A Mononuclear Copper(II) Complex of an Unsymmetrical Dinucleating Ligand†

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The unsymmetrical and potentially dinucleating ligand 4-bromo-2-(2-hydroxyethyliminomethyl)-6-(morpholin-4-ylmethyl)phenol (H_2L^1) has been prepared *via* a Mannich reaction under non-aqueous aprotic conditions. Reaction with copper(II) yielded mono- and di-nuclear complexes; the crystal structure of the mononuclear complex $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$ has been determined.

Dinucleating ligands, which can bind two metal ions within their perimeter, have been synthesised for their potential application as models of dinuclear metallobiosites.[1,2] In the majority of such ligands the donor sets that these systems present to each metal ion are identical. In dinuclear transition-metal biosites, however, the metal ions are found in chemically or geometrically distinct environments. For example, the unsymmetrical nature of the dicopper site in haemocyanin was demonstrated by the X-ray structure of deoxyhaemocyanin[3] and sequence homology studies on tyrosinases have shown that the copper sites are not always identical.[4] This observation led to the suggestion that for modelling studies unsymmetrical dinucleating ligands (*e.g.* Fig. 1) should be viewed as desirable targets.[2] Subsequently it has been noted that polydentate systems that lead to obligately asymmetric dinuclear complexes remain very rare[5] and the single example quoted was that of the unsymmetrical 'end-off' compartmental ligand HL depicted in Scheme 1.[6] This ligand was prepared by the introduction of a single pendant arm into 5-bromosalicylaldehyde, by the use of the Mannich reaction under classical aqueous acidic conditions, in moderate yields. Subsequent condensation of the Mannich bases with primary amines afforded 'side-off' unsymmetrical dinucleating Schiff-base ligands, which were complexed '*in-situ*', with copper(II) salts. This gave rise, as shown in Scheme 1, to dinucleating ligands having one donor set comprised of saturated nitrogen atoms with the second donor set comprised of unsaturated nitrogen atoms.

Two recent reports have provided new examples of unsymmetrical polypodal ligands. The heptadentate ligand 2-{[bis(2-pyridylmethyl)amino]methyl}-4-methyl-6-{[(2-pyridylmethyl)-2-hydroxyphenyl]methyl}phenol (HL^a) has been used to prepare a mixed-valence iron(II)–iron(III) complex which reproduces the co-ordination of a terminal tyrosine residue to a diiron centre as found in the purple acid phosphatase enzyme,[7] and the hexadentate ligand 6-{[(benzimidazol-2-ylmethyl)-

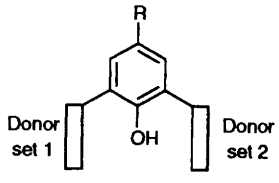
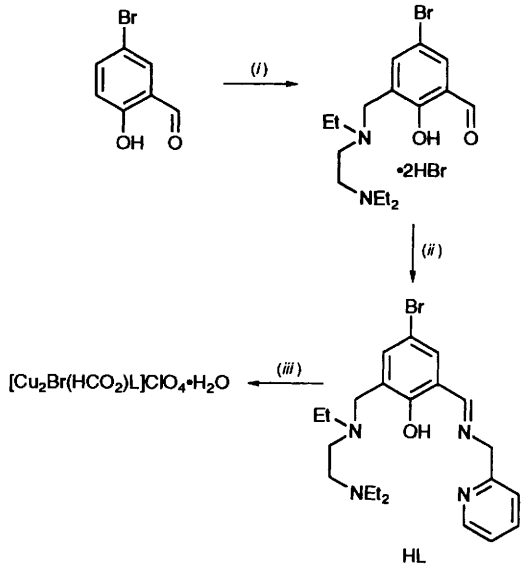
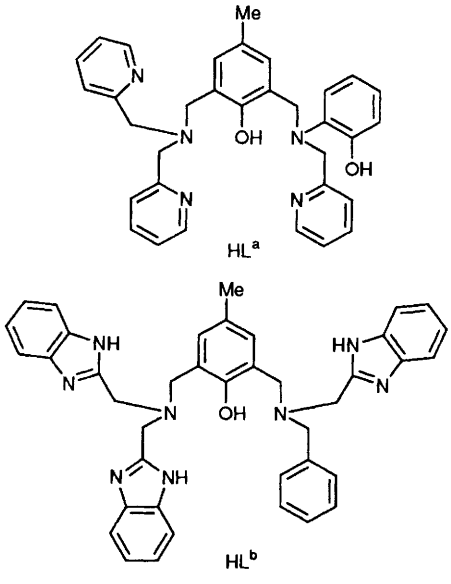


Fig. 1 Schematic representation of unsymmetrical 'end-off' compartmental ligands (R = H, Me, Cl or Br)



Scheme 1 (*i*) $Et_2NCH_2CH_2NHEt$, CH_2O(aq), EtOH, heat, HBr; (*ii*) 2-aminomethylpyridine, $HC(OEt)_3$, MeOH, heat; (*iii*) NaOH, $Cu(ClO_4)_2 \cdot 6H_2O$, heat



† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: mmHg ≈ 133 Pa.

benzylamino]methyl}-2-{[bis(benzimidazol-2-ylmethyl)-amino]-methyl}-4-methylphenol (HL^b) has been used to prepare an asymmetric dicopper(II) complex having different donor sets at each copper atom.[5]

As part of a programme[8] concerning the design and synthesis of unsymmetrical dinucleating ligands, possessing both nitrogen and oxygen donor atoms we have prepared such ligands from the functionalised Mannich bases of salicylaldehyde derivatives. Earlier experience in the development of new methodologies for the Mannich reaction, suggested that it would be more profitable to prepare Mannich bases under non-aqueous aprotic conditions rather than the more classical synthesis illustrated above.[9] We herein report the synthesis of the ligand 4-bromo-2-(2-hydroxyethyliminomethyl)-6-(morpholin-4-ylmethyl)phenol (H_2L^1) under non-aqueous aprotic conditions, and the crystal structure of a monocopper(II) complex derived from it.

Experimental

Elemental analyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1710 IR Fourier-transform spectrophotometer (4000–400 cm^{-1}), ^1H NMR spectra were recorded at 220 MHz on a Perkin-Elmer R34 spectrometer, ^{13}C NMR spectra (62.9 MHz) were recorded using a Bruker AM-250 spectrometer, electron impact (EI) mass spectra were recorded using a Kratos MS 25 spectrometer and positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS 80 spectrometer using a 3-nitrobenzyl alcohol (noba) matrix unless otherwise stated.

Syntheses.—Ethoxy-N-morpholinylmethane. Morpholine (87.12 g, 1 mol) was added dropwise to a suspension of paraformaldehyde (37.54 g, 1.25 mol) and anhydrous potassium carbonate (276.4 g, 2 mol) in ethanol (500 cm^3) with external cooling in ice. The mixture was then stirred vigorously with an overhead mechanical stirrer for 48 h allowing the temperature to reach ambient gradually. The solid was then filtered off and washed with dried diethyl ether (2 × 50 cm^3). The filtrate was then concentrated *in vacuo* to give a brown oil which was fractionally distilled through a 30 cm Vigreaux column affording the product (89.75 g, 62%), b.p. 45–47 °C (2 mm Hg) [lit.,[10] 58–63 °C (6 mm Hg)]. $\delta_H(CDCl_3)$ 1.10 (3 H, t, J = 6.2, CH_3), 2.50–2.60 (4 H, m, C^2H_2 and C^6H_2), 3.42 (2 H, q, J = 6.2 Hz, OCH_2CH_3), 3.52–3.65 (4 H, m, C^3H_2 and C^5H_2) and 3.93 (2 H, s, NCH_2O); $\delta_C(CDCl_3)$ 15.15 (CH_3), 49.82 (C^3 and C^5), 64.13 (OCH_2CH_3), 66.90 (C^2 and C^6) and 88.37 (NCH_2O).

4-Bromo-2-formyl-6-(morpholin-4-ylmethyl)phenol **I**. A mixture of 5-bromosalicylaldehyde (99%) (30.46 g, 0.15 mol) and ethoxy-*N*-morpholinylmethane (24.69 g, 0.17 mol) in acetonitrile (200 cm^3) was heated under reflux in a nitrogen atmosphere for 66 h. After cooling to room temperature the solvent was removed *in vacuo* and the residue was dissolved in 2 mol dm^{-3} HCl (100 cm^3) and extracted with diethyl ether (3 × 80 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give (3.95 g, 13%) unreacted 5-bromosalicylaldehyde. The aqueous layer was then basified to pH 9 with 2 mol dm^{-3} NaOH followed by careful addition of $NaHCO_3$ and washed with diethyl ether (3 × 100 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a light brown crystalline solid (35.57 g). Recrystallisation from diethyl ether afforded the product as pale orange crystals (32.75 g, 73%), m.p. 62–64 °C (Found: C, 48.20; H, 4.80; Br, 26.35; N, 4.65. $C_{12}H_{14}BrNO_3$ requires C, 48.00; H, 4.70; Br, 26.60; N, 4.65%); $\delta_H(CDCl_3)$ 2.45–2.67 [4 H, m, $N(CH_2)_2$], 3.62 (2 H, s, $ArCH_2N$), 3.67–3.80 [4 H, m, $O(CH_2)_2$], 7.40 (1 H, d, J = 3.1, H^3), 7.67 (1 H, d, J = 3.1 Hz, H^5), 10.20 (1 H, s, CHO) and 10.27–10.60 (1 H, br s, OH); $\delta_C(CDCl_3)$ 53.00 ($C^{3'}$ and $C^{5'}$), 59.15 ($ArCH_2N$), 66.62 ($C^{2'}$ and $C^{6'}$), 111.37 (C^4), 123.83 (C^6), 125.76 (C^2), 131.21 (C^3), 137.78 (C^5), 159.98 (C^1) and 190.49 (CHO); EI MS, m/z 299 (M^+, 22%), 271 (36), 213 (58) and 86 (100); ν_{max}(KBr) 3455 (OH), 1681 (CHO), 1588 (aromatic ring), 1456, 1231, 1117, 960, 860, 780 and 665 cm^{-1}.

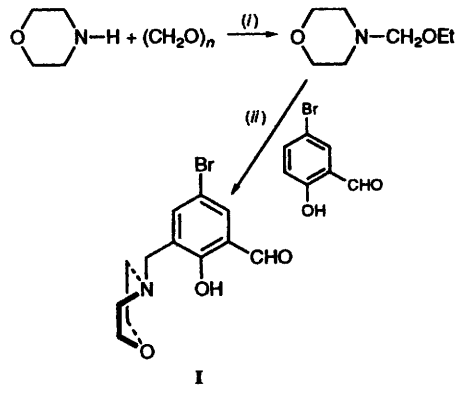
4-Bromo-2-(2-hydroxyethyliminomethyl)-6-(morpholin-4-ylmethyl)phenol (H_2L^1). A solution of the Mannich base, 4-bromo-2-formyl-6-(*N*-morpholinylmethyl)phenol **I** (9.01 g, 30 mmol), in toluene (150 cm^3) was treated with 2-aminoethanol (2.02 g, 33 mmol) in ethanol (150 cm^3) and the mixture was heated under reflux for 4 h using a Dean-Stark trap to remove the water formed as an azeotropic mixture of EtOH–toluene–water. After cooling to room temperature the solvents were removed *in vacuo* and the residue was dissolved in diethyl ether (200 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow-brown oil (10.15 g). The crude product was dissolved in the minimum amount of ether and kept in the freezer overnight. A yellow solid precipitated and was filtered off and re-crystallised from diethyl ether as yellow crystals (9.78 g, 95%), m.p. 78–80 °C (Found: C, 48.90; H, 5.65; Br, 23.05; N, 8.20. $C_{14}H_{19}BrN_2O_3$ requires C, 49.00; H, 5.60; Br, 23.30; N, 8.15%); $\delta_H(CDCl_3)$ 2.55 [4 H, t, J = 6.2, $N(CH_2)_2$], 3.55 (2 H, s, $ArCH_2N$), 3.70 [4 H, t, J = 6.2, $O(CH_2)_2$], 3.76 (3 H, t, J = 3.2, NCH_2), 3.93 (3 H, t, J = 3.2, CH_2OH), 7.33 (1 H, d, J = 3, H^6), 7.47 (1 H, d, J = 3 Hz, H^4) and 8.33 (1 H, s, ArCH=N); $\delta_C(CDCl_3)$ 53.59 ($C^{3'}$ and $C^{5'}$), 56.07 ($ArCH_2N$), 61.53 (NCH_2), 61.08 (CH_2OH), 66.90 ($C^{2'}$ and $C^{6'}$), 109.82 (C^5), 119.86 (C^1), 127.59 (C^3), 132.36 (C^4), 135.75 (C^6), 158.98 (C^2) and 165.27 (ArCH=N); EI MS, m/z 342 (M^+, 24%), 284 (22) and 257 (100); ν_{max}(KBr) 3419 (OH) 2966, 2853, 1637 (CH=N), 1604 (aromatic ring), 1449, 1289, 1115, 1078, 1021, 860, 805 and 768 cm^{-1}.

Copper(II) Complexes. General Procedure.—A solution of the ligand in methanol was treated with the copper(II) salt (2 mol equivalents) and the resulting mixture heated under reflux for 2 h. The solution was filtered whilst hot and allowed to cool slowly to room temperature; it was then concentrated to about 30% of the original volume and left standing at room temperature. The crystals that formed were collected, washed first with cold ethyl acetate and then with ether and dried in air or in a vacuum dessicator.

$[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$. A solution of H_2L^1 (1.03 g, 3 mmol) in methanol (50 cm^3) and copper(II) perchlorate hexahydrate (98%) (2.27 g, 6 mmol) gave a dark green solid (1.71 g, 87%). The solid was recrystallised from methanol affording dark blue-green crystals and light green fine needles. Both solids were confirmed by C, H, N analysis, MS and IR to conform to the above complex compound. Dark blue-green crystals (Found: C, 27.50; H, 3.80; N, 4.25. $C_{15}H_{25}BrCl_2CuN_2O_{13}$ requires C, 27.55; H, 3.85; N, 4.30%); FAB MS, m/z 506 {$[C_{14}H_{19}BrClCuN_2O_7]^+$ + 1, 100%}, 406 (15), 343 (11), 320 (19), 289 (13) and 256 (14); ν_{max}(KBr) 3459, 3100, 1646, 1548, 1458, 1438, 1387, 1318, 1264, 1217, 1116, 882, 768, 682 and 625 cm^{-1}. Light green fine needles (Found: C, 27.85; H, 3.80; N, 4.30. $C_{15}H_{25}BrCl_2CuN_2O_{13}$ requires C, 27.55; H, 3.85; N, 4.30%); FAB MS, m/z 506 {$[C_{14}H_{19}BrClCuN_2O_7]^+$ + 1, 100%}, 406 (13), 343 (9), 320 (16), 289 (13) and 256 (10); ν_{max}(KBr) 3435, 3102, 1645, 1550, 1457, 1385, 1318, 1263, 1216, 1120, 882, 768, 682 and 626 cm^{-1}.

$[Cu_2L^1]Cl_2$. A solution of H_2L^1 (0.69 g, 2 mmol) in methanol (30 cm^3) and copper(II) chloride (0.54 g, 4 mmol) gave dark green crystals (0.86 g, 80%), m.p. 208–210 °C (decomp.) (Found: C, 30.90; H, 3.35; N, 5.20. $C_{14}H_{17}BrCl_2Cu_2N_2O_3$ requires C, 31.20; H, 3.20; N, 5.20%); FAB MS, m/z 503.4 {$[C_{14}H_{17}BrClCu_2N_2O_3]^+$, 6.5%}, 441.8 (100) and 404.5 (15); ν_{max}(KBr) 3194, 1953, 2732, 1639, 1553, 1425, 1371, 1311, 1279, 1214, 1190, 1126, 1042, 1021, 914, 878, 762 and 682 cm^{-1}.

X-Ray Crystal Structure Determination.—Crystallographic data for $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$. $C_{15}H_{25}BrCl_2$-



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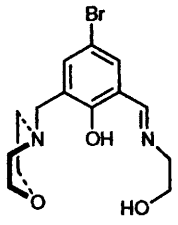
Scheme 2 (*i*) EtOH, K_2CO_3, r.t.; (*ii*) MeCN, N_2, reflux 20 h



H_2L^1

CuN_2O_{13}, M = 655.7, crystallises from methanol as blue-green oblongs; crystal dimensions 0.70 × 0.40 × 0.25 mm. Triclinic, space group $P\bar{1}$ (C^1_i, no. 2), a = 7.892(5), b = 12.156(8), c = 13.688(6) Å, α = 103.70(4), β = 98.74(4), γ = 99.73(5)°, U = 1232.1(12) Å^3, Z = 2, D_c = 1.767 g cm^{-3}, Mo-Kα radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-Kα) = 2.790 mm^{-1}, F(000) = 662. Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 45° on a Nicolet R3 diffractometer by the omega scan method. The 2040 independent reflections (of 3223 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of six azimuthal scans (minimum and maximum transmission coefficients 0.553 and 0.965). The structure was solved by direct methods and refined by full-matrix cascade least-squares methods. One perchlorate anion was disordered (0.57 : 0.43) and the two components were refined with constrained T_d symmetry with a fixed chlorine site. Hydrogen atoms were included in calculated positions, and appropriately for identified hydrogen bonds, and refined in riding mode. Refinement converged at a final R = 0.0632 (R' = 0.0758, 296 parameters, mean and maximum δ/σ 0.000, 0.001), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.55 and 0.93 e Å^{-3}. A weighting scheme w^{-1} = $\sigma^2(F) + 0.001\,34(F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL-PC[11] as implemented on the Viglen 486dx computer.

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

Results and Discussion

5-Bromosalicylaldehyde was treated with the preformed aminol ether, ethoxy-*N*-morpholinylmethane,[12] in dried acetonitrile under reflux (Scheme 2). The functionalised Mannich base I was isolated, in high yield, as a crystalline solid in the free-base form; a considerable improvement was achieved in the yield of the reaction compared to those found using the classical methods reported previously.*[,6]

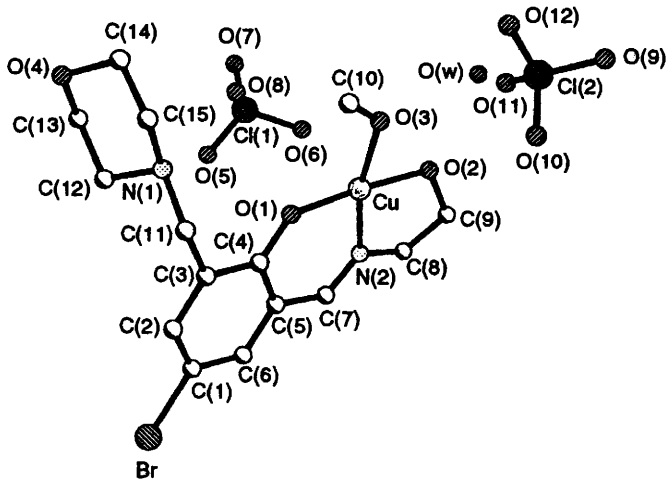


Fig. 2 Molecular structure of $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$, bond lengths in Å, angles in °: Cu–O(1) 1.907(7), Cu–O(2) 2.015(9), Cu–O(3) 2.003(8), Cu–N(2) 1.950(10), Cu–O(6) 2.496(7); O(1)–Cu–N(2) 94.8(4), O(1)–Cu–O(3) 94.6(3), O(3)–Cu–O(2) 88.2(4), O(2)–Cu–N(2) 82.1(4), O(6)–Cu–O(1) 92.2(3), O(6)–Cu–O(2) 90.5(3), O(6)–Cu–O(3) 93.2(3), O(6)–Cu–N(2) 95.9(3)

The functionalised Mannich base was successfully converted to the corresponding Schiff base by condensation with the appropriate primary amine. This gave rise to the unsymmetrical unsaturated ligand H_2L^1. The ligand was isolated as a crystalline solid in high yield and fully characterised by spectroscopic and analytical means. It was established that such transformations can be best achieved, by heating the Mannich base and a primary amine in toluene–ethanol, under Dean–Stark conditions. The products should be handled under non-aqueous conditions throughout the work-up.

The unsymmetrical ligand was treated with copper(II) chloride and copper(II) perchlorate in methanol. The ligand, in the free-base form, and the copper(II) salt were heated under reflux in methanol for about 2 h. The complexes were isolated from the reaction mixtures, on cooling, as crystalline solids. Mass spectroscopic and analytical data indicate that for copper(II) chloride the dinuclear complex $[Cu_2L^1]Cl_2$ was formed. Although crystals were obtained for this complex no crystal of a quality suitable for X-ray analysis was found. The ligand H_2L^1 and copper(II) perchlorate hexahydrate gave only a mononuclear complex, $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$, in which only the phenolic hydroxyl function had been deprotonated, with consequent protonation of the morpholino nitrogen; and there was a methanol of solvation. The X-ray crystal structure of $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$ was solved and the structure is illustrated in Fig. 2 accompanied by selected bond lengths and angles. Atomic coordinates are given in Table 1. The molecular dication does indeed comprise a tridentate O_2N ligand which co-ordinates to a copper(II) ion through alcoholic and phenolate oxygens and an imino nitrogen with a methanol of solvation; and, at a greater distance, one of the perchlorate anions [Cu–O(6) 2.50 Å] is also bonded to the copper. The co-ordination geometry of the copper is square-based pyramidal [root mean square (r.m.s.) deviation through O_3N 0.057 Å, displacement of copper 0.103 and of perchlorate oxygen 2.599 Å in the same direction]. The 'empty' co-ordination site is occupied at a distance of 3.28 Å by

* To illustrate the general case, the yield of the precursor to HL (Scheme 1) by classical methods (ref. 6) was 54% (as HL·2HBr) whereas the yield of the same compound as the free ligand prepared by the new approach was 81% (ref. 8).

Table 1 Atomic coordinates ($\times 10^4$) for $[Cu(H_2L^1)][ClO_4]_2 \cdot H_2O \cdot MeOH$

Atom	x	y	z
Cu	2725(2)	3201(1)	1624(1)
Br	1415(2)	8054(1)	−683(1)
Cl(1)	6520(4)	5103(3)	3198(2)
Cl(2)	−668(4)	110(3)	3080(2)
O(1)	2183(9)	4696(6)	1958(5)
O(2)	3189(12)	1600(7)	1159(7)
O(3)	2101(10)	2799(7)	2879(5)
O(4)	5130(11)	8548(7)	5576(5)
O(5)	6687(13)	5987(8)	2649(7)
O(6)	5889(10)	3979(7)	2452(6)
O(7)	8198(10)	5112(8)	3794(7)
O(8)	5304(10)	5323(7)	3873(6)
O(9)	−1152(25)	−1115(10)	2923(14)
O(10)	−1980(21)	454(16)	2442(12)
O(11)	949(18)	382(16)	2761(14)
O(12)	−537(23)	692(15)	4119(9)
O(9a)	519(27)	−544(19)	3434(16)
O(10a)	−191(30)	411(19)	2195(13)
O(11a)	−2401(18)	−576(19)	2808(16)
O(12a)	−567(30)	1131(14)	3863(14)
O(w)	4337(12)	233(8)	2240(7)
N(1)	2969(10)	7003(7)	3677(6)
N(2)	3008(11)	3231(8)	240(7)
C(1)	1694(14)	7007(9)	143(9)
C(2)	1478(13)	7262(10)	1158(9)
C(3)	1665(13)	6502(10)	1760(8)
C(4)	2113(13)	5414(9)	1362(8)
C(5)	2373(13)	5155(9)	310(8)
C(6)	2123(13)	5944(10)	−274(9)
C(7)	2827(14)	4047(10)	−190(9)
C(8)	3488(18)	2175(12)	−356(10)
C(9)	3079(24)	1238(12)	92(12)
C(10)	1350(19)	3495(12)	3650(10)
C(11)	1307(14)	6774(10)	2854(8)
C(12)	4221(16)	8102(10)	3696(9)
C(13)	5776(16)	8416(11)	4620(9)
C(14)	4030(17)	7464(11)	5583(8)
C(15)	2469(14)	7141(9)	4734(8)

the bromine ring substituent of an inversion related molecule [through (0, 0.5, 0)]. The phenyl ring is planar (r.m.s. deviation 0.007 Å), with perfect coplanarity of bromine and the carbimine carbon, but deviations of 0.074 and 0.091 Å for O(1) and C(11).

The ether oxygen atom of the morpholino group is not involved in co-ordination. This parallels the observation made for a tetranuclear copper(II) complex derived from 2,6-bis(morpholinomethyl)-4-methylphenol which acts as a tridentate ligand towards a dinuclear copper(II) unit using only the nitrogen atoms and the oxygen from the deprotonated phenol as donors.[13] The oxygen atoms from the morpholine ring are thrown outwards and away from the copper and the ring is found in the chair conformation. In the present complex the saturated six-membered ring also has a chair conformation [r.m.s. deviation through four carbons 0.002 Å, deviations of N(1) and O(4) +0.648 and −0.690 Å respectively] and the C–C, C–O and C–N bonds and angles in the ligand are within their accepted range of values.

There is extensive hydrogen bonding between the copper-containing cation, the two perchlorate anions, and a solvent water molecule which constitute the asymmetric unit of the crystal lattice. The terminal alcoholic residue links to a solvent water molecule [O(2)···O(w) 2.65, H(O2)···O(w) 1.69 Å]. The co-ordinated methanol forms a hydrogen bond to one oxygen of each component of the disordered perchlorate based on Cl(2) [O(3)···O(11) and O(3)···O(10a) 2.88 and 2.99; H(O3)···O(11) and H(O3)···O(10a), 1.95 and 2.06 Å]. The water molecule links two perchlorate anions, both based on Cl(2), and related by translation along the crystallographic *a* axis: to one such, a link is formed to one oxygen atom from each disorder component [O(w)···O(10^{I}) and O(w)···O($11a^{I}$) 2.84 and 2.98; H(Owa)···O(10^{I}) and H(Owa)···O($11a^{I}$) 1.88 and 2.18 Å; I $1 + x, y, z$], but the other link is only to one disorder component [O(w)···O(11) 2.90, H(Owb)···O(11) 2.20 Å], the shortest link to the second component being 3.61 Å to O(10a). This second water hydrogen atom is also linked to the ether oxygen O(4) of the morpholino group of an inversion related molecule [O(w)···O(4^{II}) 2.94, H(Owb)···O(4^{II}) 2.22 Å; II $1 - x, 1 - y, 1 - z$]. Finally, the protonated morpholino nitrogen forms a hydrogen bond to the ordered perchlorate based on Cl(1) [N(1)···O(8) 3.02, H(N1)···O(8) 2.13 Å].

Acknowledgements

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