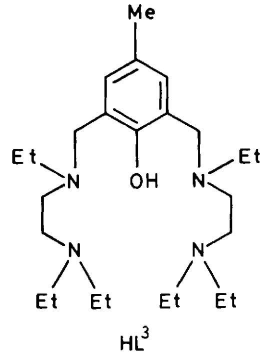
(**1**)



HL^1



HL^2



HL^3

Both copper(II) ions in the cation are five co-ordinate. There are three groups present which bridge the di-copper(II) moiety; the endogeneous phenolate group provided by L^1, a bromide, and a formate. The phenolate bridge is asymmetrically bound to the copper ions with bond lengths of 1.91 and 2.22 Å to Cu(1) and Cu(2), respectively. This marked difference does not occur in either of the parent complexes and is probably due to the unique steric constraints imposed by the ligand. The bridging bromide is also asymmetrically bound with Cu(1)–Br(1) = 2.752 Å and Cu(2)–Br(1) = 2.477 Å. This difference is similar to that seen in the bromide bridged parent complex $[L^2Cu_2(\mu\text{-}Br)Br_2]$ for which the values are 2.719 and 2.426 Å.[6] As expected, the shorter Cu–Br distance is to Cu(2), which has the longer bond to the bridging phenolate oxygen, and *vice versa* for Cu(1). The μ-formate group almost symmetrically bridges the copper ions. This formate originates from the hydrolysis of the triethylortho-

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† *Crystal data* for $[L^1Cu_2(\mu\text{-}Br)(\mu\text{-}HCO_2)]_2[Cu_2Br_4]$ (**3**). Data for the nitrate containing crystal (**2**) in square brackets. M = 1843.564, space group $P\bar{1}$, a = 10.723(13) [10.733(11)], b = 11.466(15) [11.507(19)], c = 14.168(23) [14.296(28)] Å, α = 66.34(11) [66.20(12)], β = 77.83(12) [77.74(12)], γ = 72.10(10) [71.96(10)], U = 1511(4) [1528(4)] Å^3, Z = 1, D_x = 2.03 g cm^{-3}, μ = 73.77 cm^{-1}, $F(000)$ = 909.75, 2θ range 3.5 to 40°, one check reflection every 200, no decay, empirical absorption correction (ψ-scans) $T_{\text{max.,min.}}$ = 0.336, 0.113. 1535 [1567] unique observed reflections (4 σ), 199 refined parameters, current R = 0.091 [0.106], R_w = 0.089 [0.098]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

formate used as a water scavenger in the *in situ* synthesis of the ligand. The donor set of each copper ion is completed by two nitrogen donors from the pendant arms of the ligand. The Cu(1) atom is co-ordinated to two unsaturated amines, an imine, and a pyridine. The overall geometry is a square based pyramid as is found in the parent complex $[L^2Cu_2(\mu\text{-}Br)Br_2]$.[6] The phenol, imine, and pyridine groups are almost co-planar and provide three of the donors for the square base of the pyramid, the fourth is from the formate, and the apical ligand is the bridging bromide. In contrast Cu(2) is co-ordinated to two aliphatic tertiary amines. The overall geometry is significantly distorted from both a trigonal bipyramid and a square based pyramid, and is different from that found in the parent complex $[L^3Cu_2(\mu\text{-}PhCO_2)_2][PF_6]$.[7] This change in geometry is probably due to a combination of the greater flexibility of the aliphatic pendant arm and the requirement of the other half of the complex to be planar.

The dianion is a planar dinuclear copper(I) species with two bridging bromides and two terminal bromides. This anion has previously been structurally characterised as tetra-alkylammonium and trialkylarylammonium salts.[8,9] The bond lengths and angles of the anion are in good agreement with the literature values. The copper(I) is initially formed in solution as $[CuBr_2]^-$ from copper(II) with the accompanying oxidation of Br^- to Br_2. Marsh and Trotter have reported a similar reduction in the presence of chloride ions.[10] The $[CuBr_2]^-$ anion is stable in solution and readily dimerises to the dinuclear dianion $[Cu_2Br_4]^{2-}$ seen in this structure determination.[8]

In conclusion, the synthesis of a dinucleating ligand with non-equivalent donor sets that can co-ordinate two copper ions in chemically distinct ligand environments has been achieved. In addition its asymmetric dinuclear copper(II) complex has been prepared and structurally characterised with a dinuclear copper(I) species as the counterion.

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