Complexes of Ligands providing Endogenous Bridges. Part 6.[1] The *X*-Ray Crystal Structure and Magnetic Properties of a Hexanuclear Copper(II) Aggregate bearing μ_3-$Cu_3(OH)$ Cores supported by 4-nitro-2,6-bis[(salicylideneamino)methyl]phenolate Ligands†

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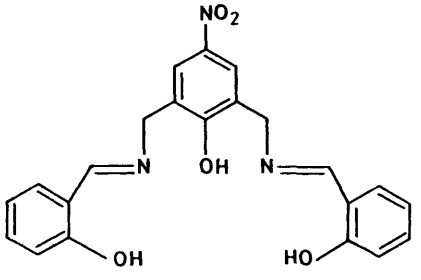
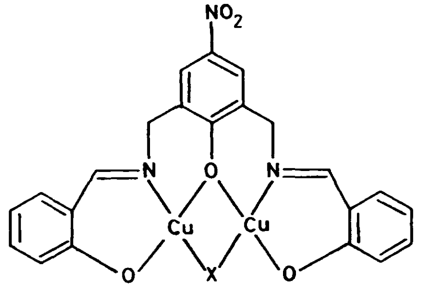
The adventitious self-assembly of a hexanuclear copper(II) aggregate $[\{Cu_3L(OH)(dmf)\}_2(\mu\text{-}Cl)(\mu\text{-}L)]\cdot 2dmf$ (dmf = dimethylformamide) during the recrystallisation of a dinuclear copper(II) hydroxo-complex derived from 4-nitro-2,6-bis[(salicylideneamino)methyl)]phenol (H_3L) is reported together with an account of the magnetic properties of the aggregate. The crystal structure of the aggregate consists of two μ_3-$Cu_3(OH)$ cores held by three peripheral bridging ligands and a μ-chloro bridge. The compound crystallises in the triclinic space group $P\bar{1}$ (C_i, no. 2) and has unit-cell dimensions a = 13.288(10), b = 14.678(7), c = 22.591(23) Å, α = 102.96(6), β = 89.07(7), γ = 113.15(5)°, and Z = 2. Antiferromagnetic coupling is observed with J values of −51, −70, and −72 cm^{-1} noted for the three dicopper pairings. The complexity of the system however leaves an uncertainty in the interpretation of the magnetic data, illustrating an inherent weakness in the capability of the technique to deal with high-nuclearity clusters.

When addressing the problem of modelling binuclear copper biosites a major feature that must be duplicated is the intermetallic distance. This distance has been found to span a domain ranging from *ca.* 3.45 Å for the metaqua- and metfluoro-derivatives of haemocyanins to 3.66 Å for metazidohaemocyanin.[2] Most model systems presented so far fail to reproduce this essential structural characteristic of the proteins. The reason for this lies in the fact that the models are built around the classical Robson unit, 2,6-di-imino-4-methylphenol,[3] or result from the incorporation of two tripodal groups onto the related 2,6-dimethylphenol.[4–5] In either case structural analyses have shown that the intercopper distance cannot be longer than 3.3 Å.[6] This effect is most important when the reactivity of the system is considered, and a good illustration of this is furnished by the co-ordination of the azide anion to binuclear copper centres. In most synthetic systems this anion co-ordinates *via* the μ-1,1 mode, accommodating short Cu–Cu separations (3.1 Å),[7] but this co-ordination mode is incompatible with the separation found in azido-derivatives of the protein.[2] The latter separation, however, is conveniently reproduced by a system involving a 3-hydroxypropyl group which gives a higher flexibility to the overall ligand system.[8]

The above considerations led us to investigate the chemistry of copper complexes derived from 2,6-bis(aminomethyl)-4-nitrophenol.[9] In this system the free rotation at the methylene group allows for geometrical distortions and the accommodation of long Cu–Cu separations is anticipated. This expectation has been confirmed by the isolation of a hexanuclear cluster in which the same ligand framework maintains the copper atoms at distances as different as 3.01 and 3.50 Å.



H_3L



$[Cu_2LX]$

The building blocks of the cluster are the organic ligands and a pair of triply bridging hydroxides. The first structural characterisation of a μ_3-OH complex was that of di-μ-aqua-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II).[10] Since that report the existence of $M_3O(H)$ cores supported by peripheral bridging ligands has been well documented. For copper(II) there has been a recent sequence of publications concerning such complexes in which the trimetal

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

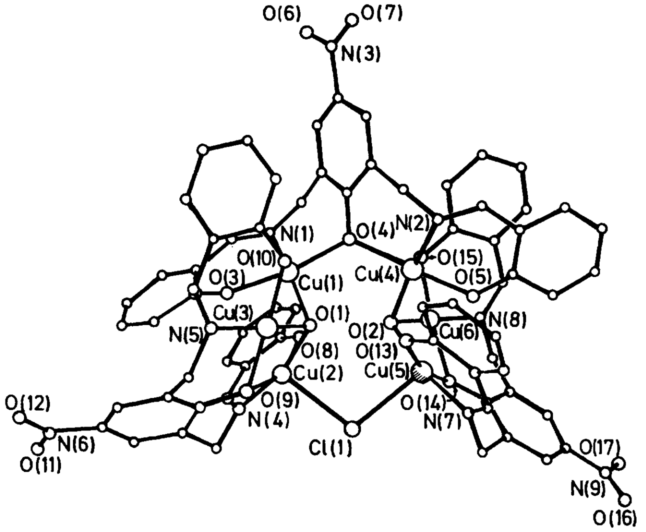


Figure 1. Molecular structure of the hexanuclear cluster. For clarity, the solvent dmf molecules on atoms Cu(3) and Cu(6) are omitted and the labelling of the carbon atoms is not shown

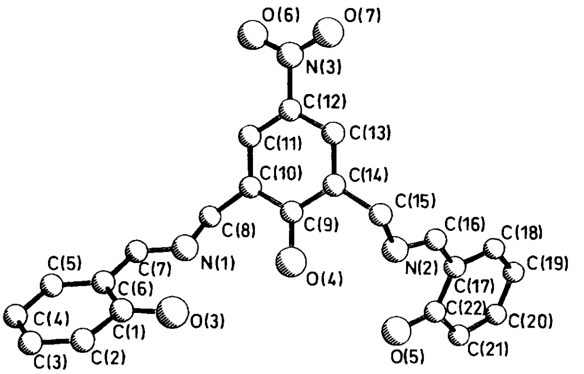


Figure 2. Atomic labelling of ligand L; the ligand shown is that which bridges Cu(1) and Cu(4) in the separate trinuclear fragments. The labellings for the other two ligands adds, respectively, 5 and 10 to the oxygen numbers, 3 and 6 to the nitrogen numbers, and 22 and 44 to the carbon numbers

core is supported by oxime ligands (pyridine-2-carbaldehyde oxime,[11] 3-methyl-3-propylaminobutan-2-one,[12] 3-phenylimino-butan-2-one oxime,[13] 2-methylimino-1,2-diphenylethanone oxime[13]), by pyrazole,[14] and by the tridentate Schiff base 7-amino-4-methyl-5-azahepten-2-one.[15] An unusual doubly μ_3-hydroxo-bridged copper(II) complex has been reported in which the peripheral ligand is the macrocycle 1,10,19-trioxa-4,7,13,16,22,25-hexa-azacycloheptacosane.[16] On a general basis these compounds exhibit antiferromagnetic interactions between the copper atoms and these interactions are favoured by the planarity of the Cu_3O core.[12] Herein the molecular structure and the magnetic properties of the hexanuclear cluster are described and analogy with the purported structure of metaqua- and metfluoro-haemocyanin is made.

Results and Discussion

Treatment of the Schiff base H_3L with copper(II) acetate in the presence of a potentially bridging ligand X^- [X = OH, OMe, N_3, p-$NO_2C_6H_4O$, pyrazolate (pz)] resulted in the formation of complexes of the type [Cu_2LX] in which the Schiff base has been fully deprotonated thus providing an endogenous bridge between the copper(II) atoms.[9]

The methoxide bridge can be introduced simply by carrying out the experiment in MeOH and so in an attempt to introduce a functionalised bridge the reaction of KH_2L with copper(II) acetate was carried out in 2-methoxyethanol. The product analysed however as Cu_2LOH and showed a band in the i.r. spectrum attributable to ν_{OH} at 3 425 cm^{-1}. In order to establish the nature of the complex and the binding modes of the likely endogenous and exogenous hydroxy bridges, determination of the crystal structure was undertaken.

The Molecular Structure.—The overall molecule (Figure 1) has approximate C_2 symmetry in which the different copper atoms associate into pairs: Cu(1) and Cu(4), Cu(2) and Cu(5), Cu(3) and Cu(6). The two tricopper units are linked through the phenoxo oxygen O(4), bridging Cu(1) and Cu(4), and the chloride ion Cl(1) which bridges Cu(2) and Cu(5). It is thus evident that two 4-nitrophenolate ligands play identical roles while the third one occupies a unique position. Each tricopper unit is constituted of a pair of copper atoms from a binuclear entity linked through a triply bridging hydroxide to a third copper atom from the unique binuclear unit. The resulting triangular aggregate is approximately equilateral with a mean Cu–Cu distance of 3.01 Å. This short intermetallic distance is undoubtedly due to the non-planarity of the system since the triply bridging oxygens lie 0.87 or 0.93 Å above the planes of the copper atoms. Within the tricopper unit two coppers are doubly bridged by the phenoxide and the hydroxide. In contrast, within the unique unit the two coppers are linked by a single phenoxide bridge but each of them interacts with a hydroxide from another pair. In relation to the single bridge and distortions described below a far greater Cu–Cu separation (3.50 Å) is observed.

Every copper atom is in a tetragonal environment whose basal plane is constituted by a phenoxo bridging oxygen, a μ_3-hydroxo ligand, and a salicylideneimino chelate group. The co-ordination sphere of every copper atom is completed by two, more remote, axial ligands. For instance, the fifth and sixth co-ordination sites of Cu(1) and Cu(4) are occupied by the salicyl oxygen atoms of the ligands which bridge the other pairs. Conversely each salicyl oxygen of the ligand which bridges Cu(1) and Cu(4) occupies a common fifth co-ordination position of both atoms of the remaining pair in the tricopper unit. Therefore these oxygen atoms can be viewed as providing a weak and asymmetric μ_3-oxygen bridge for the Cu_3 moiety. The sixth co-ordination sites of the Cu(2) and Cu(5) atoms are filled by the bridging chloride and those of the Cu(3) and Cu(6) atoms by two planar, terminal dimethylformamide (dmf) molecules; these interactions are shorter and seem to be more structurally relevant than the aforementioned interactions involving the salicyl oxygen atoms. There are also present in the structure two non-co-ordinated, planar dmf molecules. Significant distortions of the basal co-ordination planes are observed for all copper atoms: those of Cu(1) and Cu(4) are tetrahedrally twisted, while for the others the copper atoms are markedly displaced from the basal plane towards the more strongly bound axial ligands.

The presence of saturated carbon atoms as immediate substituents on the 4-nitrophenol central ring of each ligand instead of the sp^2-hybridised carbons present in the related Robson-type complexes introduces a degree of flexibility to the bonding modes of the ligand and the configurations of the two types of ligand noted in the structure differ noticeably (see Figure 1). In the two ligands related by approximate C_2 symmetry the two salicylideneimine fragments are located on the same side of the central 4-nitrophenol plane and the Cu_2O_2 units are folded along the O–O axis. The bending angles between the copper co-ordination planes [Cu(2)/Cu(3) and Cu(5)/Cu(6)] are 36.6 and 44.0°. This leads to short (3.00 and

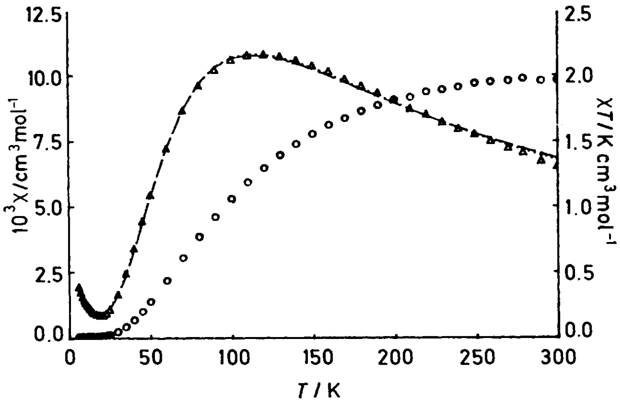


Figure 3. The temperature dependence of the molar magnetic susceptibility (χ) (△) and its product with temperature (χT) (○). The dashed curve is the theoretical susceptibility calculated according to the use of equation (2)

2.95 Å) Cu–Cu distances and reduced (100.75 and 97.9°) Cu–O–Cu angles. In the unique ligand the two salicylideneimine fragments are positioned on either side of the central 4-nitrophenol plane with approximate C_2 symmetry. The mean co-ordination planes of Cu(1) and Cu(4) present a 71.1° twisting angle. This leads to the extended intermetallic distance (3.50 Å) already noted and also the wide (126°) Cu(1)–O(4)–Cu(4) angle.

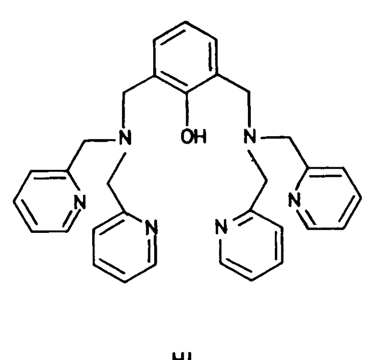
The two μ_3-hydroxy groups are each hydrogen-bonded to a co-ordinated salicylidene oxygen atom in the other triangular cluster (O ••• O 2.75 and 2.74 Å). The aggregate is proposed as arising from an adventitious self-assembly process during the recrystallisation and the chloride bridge present in the structure is believed to arise from residual contamination in the bulk sample of KH_2L.

The atomic labelling of L is shown in Figure 2.

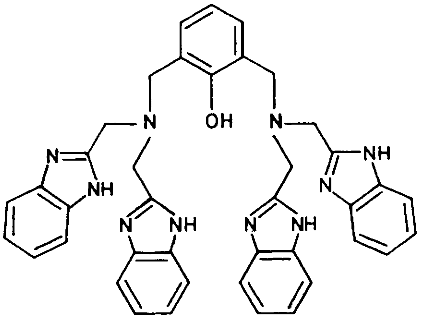
Magnetic Properties.—Figure 3 depicts the temperature dependence of the magnetic susceptibility in the form of the curves χ and χT *versus* T. The overall shape of the susceptibility curve is characteristic of an antiferromagnetically coupled system with a maximum around 120 K. The increase of the susceptibility at low temperature is attributable to the presence of a small amount of a monomeric impurity. The χT values, on the other hand, increase with temperature and reach values near $\chi T = 2$ K cm^3 mol^{-1}, which is slightly less than expected (2.25) for six independent spins of $\frac{1}{2}$.

The hexanuclear cluster can be regarded as constituted of two pairs of copper atoms [Cu(2)Cu(3) and Cu(5)Cu(6)] linked together by a chloride and to the third copper pair [Cu(1)Cu(4)] by two hydroxides. Alternatively the cluster can be viewed as a pair of trinuclear assemblies; both approaches will be considered in the following discussion. Due to the approximate symmetry the various coppers can be associated in couples [Cu(1) and Cu(4), Cu(2) and Cu(5), Cu(3) and Cu(6)] whose members play identical roles. However, examination of Table 1 reveals that significant disparities do exist in the relative structural parameters thus reducing the symmetry. For example, the intrapair CuO(H)Cu angles exhibit very different values: Cu(2)–O(1)–Cu(3) 100.75 and Cu(5)–O(2)–Cu(6) 97.92°. Accordingly the following exchange interactions must be taken into account: J_{14}, J_{23}, J_{56}, J_{25}, J_{12}, J_{13}, J_{45}, and J_{46}. All other interactions are supposed negligible since they involve multiatomic pathways.

After having identified all the interactions which can reasonably be operating, one can try to estimate their relative importance. This is not a very rigorous process since it is not possible to isolate an interaction between two particular atoms from the whole cluster; nevertheless this is helpful in building a simplistic model which will prove reasonably realistic. It is expected that the main interactions will occur between the coppers inside the pairs rather than between coppers belonging to different pairs. Two different types of pairs are present in the cluster. First Cu(2)Cu(3) and Cu(5)Cu(6) hold a mixed hydroxy–phenoxy bridging pattern; this situation is documented in the literature[7a,17–24] and values of J for these kinds of binuclear compounds with comparable Cu–O–Cu angles lie in the range -50 to -200 cm^{-1}. Lower values are expected here due to the non-planarity of the CuOCuO moiety which probably lessens both the ferromagnetic and the antiferromagnetic contributions to the exchange interaction.[25]



HL_A



HL_B

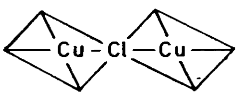
The Cu(1)Cu(4) pair, on the other hand, has a single phenoxide bridge. Single bridges are far less common for dinuclear copper complexes than double ones and, to the best of our knowledge, there are only two examples in the literature of a phenoxide singly bridging two copper(II) ions; in both cases the ligands are Karlin-type polypodal systems (HL_A and HL_B).[5,19]

Two examples of monoalkoxo-bridged compounds have recently been reported,[26,27] together with a few monohydroxo-bridged derivatives.[28–31] No correlation similar to the one derived by Hatfield and co-workers[32] for di-μ-hydroxo dicopper(II) derivatives exists for the singly bridged species. Literature data, however, show that they follow the general trend: the wider the Cu–O–Cu angle, the larger the antiferromagnetic interaction. Accordingly a significant interaction is to be expected in the present case since the Cu(1)–O(4)–Cu(4) angle is 126°, but it is not possible to estimate it precisely.

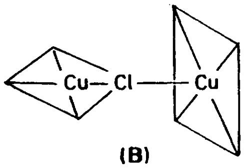
One can now focus on the interpair interactions which can occur through the chloride and hydroxide bridges. Chloro-bridged dicopper(II) complexes have been extensively studied and magnetostructural correlations have been observed when

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations for the hexanuclear cluster

Cu(1) · · · Cu(2)	2.974(2)	Cu(4) · · · Cu(5)	3.001(2)	Cu(2)–O(9)	2.062(5)	Cu(5)–O(14)	2.028(5)
Cu(1) · · · Cu(3)	3.148(2)	Cu(4) · · · Cu(6)	3.019(2)	Cu(2)–N(4)	1.897(7)	Cu(5)–N(7)	1.907(7)
Cu(2) · · · Cu(3)	2.995(2)	Cu(5) · · · Cu(6)	2.946(2)	Cu(2)–Cl(1)	2.550(3)	Cu(5)–Cl(1)	2.585(3)
Cu(1) · · · Cu(4)	3.502(3)	Cu(2) · · · Cu(5)	3.994(3)	Cu(2)–O(3)	2.817(6)	Cu(5)–O(5)	2.667(6)
Cu(1)–O(1)	1.993(5)	Cu(4)–O(2)	1.969(5)	Cu(3)–O(1)	1.937(5)	Cu(6)–O(2)	1.947(5)
Cu(1)–O(4)	1.957(5)	Cu(4)–O(4)	1.968(5)	Cu(3)–O(9)	2.071(5)	Cu(6)–O(14)	2.033(5)
Cu(1)–O(3)	1.893(6)	Cu(4)–O(5)	1.907(6)	Cu(3)–O(10)	1.891(6)	Cu(6)–O(15)	1.913(6)
Cu(1)–N(1)	1.944(7)	Cu(4)–N(2)	1.909(7)	Cu(3)–N(5)	1.918(7)	Cu(6)–N(8)	1.901(7)
Cu(1)–O(8)	2.491(6)	Cu(4)–O(13)	2.577(6)	Cu(3)–O(18)	2.392(6)	Cu(6)–O(19)	2.341(7)
Cu(1)–O(10)	3.036(6)	Cu(4)–O(15)	2.731(6)	Cu(3)–O(3)	2.727(6)	Cu(6)–O(5)	2.647(6)
Cu(2)–O(1)	1.951(5)	Cu(5)–O(2)	1.959(5)	O(1) · · · O(13)	2.751(8)	O(2) · · · O(8)	2.737(7)
Cu(2)–O(8)	1.959(6)	Cu(5)–O(13)	1.922(6)				
O(1)–Cu(1)–O(4)	95.02(21)	O(2)–Cu(4)–O(4)	93.52(21)	O(9)–Cu(2)–Cl(1)	103.13(16)	O(14)–Cu(5)–Cl(1)	102.76(16)
O(1)–Cu(1)–O(3)	84.12(22)	O(2)–Cu(4)–O(5)	83.77(22)	O(9)–Cu(2)–O(3)	79.52(19)	O(14)–Cu(5)–O(5)	80.70(19)
O(1)–Cu(1)–N(1)	165.05(25)	O(2)–Cu(4)–N(2)	173.15(19)	N(4)–Cu(2)–Cl(1)	99.36(21)	N(7)–Cu(5)–Cl(1)	97.44(21)
O(1)–Cu(1)–O(8)	73.11(19)	O(2)–Cu(4)–O(13)	70.80(19)	N(4)–Cu(2)–O(3)	100.07(23)	N(7)–Cu(5)–O(5)	100.00(24)
O(1)–Cu(1)–O(10)	60.28(19)	O(2)–Cu(4)–O(15)	68.15(18)	Cl(1)–Cu(2)–O(3)	160.24(13)	Cl(1)–Cu(5)–O(5)	162.10(13)
O(4)–Cu(1)–O(3)	163.30(23)	O(4)–Cu(4)–O(5)	172.12(23)	O(1)–Cu(3)–O(9)	81.55(21)	O(2)–Cu(6)–O(14)	81.78(21)
O(4)–Cu(1)–N(1)	91.74(25)	O(4)–Cu(4)–N(2)	90.82(25)	O(1)–Cu(3)–O(10)	88.94(24)	O(2)–Cu(6)–O(15)	89.09(24)
O(4)–Cu(1)–O(8)	106.75(20)	O(4)–Cu(4)–O(13)	105.42(20)	O(1)–Cu(3)–N(5)	169.16(26)	O(2)–Cu(6)–N(8)	165.74(26)
O(4)–Cu(1)–O(10)	86.92(19)	O(4)–Cu(4)–O(15)	92.44(20)	O(1)–Cu(3)–O(18)	98.21(21)	O(2)–Cu(6)–O(19)	98.56(22)
O(3)–Cu(1)–N(1)	93.18(26)	O(5)–Cu(4)–N(2)	92.59(26)	O(1)–Cu(3)–O(3)	65.38(19)	O(2)–Cu(6)–O(5)	66.57(19)
O(3)–Cu(1)–O(8)	89.01(21)	O(5)–Cu(4)–O(13)	80.72(21)	O(9)–Cu(3)–O(10)	167.33(24)	O(14)–Cu(6)–O(15)	162.79(24)
O(3)–Cu(1)–O(10)	78.15(21)	O(5)–Cu(4)–O(15)	79.69(21)	O(9)–Cu(3)–N(5)	93.82(26)	O(14)–Cu(6)–N(8)	92.10(26)
N(1)–Cu(1)–O(8)	92.17(23)	N(2)–Cu(4)–O(13)	102.92(24)	O(9)–Cu(3)–O(18)	85.68(21)	O(14)–Cu(6)–O(19)	84.38(22)
N(1)–Cu(1)–O(10)	133.58(23)	N(2)–Cu(4)–O(15)	116.99(24)	O(9)–Cu(3)–O(3)	81.60(19)	O(14)–Cu(6)–O(5)	81.13(19)
O(8)–Cu(1)–O(10)	132.49(17)	O(13)–Cu(4)–O(15)	135.96(18)	O(10)–Cu(3)–N(5)	94.07(29)	O(15)–Cu(6)–N(8)	93.35(28)
O(1)–Cu(2)–O(8)	87.37(22)	O(2)–Cu(5)–O(13)	87.34(22)	O(10)–Cu(3)–O(18)	104.06(24)	O(15)–Cu(6)–O(19)	111.52(24)
O(1)–Cu(2)–O(9)	81.43(21)	O(2)–Cu(5)–O(14)	81.62(21)	O(10)–Cu(3)–O(3)	86.84(23)	O(15)–Cu(6)–O(5)	81.85(22)
O(1)–Cu(2)–N(4)	162.95(25)	O(2)–Cu(5)–N(7)	165.30(25)	N(5)–Cu(3)–O(18)	91.18(26)	N(8)–Cu(6)–O(19)	93.61(27)
O(1)–Cu(2)–Cl(1)	97.57(16)	O(2)–Cu(5)–Cl(1)	96.90(16)	N(5)–Cu(3)–O(3)	104.34(24)	N(8)–Cu(6)–O(5)	99.85(25)
O(1)–Cu(2)–O(3)	63.19(10)	O(2)–Cu(5)–O(5)	65.98(19)	O(18)–Cu(3)–O(3)	160.48(19)	O(19)–Cu(6)–O(5)	160.52(20)
O(8)–Cu(2)–O(9)	158.24(22)	O(13)–Cu(5)–O(14)	158.62(23)	Cu(1)–O(1)–Cu(2)	97.83(22)	Cu(4)–O(2)–Cu(5)	99.62(23)
O(8)–Cu(2)–N(4)	92.59(26)	O(13)–Cu(5)–N(7)	94.21(26)	Cu(1)–O(1)–Cu(3)	106.47(24)	Cu(4)–O(2)–Cu(6)	100.89(23)
O(8)–Cu(2)–Cl(1)	96.78(17)	O(13)–Cu(5)–Cl(1)	96.68(18)	Cu(2)–O(1)–Cu(3)	100.75(23)	Cu(5)–O(2)–Cu(6)	97.92(22)
O(8)–Cu(2)–O(3)	78.79(20)	O(13)–Cu(5)–O(5)	78.09(21)	Cu(1)–O(4)–Cu(4)	126.3(3)	Cu(2)–O(9)–Cu(3)	92.9(2)
O(9)–Cu(2)–N(4)	92.77(25)	O(14)–Cu(5)–N(7)	92.04(25)	Cu(5)–O(14)–Cu(6)	93.0(2)	Cu(2)–Cl(1)–Cu(5)	102.13(12)



(A)



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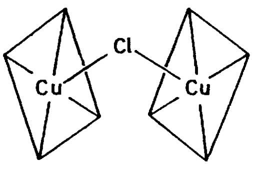

(C)

the chloro bridges occupy equatorial–equatorial[33] (**A**) or equatorial–axial[34] (**B**) positions in the co-ordination spheres of the two copper atoms. The present situation (**C**) deviates from the preceding cases since the bridging chloride is axial to both coppers. It is more similar to the one described by Hodgson and Pederson[35] where the chloro bridges are the edges shared by two trigonal bipyramids or to the one reported by Kida and co-workers[19] for a μ-phenoxo-dicopper(II) complex where the phenoxide bridge occupies the apices of both square-pyramidal copper(II) environments. In these cases, as in ours, neither magnetic orbital is pointing toward the bridging atom and the corresponding exchange integral is quite weak (< 1 cm^{-1}). We do not expect J_{23} to be larger than this value and it will not be taken into account in the calculations.

The hydroxides are involved in a triple bridge consisting of the copper pair and a third copper belonging to the Cu(1)Cu(4) pair. Tricopper complexes involving a triply bridging hydroxide have recently been described.[11,13–15,36] Although the data are still very limited and no strict magnetostructural correlation has yet appeared it seems that the magnitude of the antiferromagnetic coupling is strongly related to the planarity of the Cu_3O core: the more planar it is the higher the antiferromagnetic coupling. The present triply bridging hydroxides are the most pyramidal described so far. This observation suggests that the corresponding interactions (J_{12}, J_{13}, J_{45}, and J_{46}) will not be strongly antiferromagnetic and may even be ferromagnetic.

From the very beginning it is clear that too many variables will be present if one tries to simulate the experimental data with all the parameters allowed to vary.[37] So in order to avoid these likely intricacies we make the assumption that J_{12}, J_{13}, J_{45}, and J_{46} along with J_{23} are negligible. This leaves us with a simple model which takes only the three interpair interactions into account. The resulting Hamiltonian then takes the form of equation (1), which is identical to the sum of the interactions of three isolated dinuclear units. It is noted that, due to the

Table 2. Experimental and calculated values of the magnetic susceptibility of the hexanuclear cluster

T_0/K	χ(exp)	ψ_{calc} *
299.7	6.542	6.856
289.8	6.746	7.025
278.8	7.074	7.221
269.8	7.245	7.39
259	7.514	7.601
249.1	7.773	7.805
239.2	7.98	8.017
229.3	8.231	8.237
219.5	8.521	8.465
209.5	8.735	8.706
199.5	9.072	8.951
189.6	9.335	9.204
179.6	9.596	9.462
169.6	9.85	9.721
159.8	10.14	9.974
149.8	10.36	10.22
139.8	10.57	10.44
129.9	10.71	10.62
119.9	10.79	10.73
109.9	10.76	10.76
99.75	10.59	10.63
89.8	10.21	10.31
79.85	9.617	9.692
70	8.668	8.713
60.01	7.229	7.273
49.97	5.442	5.388
44.99	4.436	4.35
39.98	3.405	3.314
34.99	2.447	2.368
29.98	1.649	1.605
25.01	1.086	1.111
22.99	0.9459	0.9965
20.99	0.8714	0.9305
18.99	0.8689	0.9092
16.99	0.8998	0.9282
15	0.9539	0.9834
14	1.022	1.024
13	1.095	1.074
12	1.166	1.134
11	1.25	1.206
9.995	1.342	1.293
8.99	1.444	1.401
7.995	1.568	1.533
6.99	1.742	1.706
5.99	1.937	1.935

* Calculated from equation (2).

symmetry of the Hamiltonian (1), it is not possible, at this stage,

$$\mathscr{H}_0 = -2(J_{14}\vec{S}_1\vec{S}_4 + J_{23}\vec{S}_2\vec{S}_3 + J_{56}\vec{S}_5\vec{S}_6) \qquad (1)$$

unambiguously to attribute the various exchange integrals. For this reason we choose to use different subscripts to distinguish between them. The corresponding equation (2) is thus the sum

$$\psi_{calc} = \frac{N\beta^2}{4kT}g_m{}^2P + \frac{N\beta^2}{3kT}g^2(1 - P) \times [(1 + \tfrac{1}{3}e^{-2J_1/kT})^{-1} + (1 + \tfrac{1}{3}e^{-2J_2/kT})^{-1} + (1 + \tfrac{1}{3}e^{-2J_3/kT})^{-1}] + \text{t.i.p.} \qquad (2)$$

of three Bleaney–Bowers[38] terms with the usual modifications to include the monomeric impurity and the temperature-independent paramagnetism (t.i.p.).

The best fit obtained with this equation appears as the dashed line in Figure 3 (see also Table 2) and the resulting parameters are: $g_m = 2.04$, $P = 0.0123$, $g = 2.06$, $J_1 = -51$ cm^{-1}, $J_2 = -72$ cm^{-1}, $J_3 = -70$ cm^{-1}, t.i.p. = 333×10^{-4} cm^3 mol^{-1}. This simple model does work in most of the temperature domain, although in the upper part a slight discrepancy is observed. Surprisingly, two exchange integrals are set almost equal while, according to the previous discussion, structural data seemed to warrant that every interaction would be unique.

As discussed above the data on μ_3-hydroxo-tricopper(II) derivatives do not exclude the possibility of the interactions between the central pair [Cu(1)Cu(4)] and the two lateral ones [Cu(2)Cu(3) and Cu(5)Cu(6)] being important in the present cluster. However, attempts to treat the entire cluster by a six-*J* model using techniques we have described elsewhere[39,40] lead to unreasonably high ferromagnetic values for the inter-trimer terms. These are compensated for by more negative intra-trimer interactions and detailed analysis of the fit operation that has shown that strong correlations exist between several parameters. Such problems are not unusual for polynuclear clusters[37,41,42] and preclude a more precise evaluation of the various exchange integrals than that obtained from the simple model above.

Conclusions

The structure determination of the hexanuclear cluster has confirmed the expectation that the new ligand system is flexible enough to accommodate very different intercopper distances in binuclear copper complexes derived from it. Although only single-atom hydroxo bridges are observed in the present case the longer Cu–Cu separation reported is compatible with μ-1,2- and even μ-1,3-bridging entities.

It is worth noting that this Cu–Cu separation is the largest observed so far with this kind of binucleating ligand. In a related dinuclear copper(II) complex of a polypodal ligand in which the pyrazolate-bearing arms are directly linked to the phenol *via* C–N bonds and the exogenous azide is in the 1,3-bridging mode a Cu–Cu separation of 3.756 Å has been reported.[43] From the bioinorganic viewpoint the μ-phenoxy–dicopper unit may be compared with the metaqua- and metfluoro-haemocyanins for which there is evidence for a singly bridged dicopper unit with intercopper separations of 3.39—3.45 and 3.50 Å respectively.[2,44] To our knowledge the present arrangement represents the first model for methaemocyanins derived from binucleating Schiff-base ligands; the polypodal ligands L_A and L_B both give dinuclear copper(II) complexes in which there is an endogenous phenoxide bridge and exogenous monodentate ligation of the Cu^{II} atoms: $[Cu_2L_ACl_2]^+$ (ref. 19) and $[Cu_2L_B(H_2O)]^{3+}$ (ref. 5) (the Cu . . . Cu separations are 4.128 and 3.785 Å respectively, much in excess of the EXAFS determined distances in methaemocyanins).

The nature of the natural endogenous bridge is not yet defined and sequential studies on various haemocyanins have indicated that tyrosine is unlikely to provide the bridge in deoxy- or oxy-haemocyanins.[45] Consequently it is necessary to view the phenoxide in this study as a 'suppositional' bridging species within a speculative model for the metsites. As mentioned earlier such mono-bridged dicopper entities are not numerous and studies of their physical and, especially, magnetic properties can contribute considerably to our understanding of the behaviour of the protein.

Unfortunately the present magnetic susceptibility analysis has not permitted the determination of all of the values for the exchange integrals operative in the cluster. A similar uncertainty in the quantitative evaluation of the parameters has already been observed in the treatment of the magnetic susceptibility data for tetra-[41] and penta-nuclear clusters.[42] However, in the latter case e.s.r. experiments allow for discrimination between the various possibilities; unfortunately in the present study the e.s.r. technique does not help. The magnetic problem to be solved here is more complex than in the above examples and difficulties in obtaining data, as outlined in the Experimental section, are likely to lower the accuracy of the experimental values. Overall this illustrates the inherent weakness of the magnetic susceptibility experiments unambiguously to assign the magnetic properties of high-nuclearity clusters in the absence of another complementary technique.

Experimental

Synthesis.—(*a*) *2,6-Bis(aminomethyl)-4-nitrophenol dihydrochloride*, (**1**). *N*-Hydroxymethylphthalimide was prepared by the method of Buc.[46] 2,6-Bis(phthaloylmethyl)-4-nitrophenol was prepared by adaptation of the Tscherniac–Einhorn reaction.[47] *N*-Hydroxymethylphthalimide (34.0 g, 192 mmol) and 4-nitrophenol (13.35 g, 96 mmol) were ground together to form an intimate mixture and added over 5 min to concentrated H_2SO_4 (350 cm^3) with stirring and cooling in ice. When the addition was complete the clear orange solution was allowed to warm to room temperature and stirred for a further 2 h. The solution was poured into crushed ice with stirring and the white precipitate filtered off. This was washed with copious amounts of water until the filtrate was no longer acidic (6 × 1 000 cm^3). The product was dried *in vacuo*, or in an oven at 105 °C. Yields averaged *ca.* 90%. An analytical sample was recrystallised from dmf (Found: C, 63.0; H, 3.6; N, 9.0. Calc. for $C_{24}H_{15}N_3O_7$: C, 63.0; H, 3.3; N, 9.2%). I.r.: 1 700 [ν(C=O)], 1 520 [$\nu_{asym}(NO_2)$], 1 340 cm^{-1} [$\nu_{sym}(NO_2)$].

2,6-Bis(phthaloylmethyl)-4-nitrophenol (30.0 g, 65.6 mmol) was suspended in methanol (600 cm^3) and heated to reflux. Hydrazine hydrate (6.75 g, 131.2 mmol) was added and the mixture was refluxed for a further 2 h. The intense yellow suspension was reduced to dryness on a rotary evaporator and dilute HCl (500 cm^3, 0.5 mol dm^{-3}) was added. This suspension was heated at 50 °C for 1 h then refrigerated overnight. The precipitate of phthalohydrazide was filtered off and the filtrate reduced to dryness to yield the crude product. Recrystallisation from acidified propan-1-ol–water gave pale yellow plates. Yields were *ca.* 60% (Found: C, 33.9; H, 5.4; Cl, 23.5; N, 15.0. Calc. for $C_8H_{13}Cl_2N_3O_3$: C, 33.4; H, 5.3; Cl, 24.6; N, 14.6%).

(*b*) *The dinuclear copper*(II) *complex.* The diamine (**1**) (2.7 g, 10 mmol) was suspended in ethanol (100 cm^3) and treated with an ethanolic solution of KOH (1.68 g, 30 mmol). The resulting solution was refluxed for 15 min. Salicylaldehyde (2.44 g, 20 mmol) was added dropwise and heating continued for 4 h. The potassium salt of the Schiff base (KH_2L) was isolated as a yellow powder in 75% yield by filtration and dried over silica gel *in vacuo* (Found: C, 59.0; H, 4.3; N, 9.1. Calc. for $C_{22}H_{18}KN_3O_5$: C, 59.6; H, 4.1; N, 9.5%).

The salt KH_2L (0.1 g, 0.23 mmol) was suspended in 2-methoxyethanol (25 cm^3) and treated with a solution of copper(II) acetate (0.09 g, 0.46 mmol) in the same solvent (25 cm^3). The mixture was refluxed for 1 h and then allowed to cool to ambient temperature. The bright green precipitate was filtered off and dried over silica gel *in vacuo* (yield 0.05 g) (Found: C, 48.25; H, 4.10; N, 7.05. Calc. for $C_{22}H_{17}Cu_2N_3O_6$: C, 48.6; H, 3.15; N, 7.70%). I.r.: 3 425 [ν(OH)], 1 635 [ν(C=N)], 1 600, 1 590 [ν(C=C)], 1 300 cm^{-1} [$\nu(NO_2)$].

Physical Measurements.—Elemental analyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrophotometer.

Table 3. Summary of crystal data

Compound	$[\{Cu_3L(OH)(dmf)\}_2(\mu\text{-}Cl)(\mu\text{-}L)]\cdot 2dmf$
Formula	$C_{78}H_{78}ClCu_6N_{13}O_{21}$
M	1 950.23
a/Å	13.288(10)
b/Å	14.678(7)
c/Å	22.591(23)
α/°	102.96(6)
β/°	89.07(7)
γ/°	113.15(5)
U/Å^3	3 935(5)
Z	2
F(000)	1 992
D_m/g cm^{-3}	1.61
D_c/g cm^{-3}	1.646
Space group	$P\bar{1}$ (C_i, no. 2)
Radiation	Graphite-monochromated Mo-K_α ($\bar{\lambda}$ = 0.710 69 Å)
Linear absorption coefficient	μ(Mo-K_α) = 17.12 cm^{-1}

Magnetic susceptibility measurements were carried out using a variable-temperature superconducting magnetometer SHE 900 operating at 5 kG (0.5 T) in the range 6—300 K. The sample was constituted of a few crystals (weight 2.7 mg) contained in a Nylon bucket which was calibrated independently. Data were corrected for a small amount of saturated ferromagnetic impurity. Diamagnetic corrections were evaluated using Pascal's constants. The data were least-squares fitted to equation (2). The quantity minimized in the fitting process was $\Sigma(\psi_{obs} - \psi_{calc})^2$. The quality of the fit was estimated through the statistical indicator *R* (see below), where

$$R = \frac{\Sigma(\psi_{obs} - \psi_{calc})^2}{N\Sigma(\psi_{obs}{}^2)}$$

N is the number of measurements; *R* amounted to 4.7 × 10^{-6} when the Hamiltonian of equation (1) was used.

Crystal Structure Determination.—The complex was crystallised from dmf as irregular green blocks. The selected crystal was of dimensions 0.48 × 0.28 × 0.25 mm. Three-dimensional *X*-ray diffraction data were collected (Table 3) in the range $3.5 < 2\theta < 50°$ on a Nicolet R3m diffractometer by the omega-scan method. The 6 846 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by image-seeking Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.97, O–H 0.91 Å, N–C–H 112°); their contributions were included in structure factor calculations (B = 7.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at *R* 0.0471 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper and chlorine. Table 4 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 48; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system. Selected bond lengths and angles are presented in Table 1.

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

Table 4. Atomic positional parameters with estimated standard deviations for the hexanuclear cluster*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.034 79(8)	−0.194 76(7)	−0.287 23(4)	C(20)	0.638 1(8)	0.316 0(7)	−0.322 8(5)
Cu(2)	0.017 17(8)	−0.102 92(7)	−0.158 12(4)	C(21)	0.562 0(7)	0.265 5(6)	−0.287 0(4)
Cu(3)	−0.128 87(8)	−0.087 64(7)	−0.251 63(4)	C(22)	0.458 7(7)	0.189 5(6)	−0.313 7(4)
Cu(4)	0.265 38(8)	0.014 89(7)	−0.308 02(4)	C(23)	0.140 8(6)	−0.232 3(5)	−0.165 2(3)
Cu(5)	0.285 01(8)	0.134 26(7)	−0.179 04(4)	C(24)	0.217 8(7)	−0.268 6(6)	−0.192 1(4)
Cu(6)	0.430 57(8)	−0.026 10(7)	−0.213 49(4)	C(25)	0.233 8(7)	−0.346 1(6)	−0.174 4(4)
Cl(1)	0.152 27(17)	0.071 07(15)	−0.098 15(9)	C(26)	0.176 0(8)	−0.389 8(7)	−0.130 0(5)
O(1)	0.021 7(4)	−0.069 9(3)	−0.237 39(22)	C(27)	0.101 8(7)	−0.355 7(7)	−0.102 9(4)
O(2)	0.275 8(4)	0.000 3(3)	−0.224 07(21)	C(28)	0.083 5(6)	−0.275 7(6)	−0.118 9(4)
O(3)	−0.101 6(5)	−0.264 1(4)	−0.257 63(25)	C(29)	0.006 8(6)	−0.241 6(6)	−0.085 3(4)
O(4)	0.147 8(4)	−0.122 0(4)	−0.336 14(21)	C(30)	−0.098 8(6)	−0.144 7(7)	−0.053 2(4)
O(5)	0.392 2(4)	0.138 1(4)	−0.279 93(23)	C(31)	−0.218 3(6)	−0.142 6(5)	−0.136 6(4)
O(6)	0.099 2(7)	−0.428 2(5)	−0.584 32(30)	C(32)	−0.208 0(6)	−0.180 3(6)	−0.086 7(3)
O(7)	0.105 4(7)	−0.299 0(6)	−0.616 30(28)	C(33)	−0.299 1(7)	−0.252 4(6)	−0.069 8(3)
O(8)	0.126 1(4)	−0.159 7(4)	−0.184 32(23)	C(34)	−0.399 5(6)	−0.281 9(6)	−0.100 9(4)
O(9)	−0.128 9(4)	−0.084 8(4)	−0.159 56(23)	C(35)	−0.413 8(6)	−0.236 3(6)	−0.144 5(4)
O(10)	−0.111 0(5)	−0.108 3(5)	−0.336 17(25)	C(36)	−0.323 6(6)	−0.165 1(5)	−0.162 1(4)
O(11)	−0.479 9(5)	−0.407 9(5)	−0.049 10(31)	C(37)	−0.337 2(7)	−0.109 1(7)	−0.206 6(4)
O(12)	−0.580 0(5)	−0.394 1(6)	−0.115 72(38)	C(38)	−0.342 0(7)	−0.170 2(6)	−0.313 0(4)
O(13)	0.175 4(4)	0.121 3(4)	−0.238 50(24)	C(39)	−0.301 7(7)	−0.190 2(6)	−0.370 7(4)
O(14)	0.429 2(4)	0.142 1(4)	−0.145 04(22)	C(40)	−0.378 2(8)	−0.243 3(8)	−0.421 1(5)
O(15)	0.416 7(5)	−0.062 4(4)	−0.292 05(25)	C(41)	−0.347 1(8)	−0.263 3(8)	−0.478 3(5)
O(16)	0.776 3(6)	0.570 2(5)	−0.015 15(37)	C(42)	−0.236 6(9)	−0.229 0(8)	−0.487 5(4)
O(17)	0.876 6(5)	0.483 9(5)	−0.029 89(38)	C(43)	−0.159 3(8)	−0.175 5(7)	−0.440 0(4)
O(18)	−0.102 4(5)	0.087 6(4)	−0.220 45(27)	C(44)	−0.187 3(7)	−0.155 3(7)	−0.380 7(4)
O(19)	0.420 9(5)	−0.057 6(4)	−0.135 39(27)	C(45)	0.169 1(6)	0.196 7(6)	−0.257 7(4)
O(20)	0.584 7(8)	0.336 4(7)	0.285 28(49)	C(46)	0.099 0(8)	0.176 2(7)	−0.308 8(4)
O(21)	0.167 7(9)	0.454 1(7)	0.553 93(48)	C(47)	0.091 1(9)	0.253 3(8)	−0.331 5(5)
N(1)	0.060 4(5)	−0.318 5(4)	−0.315 39(28)	C(48)	0.151 6(10)	0.355 3(9)	−0.302 6(6)
N(2)	0.253 9(5)	0.044 2(4)	−0.385 21(29)	C(49)	0.217 7(9)	0.377 0(7)	−0.251 7(5)
N(3)	0.106 2(7)	−0.339 9(7)	−0.575 63(32)	C(50)	0.229 0(7)	0.301 2(6)	−0.227 8(4)
N(4)	−0.020 8(5)	−0.171 4(5)	−0.093 96(27)	C(51)	0.299 7(7)	0.333 4(6)	−0.173 5(4)
N(5)	−0.284 8(5)	−0.129 7(5)	−0.262 15(31)	C(52)	0.390 1(6)	0.319 9(6)	−0.089 1(4)
N(6)	−0.493 3(6)	−0.366 5(5)	−0.086 61(34)	C(53)	0.516 1(6)	0.226 6(5)	−0.120 0(3)
N(7)	0.325 2(5)	0.276 8(5)	−0.147 30(29)	C(54)	0.502 9(7)	0.317 4(6)	−0.092 9(4)
N(8)	0.586 6(5)	0.081 7(5)	−0.208 96(29)	C(55)	0.594 1(7)	0.403 4(6)	−0.064 3(4)
N(9)	0.788 4(6)	0.491 0(6)	−0.033 30(36)	C(56)	0.695 3(7)	0.399 5(6)	−0.063 2(4)
N(10)	−0.021 1(6)	0.236 9(5)	−0.151 79(36)	C(57)	0.710 0(6)	0.313 2(6)	−0.089 6(4)
N(11)	0.350 0(6)	−0.081 3(6)	−0.046 13(31)	C(58)	0.621 4(6)	0.226 0(5)	−0.119 1(3)
N(12)	0.561 1(7)	0.482 4(7)	0.321 83(40)	C(59)	0.641 0(7)	0.132 1(6)	−0.146 9(4)
N(13)	0.247 8(7)	0.460 2(7)	0.463 62(46)	C(60)	0.643 2(7)	0.081 1(6)	−0.255 4(4)
C(1)	−0.128 1(6)	−0.350 5(5)	−0.241 2(4)	C(61)	0.597 4(7)	0.032 2(7)	−0.316 7(4)
C(2)	−0.218 2(7)	−0.378 9(6)	−0.205 2(4)	C(62)	0.667 0(9)	0.056 3(8)	−0.362 2(5)
C(3)	−0.244 6(7)	−0.463 8(7)	−0.183 0(4)	C(63)	0.628 7(10)	0.016 1(9)	−0.422 0(5)
C(4)	−0.186 8(8)	−0.525 5(7)	−0.195 9(5)	C(64)	0.522 5(10)	−0.051 6(9)	−0.437 3(5)
C(5)	−0.103 7(7)	−0.503 0(6)	−0.233 9(4)	C(65)	0.452 5(8)	−0.080 5(8)	−0.393 9(4)
C(6)	−0.074 8(7)	−0.416 2(6)	−0.256 7(3)	C(66)	0.486 6(7)	−0.036 9(6)	−0.332 2(4)
C(7)	0.014 1(6)	−0.398 6(5)	−0.295 2(4)	C(67)	−0.048 9(7)	0.137 0(7)	−0.172 3(5)
C(8)	0.151 1(7)	−0.313 6(6)	−0.354 4(4)	C(68)	−0.046 5(9)	0.294 8(7)	−0.187 5(5)
C(9)	0.141 6(6)	−0.172 8(5)	−0.394 5(3)	C(69)	0.045 1(11)	0.292 4(9)	−0.094 8(5)
C(10)	0.141 1(7)	−0.272 0(6)	−0.406 8(4)	C(70)	0.361 3(7)	−0.044 3(6)	−0.094 8(4)
C(11)	0.127 8(6)	−0.325 8(6)	−0.466 5(4)	C(71)	0.404 9(10)	−0.143 6(8)	−0.037 1(5)
C(12)	0.123 1(6)	−0.280 8(6)	−0.512 3(3)	C(72)	0.277 1(10)	−0.061 1(9)	−0.001 4(5)
C(13)	0.130 7(7)	−0.181 7(7)	−0.501 2(4)	C(73)	0.610 5(10)	0.418 3(9)	0.321 8(5)
C(14)	0.141 5(6)	−0.127 2(6)	−0.442 0(3)	C(74)	0.475 8(13)	0.456 3(14)	0.277 5(7)
C(15)	0.152 6(7)	−0.018 9(6)	−0.425 9(4)	C(75)	0.595 5(13)	0.578 7(11)	0.364 7(7)
C(16)	0.332 4(7)	0.106 2(6)	−0.408 1(4)	C(76)	0.166 4(11)	0.428 1(10)	0.497 7(7)
C(17)	0.437 4(7)	0.174 9(6)	−0.376 9(4)	C(77)	0.349 9(12)	0.532 8(11)	0.493 3(8)
C(18)	0.518 1(8)	0.229 2(7)	−0.410 7(4)	C(78)	0.237 9(13)	0.422 7(11)	0.399 8(6)
C(19)	0.618 6(8)	0.299 0(8)	−0.383 7(5)				

* Atoms [O(18), N(10), C(67)—C(69)], [O(19), N(11), C(70)—C(72)], [O(20), N(12), C(73)—C(75)], [O(21), N(13), C(76)—C(78)] comprise the four dimethylformamide molecules; the latter pair are not co-ordinated to the copper atoms. The three ligands (L) are labelled as shown in Figure 2.

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