Compartmental Ligands. Part 10.[1] Syntheses and Crystal and Molecular Structures † of the Copper(II) Complexes of Schiff Bases derived from 1-(Pyrrol-2-yl)butane-1,3-dione and 1,3-Bis-(2-aminophenoxy)propane, and from Pyrrole-2-carbaldehyde and 3,6-Dioxaoctane-1,8-diamine

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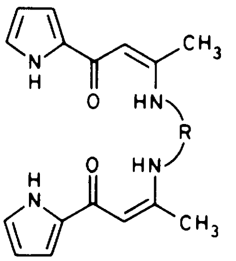
The synthesis of the acyclic Schiff bases H_4L^7 and H_2L^8, derived from 1-(pyrrol-2-yl)butane-1,3-dione and 1,3-bis(2-aminophenoxy)propane, and from pyrrole-2-carbaldehyde and 3,6-dioxaoctane-1,8-diamine, respectively are reported, together with their respective copper(II) complexes. Crystals of $[Cu(H_2L^7)]$ are monoclinic; R = 0.0549 for 1 901 observed reflections. The copper is co-ordinated in the inner (N_2O_2) compartment with a *trans* mode of attachment by the ligand; the approximately square-planar co-ordination geometry shows a significant tetrahedral distortion. The pyrrole and ether functions are not bonded to the copper. In the structure of $[Cu(HL^8)(O_2CMe)]$ (R = 0.0363, 4 800 reflections), the co-ordination geometries of the copper atoms in the two independent molecules are tetragonally-distorted octahedral, the two long axial bonds being to one acetate oxygen and to one of the ether oxygen atoms; one pyrrole residue is not co-ordinated to copper.

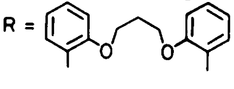
We have earlier reported the synthesis and properties of a series of copper(II) complexes of compartmental Schiff bases, H_4L, derived from 1-(pyrrol-2-yl)butane-1,3-dione.[2] The bridging units were either oligomethylenic chains, $(CH_2)_n$ (n = 2—5), or five-atom chains provided through use of the facultative alkane-α,ω-diamines, $NH_2(CH_2)_2E(CH_2)_2NH_2$ (E = O or S). The copper(II) was shown, through i.r. monitoring of the pyrrole NH stretch at *ca.* 3 300 cm^{-1}, to occupy the inner ligand compartment for chains up to three atoms long, and the outer compartment for the longer chains. *X*-Ray crystal structures of the mononuclear copper(II) complexes of H_4L^1 (ref. 3) and H_4L^5 (ref. 2) have confirmed the respective inner- and outer-compartmental occupancies.

This paper reports the synthesis and crystal and molecular structure of the copper(II) complex of H_4L^7, in which a nine-atom bridge is present. The copper(II) complex of the related single-compartment Schiff base, H_2L^8, having present an eight-atom bridge is also discussed, together with its crystal and molecular structure.



H_4L

H_4L^1; R = $(CH_2)_2$
H_4L^2; R = $(CH_2)_3$
H_4L^3; R = $(CH_2)_4$
H_4L^4; R = $(CH_2)_5$
H_4L^5; R = $(CH_2)_2O(CH_2)_2$
H_4L^6; R = $(CH_2)_2S(CH_2)_2$
H_4L^7; R =



Results and Discussion

The Schiff-base H_4L^7 was prepared by the reaction of 1-(pyrrol-2-yl)butane-1,3-dione and 1,3-bis(2-aminophenoxy)propane in ethanol and characterised by microanalysis, i.r., and m.s. The ligand was then reacted with copper(II) ethanoate to give a mononuclear copper(II) complex, $[Cu(H_2L^7)]$ (1), the i.r. of which gave bands at 3 405 and 3 380 cm^{-1} ascribable to the pyrrole NH stretching frequency. The presence of these bands is indicative of an inner compartmental occupancy and because of the long bridging unit several modes of copper(II) co-ordination can be envisaged.

Tetradentate Schiff-base complexes having long alkyl chains (n = 4—12) have been reported in the literature [4-8] and dimeric or polymeric association,[4,5] or the existence of a tetrahedral environment [6-8] for the metal in the monomeric complexes has been proven or inferred. The diffuse reflectance spectrum (d.r.s.) of complex (1) is dominated by a very broad and strong band centred on 408 nm, with a small shoulder at *ca.* 500 nm, and is indicative of a distorted square-planar geometry for copper(II). The crystal structure of the mononuclear copper(II) complex (1) was therefore undertaken in order to resolve the nature of the structure type present.

The structure of $[Cu(H_2L^7)]$ (1) is illustrated in Figure 1 with the atom labelling used in the corresponding Tables: selected bond lengths and angles (together with estimated standard deviations) are given in Table 1.

The molecule contains a copper atom in a tetrahedrally-distorted (28.2°) square-planar environment which, together with the extended chain between donor imino-nitrogen atoms, allows the latter to occupy relatively *trans* co-ordination sites at the copper. The remaining mutually *trans* co-ordination

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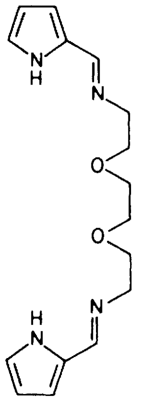
† *Supplementary data available* (No. SUP 56062, 16 pp.): anisotropic thermal parameters, H-atom co-ordinates, full bond lengths and angles, least-squares planes data. See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



H$_2$L^8

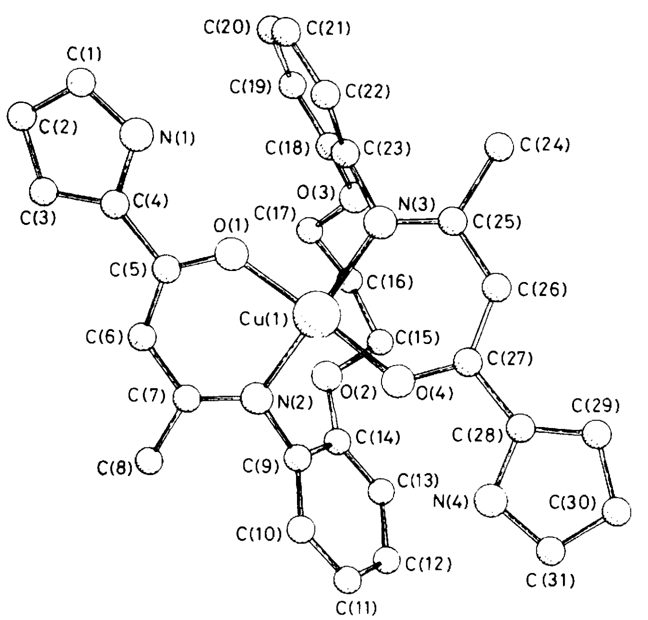
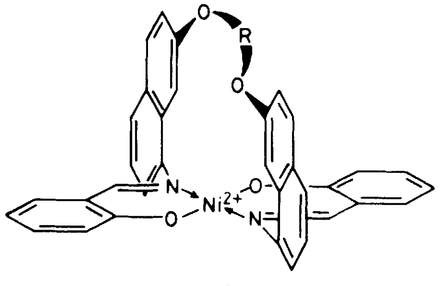


Figure 1. The molecular structure with atom labelling for [Cu(H$_2$L^7)] (1) showing the approximate C_2 symmetry

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations for [Cu(H$_2$L^7)] (1)

Cu(1)–O(1)	1.910(6)	Cu(1)–O(4)	1.909(6)
Cu(1)–N(2)	2.016(7)	Cu(1)–N(3)	2.013(7)
C(4)–C(5)	1.471(14)	C(27)–C(28)	1.484(14)
O(1)–C(5)	1.272(11)	O(4)–C(27)	1.289(12)
C(5)–C(6)	1.426(13)	C(26)–C(27)	1.418(14)
C(6)–C(7)	1.433(14)	C(25)–C(26)	1.415(13)
C(7)–C(8)	1.540(15)	C(24)–C(25)	1.554(14)
N(2)–C(7)	1.309(12)	N(3)–C(25)	1.303(11)
N(2)–C(9)	1.458(11)	N(3)–C(23)	1.442(12)
C(9)–C(14)	1.370(13)	C(18)–C(23)	1.383(14)
O(2)–C(14)	1.386(12)	O(3)–C(18)	1.382(13)
O(2)–C(15)	1.411(13)	O(3)–C(17)	1.411(14)
C(15)–C(16)	1.539(17)	C(16)–C(17)	1.527(17)
O(1)–Cu(1)–O(4)	156.8(3)	N(2)–Cu(1)–N(3)	162.8(3)
O(1)–Cu(1)–N(2)	93.7(3)	O(4)–Cu(1)–N(3)	93.6(3)
O(1)–Cu(1)–N(3)	89.3(3)	O(4)–Cu(1)–N(2)	90.4(3)
Cu(1)–O(1)–C(5)	126.1(6)	Cu(1)–O(4)–C(27)	125.9(6)
Cu(1)–N(2)–C(7)	125.2(6)	Cu(1)–N(3)–C(25)	125.3(6)
Cu(1)–N(2)–C(9)	116.2(5)	Cu(1)–N(3)–C(23)	117.0(6)
C(7)–N(2)–C(9)	118.1(7)	C(23)–N(3)–C(25)	117.2(7)
N(2)–C(9)–C(14)	116.0(8)	N(3)–C(23)–C(18)	117.3(8)
O(2)–C(14)–C(9)	115.7(8)	O(3)–C(18)–C(23)	117.2(9)
C(14)–O(2)–C(15)	120.7(8)	C(17)–O(3)–C(18)	119.7(8)
O(2)–C(15)–C(16)	106.9(9)	O(3)–C(17)–C(16)	108.3(9)
C(15)–C(16)–C(17)	115.8(10)		



(2) R = (CH$_2$)$_4$

sites are occupied by the ketonic oxygen atoms: the ether oxygen atoms and the pyrrole nitrogen atoms are not in the first co-ordination sphere of the metal. The molecule possesses approximate C_2 symmetry perpendicular to the mean co-ordination plane. The copper atom deviates by relatively small distances (0.14 and 0.05 Å) from the planes of the two keto-imine chelate groups. Bond lengths indicate that there is substantially complete π-electron delocalisation within each of the planar pyrrole, keto-imine, and phenyl fragments, but each conjugated system is independent, as evidenced by the essentially single bonds which link them and by their deviations from coplanarity (mean values of interplanar angles from keto-imine to pyrrole of 10° and to phenyl of 76°). The torsion angles in the diether chain [C(14) $\cdots$ C(18)] are close to 180 and 60° and the cumulative small deviations from C_2 molecular symmetry serve to bring atom O(2) closer to the copper atom at 3.18 Å than is atom O(3) at 3.42 Å. The differences in the exocyclic bond angles at atoms C(4) and C(28) suggest some slight intramolecular hydrogen bonding to the ketonic oxygen atoms, NH $\cdots$ O 2.45 Å in both cases.

Such a 'capped' environment has been reported for a series of complexes of Schiff bases derived from salicylaldehyde, or pyrrole-2-carbaldehyde, and the more rigid and sterically constrained bis(8-aminonaphthyl)-n-alkyl diethers.[9] In order to retain a square-planar geometry at the metal ion the ligand must accommodate the metal ion in the style of a 'capped' porphyrin. The crystal structure of the nickel(II) complex of 2,2′-tetramethylenedioxydi(8-*N*-salicylideneiminonaphthalene), (2), has been solved and clearly demonstrated the 'fly-over' arrangement of the ligand.[10] A further complex exhibiting a 'fly-over' ligand is (3) in which the ligand chain incorporates a metal atom.[11] Both of these examples contain the Schiff base in a '*trans*' configuration.

The synthesis of molecules with sterically hindered sites such as these can be viewed as extending the versatility of Schiff-base ligands by incorporating the protective features displayed by biological and model porphyrin systems, thereby permitting the investigation of the reactivity of the metal site towards small substrate molecules such as dioxygen and carbon dioxide.

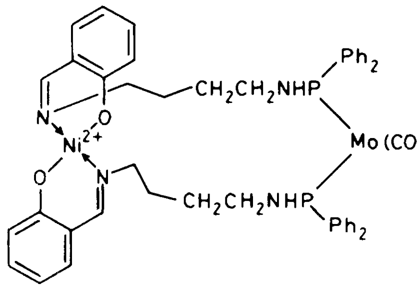
The related monocompartmental Schiff-base ligand derived from pyrrole-2-carbaldehyde and 3,6-dioxaoctane-1,8-diamine, H$_2$L^8, also provides an unusual co-ordination environment for copper(II). The free Schiff base was prepared by the stoicheiometric reaction of the components in ethanol,

Table 2. Bond lengths (Å) and selected bond angles (°) with estimated standard deviations for [Cu(HL^8)(O$_2$CMe)] (4)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Cu(1)–O(2)	2.527(3)	2.707(3)	C(9)–O(2)	1.439(6)	1.428(6)
Cu(1)–O(3)	1.979(3)	1.969(3)	O(2)–C(10)	1.423(5)	1.429(5)
Cu(1)–O(4)	2.765(3)	2.612(3)	C(10)–C(11)	1.508(6)	1.495(6)
Cu(1)–N(1)	1.959(3)	1.955(3)	C(11)–N(3)	1.483(5)	1.486(5)
Cu(1)–N(2)	2.018(4)	2.021(3)	N(3)–C(12)	1.279(5)	1.283(5)
Cu(1)–N(3)	2.018(3)	2.012(3)	C(12)–C(13)	1.419(5)	1.423(6)
N(1)–C(1)	1.343(6)	1.341(6)	C(13)–N(4)	1.383(5)	1.374(5)
C(1)–C(2)	1.397(7)	1.400(7)	C(13)–C(14)	1.378(6)	1.385(7)
C(2)–C(3)	1.384(7)	1.385(7)	C(14)–C(15)	1.392(7)	1.397(7)
C(3)–C(4)	1.388(6)	1.391(6)	C(15)–C(16)	1.366(7)	1.377(7)
C(4)–N(1)	1.380(5)	1.382(5)	C(16)–N(4)	1.349(6)	1.359(6)
C(4)–C(5)	1.415(6)	1.406(6)	O(3)–C(17)	1.276(5)	1.280(5)
C(5)–N(2)	1.293(6)	1.290(5)	O(4)–C(17)	1.235(5)	1.242(5)
N(2)–C(6)	1.463(7)	1.450(6)	C(17)–C(18)	1.504(6)	1.507(6)
C(6)–C(7)	1.509(8)	1.514(6)	O(4) · · · N(4)	2.807(5)	2.791(5)
C(7)–O(1)	1.407(7)	1.425(6)	O(3) · · · O(5)	3.005(6)	
O(1)–C(8)	1.432(7)	1.425(6)	O(4) · · · O(5) [a]	3.001(6)	
C(8)–C(9)	1.498(8)	1.494(8)	O(4) · · · HN(4) [b]	1.97	1.92

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
O(2)–Cu(1)–O(3)	94.64(10)	94.80(10)	Cu(1)–N(1)–C(1)	140.8(3)	141.3(3)
O(2)–Cu(1)–O(4)	146.95(9)	150.53(9)	Cu(1)–N(1)–C(4)	112.4(3)	111.7(3)
O(2)–Cu(1)–N(1)	98.28(12)	97.94(11)	Cu(1)–N(2)–C(5)	112.1(3)	111.1(3)
O(2)–Cu(1)–N(2)	90.54(12)	88.42(11)	Cu(1)–N(2)–C(6)	126.4(3)	127.2(3)
O(2)–Cu(1)–N(3)	78.67(11)	77.27(11)	C(5)–N(2)–C(6)	120.3(4)	120.6(4)
O(3)–Cu(1)–O(4)	52.48(10)	55.74(10)	Cu(1)–O(2)–C(9)	120.4(3)	121.8(3)
O(3)–Cu(1)–N(1)	166.12(13)	166.10(12)	Cu(1)–O(2)–C(10)	97.2(2)	93.0(2)
O(3)–Cu(1)–N(2)	92.83(13)	92.16(12)	C(9)–O(2)–C(10)	111.5(3)	111.1(3)
O(3)–Cu(1)–N(3)	92.61(12)	91.80(12)	Cu(1)–N(3)–C(11)	111.7(2)	111.0(2)
O(4)–Cu(1)–N(1)	114.20(12)	111.40(12)	Cu(1)–N(3)–C(12)	131.1(3)	132.3(3)
O(4)–Cu(1)–N(2)	88.17(12)	92.53(11)	C(11)–N(3)–C(12)	116.8(3)	116.2(3)
O(4)–Cu(1)–N(3)	103.36(11)	101.28(11)	Cu(1)–O(3)–C(17)	109.7(2)	105.0(2)
N(1)–Cu(1)–N(2)	82.04(14)	82.68(13)	Cu(1)–O(4)–C(17)	73.7(2)	76.2(2)
N(1)–Cu(1)–N(3)	94.88(13)	96.41(13)	O(3) · · · O(5) · · · O(4) [a]		101.6(2)
N(2)–Cu(1)–N(3)	168.28(14)	165.43(13)			

[a] 1 − *x*, −*y*, −*z*. [b] This value is based on an *X*-ray N–H bond length of 0.92 Å.



(3)

and was characterised by microanalysis, i.r., m.s., and ^{1}H n.m.r. The reaction of H$_2$L^8 with copper(II) ethanoate in ethanol in 1 : 1 or 1 : 2 ratios gave a dark green precipitate which was recrystallised from methanol to give green plates. The i.r. spectrum showed a band at 3 150 cm^{-1} ascribable to the pyrrole NH stretching frequency and as the stoicheiometry of the product indicated a product of formula [Cu(HL^8)(O$_2$CMe)] (4), in which only one pyrrole was deprotonated, a crystal structure was undertaken to reveal the co-ordination mode and geometry.

The structure of one of the two crystallographic independent molecules of [Cu(HL^8)(O$_2$CMe)] (4) is illustrated in Figure 2, with the atom labelling used in the corresponding Tables. Selected bond lengths and angles (with estimated standard deviations) are given in Table 2.

The two crystallographically independent molecules have identical conformations and are very similar in geometry. In both molecules, the copper atom is in a distorted octahedral co-ordination environment (two long axial bonds) with an asymmetrically bidentate acetate ligand and with the tetradentate ligand occupying three equatorial sites (one pyrrole and two imino-nitrogens) and making one more remote axial bond to an ether oxygen atom. The remaining ether oxygen and pyrrole nitrogen atoms are not co-ordinated to the metal. The equatorial co-ordination planes show substantial (17.0 and 19.4°) tetrahedral distortions: the imino-nitrogen atoms are displaced by up to 0.1 Å from the planes of their immediate neighbours, the atoms of the co-ordinated pyrrole-imine fragments deviate only slightly from coplanarity, and the acetate groups are both hinged (8.6 and 4.0°) about the O · · · O line. The hydrogen atoms on the nitrogens of the free pyrrole groups are directed towards the axially-bonded acetate oxygen atoms, to which they form intramolecular hydrogen bonds. The equatorially bonded acetate oxygen atom of molecule 1 is also hydrogen bonded, *via* a water molecule of crystallisation, to the axially bonded acetate oxygen atom of an inversion symmetry-related molecule: there are no such interactions involving molecule 2. There is only one significant geometric difference between the two independent molecules; the two pairs of long axial copper–oxygen bonds differ in relative length. Since the sum of the two bond lengths is approximately the same in the two molecules (O · · · O 5.305 ± 0.014 Å) the difference is best described as an axial displacement of the copper square plane by 0.165 Å. Since the

Table 3. Atomic positional parameters * with estimated standard deviations for [Cu(HL^8)(O$_2$CMe)] (4)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.246 05(3)	−0.040 82(5)	−0.062 84(3)	C(9)	0.080 1(3)	0.154 1(5)	−0.002 6(4)
Cu(1′)	−0.277 18(3)	0.345 11(5)	−0.434 17(3)	C(10)	0.149 8(3)	0.032 9(5)	0.124 1(3)
O(1)	0.120 71(22)	0.281 5(4)	−0.152 4(3)	C(11)	0.235 4(3)	−0.009 9(5)	0.158 2(3)
O(2)	0.160 23(17)	0.117 4(3)	0.039 4(2)	C(12)	0.289 9(2)	−0.220 0(4)	0.110 2(3)
O(3)	0.350 81(16)	0.088 1(3)	−0.048 9(2)	C(13)	0.324 4(2)	−0.324 6(4)	0.050 2(3)
O(4)	0.397 78(19)	−0.074 0(3)	−0.150 2(2)	C(14)	0.341 6(3)	−0.453 3(5)	0.081 2(4)
O(1′)	−0.117 36(19)	0.695 4(3)	−0.404 0(2)	C(15)	0.378 5(4)	−0.520 4(5)	0.001 0(4)
O(2′)	−0.199 83(17)	0.498 6(3)	−0.574 6(2)	C(16)	0.384 4(3)	−0.431 6(5)	−0.076 3(4)
O(3′)	−0.375 62(16)	0.454 3(3)	−0.429 2(2)	C(17)	0.406 0(2)	0.042 3(4)	−0.105 6(3)
O(4′)	−0.403 77(19)	0.293 4(3)	−0.318 9(2)	C(18)	0.485 1(3)	0.136 9(5)	−0.116 8(4)
O(5)	0.437 8(3)	0.203 9(6)	0.151 4(4)	C(1′)	−0.161 6(3)	0.1020 (5)	−0.435 9(4)
N(1)	0.155 28(20)	−0.187 0(4)	−0.105 3(3)	C(2′)	−0.086 5(3)	0.079 8(5)	−0.380 4(4)
N(2)	0.204 97(22)	0.038 5(4)	−0.194 0(3)	C(3′)	−0.066 1(3)	0.194 8(5)	−0.313 3(4)
N(3)	0.265 53(19)	−0.106 2(3)	0.079 5(2)	C(4′)	−0.128 3(2)	0.284 5(4)	−0.330 7(3)
N(4)	0.350 76(21)	−0.313 6(4)	−0.048 0(3)	C(5′)	−0.143 6(3)	0.416 7(5)	−0.290 9(3)
N(1′)	−0.187 08(20)	0.225 2(3)	−0.406 1(3)	C(6′)	−0.223 0(3)	0.613 3(5)	−0.294 8(3)
N(2′)	−0.210 92(20)	0.470 2(3)	−0.323 3(2)	C(7′)	−0.204 1(3)	0.702 4(5)	−0.383 6(3)
N(3′)	−0.322 79(20)	0.245 9(3)	−0.567 6(2)	C(8′)	−0.100 9(3)	0.690 5(6)	−0.509 8(4)
N(4′)	−0.384 79(22)	0.036 9(4)	−0.417 7(3)	C(9′)	−0.112 1(3)	0.548 3(6)	−0.561 6(4)
C(1)	0.121 6(3)	−0.310 4(5)	−0.077 1(4)	C(10′)	−0.214 1(3)	0.388 7(5)	−0.652 7(3)
C(2)	0.054 8(3)	−0.362 3(5)	−0.146 9(4)	C(11′)	−0.305 3(3)	0.333 2(5)	−0.655 2(3)
C(3)	0.046 3(3)	−0.264 8(5)	−0.219 3(4)	C(12′)	−0.355 2(3)	0.121 1(4)	−0.590 5(3)
C(4)	0.109 5(3)	−0.158 0(5)	−0.193 0(3)	C(13′)	−0.378 6(3)	0.017 8(4)	−0.521 5(3)
C(5)	0.138 3(3)	−0.033 3(6)	−0.236 8(3)	C(14′)	−0.394 6(3)	−0.123 1(5)	−0.547 1(4)
C(6)	0.232 3(3)	0.174 9(7)	−0.229 6(4)	C(15′)	−0.410 8(3)	−0.188 9(5)	−0.457 1(4)
C(7)	0.209 5(4)	0.287 3(6)	−0.154 9(5)	C(16′)	−0.405 5(3)	−0.087 8(5)	−0.378 4(4)
C(8)	0.089 8(4)	0.290 0(6)	−0.052 0(5)	C(17′)	−0.421 3(3)	0.399 0(4)	−0.362 1(3)
				C(18′)	−0.497 9(3)	0.470 7(5)	−0.335 0(4)

* Atoms indicated by a prime comprise molecule 2. Atom O(5) is the oxygen atom of the water molecule of crystallisation.

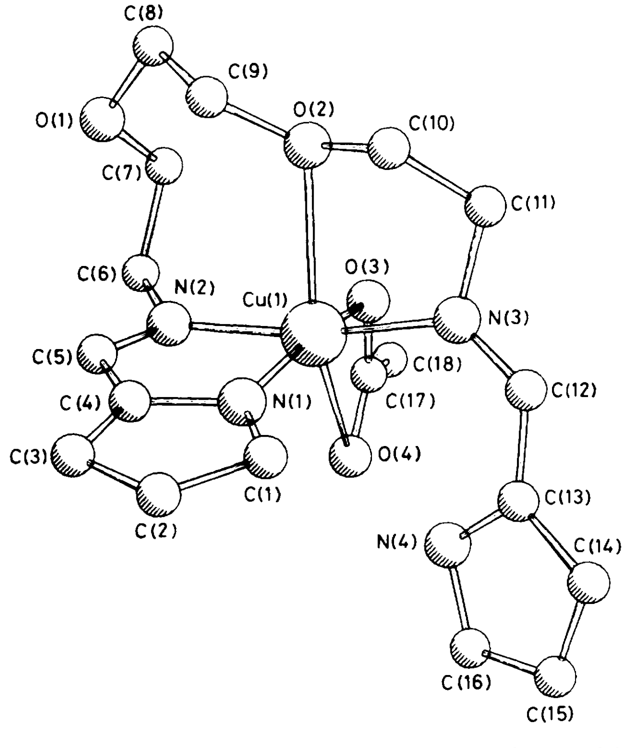
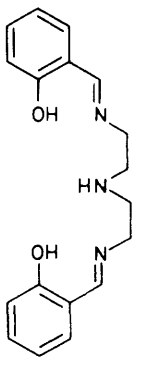


Figure 2. The molecular structure with atom labelling for one of the crystallographically independent molecules of [Cu(HL^8)(O$_2$CMe)] (4), the second molecule is visually indistinguishable



H_3L^9

axial copper–oxygen(acetate) is longer, and the copper–oxygen(ether) is shorter, in the molecule in which the acetate ligand takes part in intermolecular hydrogen bonding, it is tempting to see a connection between these two observations; however the magnitude of the displacement seems much larger than the type of bond length variation that normally accompanies such hydrogen bonding.

The mononuclear nature of the complex was of interest as the copper(II) complex of the potentially quinquedentate ligand H_3L^9 had been shown to be a dimer,[12] and so it was not improbable that a similar dimerisation could have occurred here. Clearly the options open for co-ordination are many when facultative bridges are introduced into Schiff-base ligands, and for copper(II) then if the prime option offers square-planar geometry this will be taken, as evidenced in the compartmental shifts noted on changing the bridging chain length in the compartmental pyrrole-based ligands. If there is no such option then a distorted co-ordination geometry arises which can include, as in the present instance, interactions with donor atoms which would not normally be expected to act as good donors.*

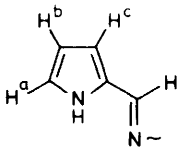
Experimental

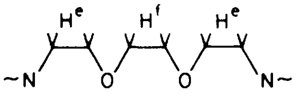
Details of physical measurements were given in ref. 2.

Preparation of H_4L^7.—1-(Pyrrol-2-yl)butane-1,3-dione (0.01 mol) was dissolved in hot absolute ethanol (30 cm^3) and to it was added 1,3-bis(2-aminophenoxy)propane (0.005 mol) dissolved in $CHCl_3$ (20 cm^3). After warming on a steam-bath for *ca.* 30 min the solution was allowed to cool. The acyclic Schiff base was recovered as a pale yellow solid, filtered off, and dried under vacuum over silica gel (Found: C, 69.3; H, 6.3; N, 10.3%; M^+, 524. Calc. for $C_{31}H_{32}N_4O_4 \cdot 0.5H_2O$: C, 69.8, H, 6.2; N, 10.5%; *M*, 524). I.r.: 3 230m br (ν_{NH}), 1 610s, 1 590s, and 1 540w cm^{-1} ($\nu_{C=O}$, $\nu_{C=N}$).

The copper(II) complex $[Cu(H_2L^7)]$ (1) was synthesised by the reaction of copper(II) ethanoate (0.01 mol) dissolved in hot ethanolic solution (20 cm^3) with the Schiff base (0.01 mol) dissolved in hot CH_2Cl_2 (30 cm^3). The mixture was allowed to warm on a steam-bath for 30 min and was then filtered hot. A red-brown solid was recovered and dried under vacuum over silica gel (Found: C, 63.3; H, 5.2; N, 9.2%; M^+, 585. Calc. for $C_{31}H_{30}CuN_4O_4$: C, 63.6; H, 5.2; N, 9.6%; *M*, 585). I.r.: 3 405m, 3 380m (ν_{NH}), 1 570m, 1 540s, and 1 500s cm^{-1} ($\nu_{C=O}$, $\nu_{C=N}$). D.r.s.: 500 (sh), 408br, and 377 (sh) nm.

Preparation of H_2L^8.—Pyrrole-2-carbaldehyde (0.01 mol) and 3,6-dioxaoctane-1,8-diamine (0.005 mol) were refluxed together in ethanol (50 cm^3) for 1 h. The reaction mixture was cooled and the Schiff base recovered as an oil and used without further purification.





Mass spectra: found 302; calc. 302. I.r.: 3 250br (ν_{NH}, ν_{OH}), 1 640, 1 560 cm^{-1} ($\nu_{C=N}$, $\nu_{C=C}$). ^1H N.m.r. ($CDCl_3$): δ, 3.57 (s, 4 H, H^f), 3.65 (s, 8 H, H^e), 6.20 (t, 2 H, H^b), 6.50 (d, 2 H, H^a), 6.74 (d, 2 H, H^c), and 8.02 p.p.m. (s, 2 H, H^d).

The copper(II) complex $[Cu(HL^8)(O_2CMe)]$ (4) was prepared by (*i*) addition of a solution of copper(II) ethanoate (0.0005 mol) in ethanol (25 cm^3) to a solution of the Schiff base (0.0005 mol) in ethanol (25 cm^3), dropwise, with stirring. The green solution was evaporated down to reduce the volume and a green solid precipitated out. An alternative method (*ii*) was addition of a solution of the Schiff base (0.0005 mol) in ethanol (25 cm^3) to a solution of copper(II) ethanoate (0.001 mol) in ethanol (25 cm^3) dropwise with stirring. The solution turned dark green and, after the volume was reduced, was left to stand. Dark green crystals of the product were obtained (Found: C, 48.3; H, 5.8; N, 11.4. Calc. for $C_{18}H_{24}CuN_4O_4 \cdot H_2O$: C, 48.9; H, 5.9; N, 12.6%; this was the best-fit for the bulk sample analysis). I.r.: 3 150 (ν_{NH}), 1 630, 1 600, 1 570, 1 560 cm^{-1} ($\nu_{C=O}$, $\nu_{C=O}$).

Table 4. Atomic positional parameters with estimated standard deviations for $[Cu(H_2L^7)]$ (1)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	−0.110 78(10)	0.057 52(6)	0.213 86(10)
O(1)	−0.200 1(5)	−0.008 8(3)	0.250 0(5)
O(2)	−0.260 1(6)	0.158 9(3)	0.010 5(6)
O(3)	−0.277 5(6)	0.165 5(3)	0.294 7(7)
O(4)	0.025 7(5)	0.096 7(3)	0.199 4(5)
N(1)	−0.323 2(7)	−0.078 3(4)	0.351 0(7)
N(2)	−0.185 7(6)	0.040 1(3)	0.032 4(6)
N(3)	−0.073 4(6)	0.095 9(3)	0.379 7(6)
N(4)	0.173 9(7)	0.152 7(4)	0.111 1(7)
C(1)	−0.404 8(9)	−0.112 0(5)	0.379 0(10)
C(2)	−0.492 8(10)	−0.134 3(5)	0.273 6(11)
C(3)	−0.463 2(10)	−0.112 3(5)	0.175 0(10)
C(4)	−0.358 3(8)	−0.077 6(4)	0.225 1(9)
C(5)	−0.288 1(8)	−0.040 0(4)	0.172 4(8)
C(6)	−0.323 8(8)	−0.039 9(4)	0.043 2(9)
C(7)	−0.273 1(8)	−0.000 8(4)	−0.022 6(8)
C(8)	−0.330 4(10)	−0.008 3(5)	−0.162 7(9)
C(9)	−0.149 2(8)	0.082 6(4)	−0.043 2(7)
C(10)	−0.075 1(9)	0.062 7(5)	−0.102 2(8)
C(11)	−0.033 2(9)	0.108 3(5)	−0.160 4(9)
C(12)	−0.063 6(9)	0.171 5(5)	−0.161 7(9)
C(13)	−0.139 8(9)	0.191 1(5)	−0.104 9(9)
C(14)	−0.182 3(8)	0.145 4(4)	−0.045 5(8)
C(15)	−0.253 4(10)	0.217 9(5)	0.070 0(10)
C(16)	−0.363 2(10)	0.220 8(5)	0.104 3(10)
C(17)	−0.376 6(9)	0.164 6(6)	0.179 4(10)
C(18)	−0.268 8(9)	0.119 4(5)	0.380 6(9)
C(19)	−0.361 8(9)	0.107 1(5)	0.422 0(12)
C(20)	−0.339 7(10)	0.062 0(6)	0.515 6(11)
C(21)	−0.233 3(9)	0.029 8(5)	0.567 5(10)
C(22)	−0.142 4(9)	0.041 8(5)	0.527 1(9)
C(23)	−0.161 2(8)	0.085 7(4)	0.431 3(8)
C(24)	0.035 4(9)	0.164 9(5)	0.563 0(8)
C(25)	0.015 7(7)	0.134 9(4)	0.437 4(8)
C(26)	0.100 6(8)	0.154 7(5)	0.390 6(9)
C(27)	0.100 2(8)	0.136 1(4)	0.276 3(9)
C(28)	0.186 8(8)	0.165 3(5)	0.231 7(9)
C(29)	0.280 8(10)	0.205 3(5)	0.283 4(11)
C(30)	0.328 4(10)	0.219 9(5)	0.195 4(12)
C(31)	0.261 7(10)	0.187 0(5)	0.091 4(11)

Crystal Data for $[Cu(HL^8)(O_2CMe)]$ (4).—$C_{18}H_{24}CuN_4O_4 \cdot 0.5H_2O$, $M = 432.96$, crystallises from methanol as thick, green plates, crystal dimensions 0.123 × 0.29 × 0.380 mm, triclinic, $a = 15.873(15)$, $b = 9.693(9)$, $c = 13.104(22)$ Å, $\alpha = 93.080(8)$, $\beta = 93.378(8)$, $\gamma = 95.290(7)^\circ$, $U = 2\,000(4)$ Å^3, $D_m = 1.48$, $Z = 4$, $D_c = 1.438$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2; assumed and confirmed by the analysis), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 11.25 cm^{-1}, $F(000) = 904$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50^\circ$ on a Stoe Stadi-2 diffractometer by the ω-scan method. 4 800 Independent observed reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms (with the exception of those of the water molecule for which there was no strong evidence in the difference electron-density synthesis) were placed in calculated positions [C–H 0.97, N–H 0.92 Å, C–C–H(methyl) 111°]; 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* 0.0363 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the

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* It has been suggested that simple bis(2-aminoethyl) ether complexes of copper(II) are less stable than those of the corresponding diethylenetriamine complexes as the co-ordination of the oxygen atom is an endothermic process (R. Barbucci and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1974, **2363**).

anomalous scattering of copper. Table 3 lists the atomic positional parameters with estimated standard deviations.

Crystal Data for [Cu(H_2L^7)] (1).—$C_{31}H_{30}CuN_4O_4$, M = 586.38, crystallises from methanol–chloroform as red-brown needles, crystal dimensions 0.08 × 0.114 × 0.565 mm, monoclinic, a = 12.069(17), b = 20.909(29), c = 11.958(14) Å, β = 113.95(5)°, U = 2 758(6) Å^3, D_m = 1.43, Z = 4, D_c = 1.412 g cm^{-3}, space group $P2_1/c$ (C_{2h}^5, no. 14), Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8.33 cm^{-1}, $F(000)$ = 1 220.

The data were collected and processed (1 901 independent reflections) and the structure solved and refined (R 0.0549) as for (4) above (for hydrogen atoms B = 10.0 Å^2). Table 4 lists atomic positions with estimated standard deviations.

Scattering factors were taken from ref. 13; unit weights were used throughout the refinements; computer programs formed part of the Sheffield X-ray system.

Acknowledgements

We thank the S.E.R.C. and the Consejo Nacional de Ciencia y Tecnologia (Mexico) for support, and E. Merck for a gift of 3,6-dioxaoctane-1,8-diamine.

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Received 6*th February* 1984; *Paper* 4/212