Compartmental Ligands. Part 11.[1] Copper(II) Complexes of 'Half-unit' Schiff Bases: Crystal and Molecular Structures† of One Monomeric and of One Dimeric Complex

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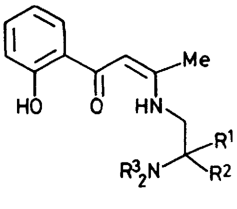
The syntheses of 'half-unit' Schiff bases derived from 1-(2'-hydroxyphenyl)butane-1,3-dione (Hhpbdo) and α,ω-alkanediamines are reported, together with that of the related compound derived from Hhpbdo and 2-(2'-aminoethyl)pyridine. The copper(II) complexes of these ligands are reported and three-dimensional *X*-ray crystal structure analyses were carried out for acetato[1-(2'-hydroxyphenyl)-3-methyl-6-(2'-pyridyl)-4-azahex-2-en-1-onato-*O,N,N'*]copper(II), [Cu(HL^5)(O$_2$CMe)], and acetato[6-amino-1-(2'-hydroxyphenyl)-3-methyl-4-azahept-2-en-1-onato-*O,N,N'*]copper(II), [Cu(HL^1)(O$_2$CMe)]. The crystal structure of [Cu(HL^5)(O$_2$CMe)] is triclinic, *R* = 0.0332, for 2 529 reflections. The copper(II) atom is five-co-ordinate, with the nitrogen atoms, ketonic oxygen of the ligand, and one acetate oxygen providing a tetrahedrally distorted (15°) square plane, with a further acetate oxygen at 2.55 Å. The structure of [Cu(HL^1)(O$_2$CMe)] (*R* = 0.0476, 1 550 reflections) shows an acetate-bridged, dinuclear dimer in which there is a copper–copper distance of 3.51 Å. The co-ordinating atoms comprise four short interactions (ketonic oxygen, imino-nitrogen, primary amine nitrogen, and acetate oxygen) with two longer interactions, one towards the bridging acetate oxygen, and the other to the second oxygen of the acetate anion which is the more strongly bound to the copper(II). The application of the 'half-units' to the synthesis of unsymmetrical Schiff bases and the metal complexation properties of these bases are discussed briefly.

In a previous Part[2] of this Series we reported the synthesis of singly condensed (or 'half-unit') Schiff-base derivatives of β-diketones and discussed their application to the derivation of unsymmetrical, acyclic, compartmental ligands. The corresponding literature was reviewed. Here we report the synthesis of a group of 'half-unit' Schiff bases and their complexation of copper(II), together with the crystal and molecular structures of a monomeric and of a dimeric derivative.

Results and Discussion

The Schiff Base Ligands.—It is generally found that under normal conditions the reaction of 1-(2'-hydroxyphenyl)butane-1,3-dione (Hhpbdo) and an aliphatic diamine leads to a compartmental Schiff base.[3] In order to form the corresponding unsymmetrical 'half-unit' it is necessary to leave one end of the diamine unreacted. The reaction between a primary diamine and carbonyl moieties often proceeds rapidly under mild conditions rendering it difficult to prevent the second condensation from occurring. Furthermore there is the availability, in the case of β-diketone precursors, of an intramolecular condensation leading to a diazepine; this is found in the reaction of Hhpbdo and 1,2-diaminobenzene.[4] In order to induce a reaction between Hhpbdo and an aliphatic diamine in 1 : 1 ratio, 'conditions of dilution' were employed and the Hhpbdo was added to the diamine in solution, thus maintaining an excess of the diamine. The diamines initially chosen were sterically hindered by having methyl groups substituted at the carbon adjacent to the proposed terminal amine group in order to restrain its attack on the carbonyl function.



	R^1	R^2	R^3
H$_2$L^1	Me	H	H
H$_2$L^2	Me	Me	H
H$_2$L^3	H	H	Me
H$_2$L^4	H	H	H

The reaction of Hhpbdo and 1,2-diaminopropane (pn) in 1 : 1 ratio, under 'conditions of dilution,' yielded the 'half-unit' H$_2$L^1. Similarly reaction with 1,2-diamino-2-methylpropane gave H$_2$L^2. The i.r. spectra of these compounds both show a sharp, intense band in the region of 3 400 cm^{-1} indicative of free NH stretching modes. In addition strong, slightly broadened bands are found at 1 600 and 1 540 cm^{-1}, ascribed to C=O and C=C stretches. The band found at 760 cm^{-1} is typical of that for *ortho*-substituted aromatic rings and a band at 1 255 cm^{-1} is due to the C–O stretch of the phenol. The parent peaks found in the mass spectrum are consistent with the structures shown. This reinforces the evidence that no intramolecular condensation has occurred to give a diazepine: furthermore no peaks at higher mass are detected, showing the absence of the compartmental ligand.

The ^{1}H n.m.r. spectra (Table 1) show that both compounds are in the enamine form. The free primary amine protons are not clearly observed, though bands of low intensity are found in the region of the spectrum where the amine protons are most likely to be found. The compound H$_2$L^3 was synthesised, by reaction of Hhpbdo and *N,N*-dimethyl-1,2-diaminoethane, in order to

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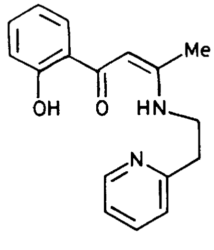
† *Supplementary data available* (No. SUP 56223, 15 pp.): H-atom co-ordinates, thermal parameters, full bond lengths and angles, details of planar fragments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, 1985, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Proton n.m.r. spectra for the Schiff bases

Assignment	δ/p.p.m.[a] H_2L^1	H_2L^2	H_2L^3	H_2L^5
CH_3	2.05 (s, 3 H)	2.07 (s, 3 H)	2.07 (s, 3 H)	2.01 (s, 3 H)
CH_2(amine)	1.13 (d, 3 H)	1.18 (s, 6 H)	2.28 (s, 6 H)	
CH_2,CH (amine)	3.13 (m, 3 H)	3.19 (d, 2 H)	2.52 (t, 2 H) 3.39 (q, 2 H)	3.07 (t, 2 H) 3.75 (q, 2 H)
CH (vinyl)	5.67 (s, 1 H)	5.69 (s, 1 H)	5.66 (s, 1 H)	5.60 (s, 1 H)
Aromatic protons (phenol)	6.75 (t, 1 H) 6.88 (d, 1 H)	6.77 (t, 1 H) 6.89 (d, 1 H)	6.76 (t, 1 H) 6.97 (d, 1 H)	*b* *b*
Pyridyl protons	7.28 (t, 1 H) 7.60 (d, 1 H)	7.29 (t, 1 H) 7.61 (d, 1 H)	7.28 (t, 1 H) 7.59 (d, 1 H)	*b* *b*
–OH (phenol)	10.97 (s, 1 H)	11.27 (s, 1 H)	10.97 (s, 1 H)	10.98 (s, 1 H)
–NH (secondary amine)	13.64 (br, 1 H)	13.57 (br, 1 H)	13.64 (br, 1 H)	13.50 (br, 1 H)

[a] $CHCl_3$ solution; br = broad. [b] The signal in this region consisted of a series of multiplets: clearly defined signals were noted at 6.74 (t, 1 H), 6.87 (d, 1 H), 7.20 (m, 3 H), 7.58 (q, 2 H), and 8.54 p.p.m. (d, 1 H).



H_2L^5

provide some comparison. The ^1H n.m.r. spectrum was similar to those of the 'half-units'.

The related Schiff base H_2L^5 was also synthesised from Hhpbdo and the corresponding amine. The ^1H n.m.r. data are given in Table 1 and the mass spectrum showed a parent peak at *m*/*e* = 282. The 'half-unit' ligand derived from the reaction of Hhpbdo and 1,2-diaminoethane (H_2L^4) was also synthesised under 'conditions of dilution'. The characterisation of H_2L^4 and its application to the synthesis of unsymmetric compartmental ligands has previously been reported.[2]

Copper(II) *Complexes of the Schiff Base Ligands*.—An ethanolic solution of copper(II) acetate reacts with H_2L^1 in chloroform, to yield a blue compound of the type $[Cu(HL^1)(O_2CMe)]$. The ligands H_2L^2 and H_2L^4 react in a similar manner to give $[Cu(HL^2)(O_2CMe)]$ and $[Cu(HL^4)(O_2CMe)]$ respectively. The i.r. spectra of these compounds display a double band at 1 600 cm^{-1} and a strong band at 1 500 cm^{-1}. The double band is assigned to the C=O stretching mode of the ligand and the acetate molecules, while the band at lower frequency is attributed to the C=C vibration of the ligand. A sharp band is present at 3 250 cm^{-1}, which is attributed to N–H vibrations arising from the primary amine group. In addition a fairly broad band is centred at 3 400 cm^{-1} due to the O–H of the phenol, probably involved in intramolecular hydrogen bonding. The presence of the phenolic O–H vibration indicates that the copper ion is bound in the inner N_2O site. This would account for the broadening of the normally very sharp N–H vibrational bands. Single crystals of $[Cu(HL^1)(O_2CMe)]$, suitable for structure determination by *X*-ray diffraction, were grown from ethanol.

Table 2 gives selected bond lengths and angles with estimated standard deviations. The binuclear copper complex $[\{Cu(HL^1)(O_2CMe)\}_2]$ (Figure 1) consists of two almost identical $Cu(HL^1)$ fragments which are asymmetrically bridged by two acetate ligands, giving a dimeric complex with an approximate centre of symmetry: the copper–copper distance of 3.51 Å is long. Each copper atom forms four short bonds to a ketonic oxygen, an imino-nitrogen, a primary amino-nitrogen, and to an oxygen atom of one of the bridging acetate groups. The co-ordination polyhedra are each approximately square planar with closely coplanar sets of donor atoms (r.m.s. deviations 0.004 Å); the copper atoms are slightly displaced from the mean planes (by 0.082 and 0.039 Å) towards the second, somewhat more distant (2.49 and 2.54 Å) bridging acetate oxygen atoms. The remaining sixth co-ordination site at each copper is occupied, at greater distances (2.85 and 2.90 Å) by the second oxygen atom of the bridging acetate which is the more strongly bonded to that copper. The two copper square planes are almost parallel (2.1°) but 'stepped' by 2.51 Å; they are almost perpendicular to the bridge plane, the atoms of which are almost coplanar (0.012 Å). The phenyl rings are each almost planar (r.m.s. deviations 0.012 and 0.015 Å) and, although the linking carbon–carbon bonds are long, they are twisted away very little (6.9 and 7.5°) from their adjacent keto-imine chelate planes:

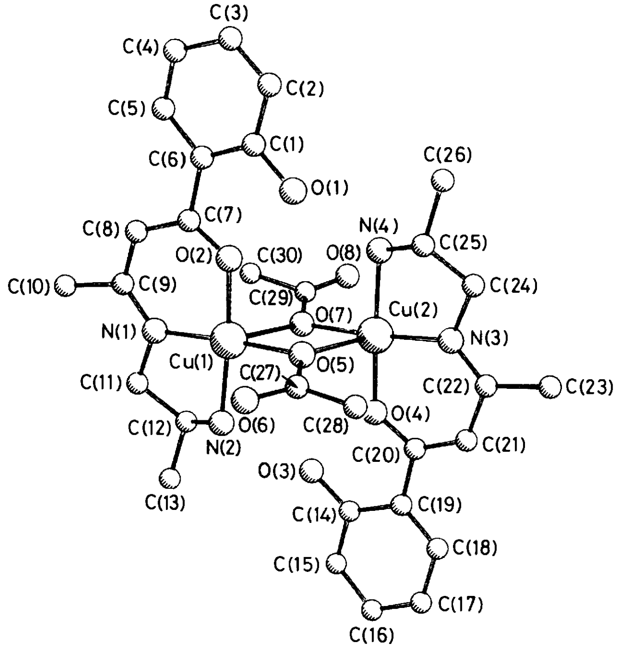


Figure 1. The molecular structure of $[\{Cu(HL^1)(O_2CMe)\}_2]$ with atom labelling

Table 2. Selected bond lengths (Å) and bond angles(°) with estimated standard deviations for $[\{Cu(HL^1)(O_2CMe)\}_2]\cdot 1.2H_2O$

Cu(1)–Cu(2)	3.507(3)		
Cu(1)–O(2)	1.933(10)	Cu(2)–O(4)	1.926(10)
Cu(1)–O(5)	1.973(10)	Cu(2)–O(7)	1.980(10)
Cu(1)–O(6)	2.845(13)	Cu(2)–O(8)	2.901(13)
Cu(1)–O(7)	2.485(10)	Cu(2)–O(5)	2.540(10)
Cu(1)–N(1)	1.967(12)	Cu(2)–N(3)	1.914(12)
Cu(1)–N(2)	2.003(12)	Cu(2)–N(4)	2.039(14)
O(1)–C(1)	1.385(20)	O(3)–C(14)	1.362(21)
C(6)–C(7)	1.529(20)	C(19)–C(20)	1.501(21)
O(2)–C(7)	1.263(18)	O(4)–C(20)	1.295(18)
C(7)–C(8)	1.408(21)	C(20)–C(21)	1.341(21)
C(8)–C(9)	1.361(20)	C(21)–C(22)	1.495(21)
C(9)–C(10)	1.557(23)	C(22)–C(23)	1.513(24)
N(1)–C(9)	1.312(18)	N(3)–C(22)	1.320(18)
N(1)–C(11)	1.475(20)	N(3)–C(24)	1.469(20)
C(11)–C(12)	1.494(23)	C(24)–C(25)	1.480(24)
C(12)–C(13)	1.528(25)	C(25)–C(26)	1.527(27)
N(2)–C(12)	1.476(20)	N(4)–C(25)	1.494(22)
O(5)–C(27)	1.279(20)	O(7)–C(29)	1.299(19)
O(6)–C(27)	1.239(21)	O(8)–C(29)	1.213(21)
C(27)–C(28)	1.492(27)	C(29)–C(30)	1.544(26)
O(1) ··· O(2)	2.451(16)	O(3) ··· O(4)	2.437(16)
O(6) ··· O(10)	2.52(15)	O(8) ··· O(9)	2.848(22)
N(2) ··· O(10)	3.10(15)	N(4) ··· O(9)	2.990(22)
O(6) ··· O(9$^{\rm I}$)	2.753(22)		

O(2)–Cu(1)–O(5)	89.2(4)	O(4)–Cu(2)–O(7)	89.3(4)
O(2)–Cu(1)–O(6)	98.9(4)	O(4)–Cu(2)–O(8)	102.9(4)
O(2)–Cu(1)–O(7)	93.5(4)	O(4)–Cu(2)–O(5)	93.5(4)
O(2)–Cu(1)–N(1)	92.5(5)	O(4)–Cu(2)–N(3)	94.0(5)
O(2)–Cu(1)–N(2)	174.9(5)	O(4)–Cu(2)–N(4)	177.2(5)
O(5)–Cu(1)–O(6)	50.0(4)	O(7)–Cu(2)–O(8)	50.0(4)
O(5)–Cu(1)–O(7)	78.6(4)	O(7)–Cu(2)–O(5)	77.1(4)
O(5)–Cu(1)–N(1)	174.6(5)	O(7)–Cu(2)–N(3)	175.8(5)
O(5)–Cu(1)–N(2)	92.9(5)	O(7)–Cu(2)–N(4)	92.5(5)
O(6)–Cu(1)–O(7)	126.5(4)	O(8)–Cu(2)–O(5)	123.5(4)
O(6)–Cu(1)–N(1)	124.7(4)	O(8)–Cu(2)–N(3)	126.6(4)
O(6)–Cu(1)–N(2)	79.0(4)	O(8)–Cu(2)–N(4)	76.8(5)
O(7)–Cu(1)–N(1)	106.4(4)	O(5)–Cu(2)–N(3)	105.2(4)
O(7)–Cu(1)–N(2)	91.5(4)	O(5)–Cu(2)–N(4)	89.0(5)
N(1)–Cu(1)–N(2)	85.0(5)	N(3)–Cu(2)–N(4)	84.1(5)
Cu(1)–O(2)–C(7)	126.6(10)	Cu(2)–O(4)–C(20)	127.4(9)
Cu(1)–N(1)–C(9)	123.7(10)	Cu(2)–N(3)–C(22)	125.7(10)
Cu(1)–N(1)–C(11)	111.9(9)	Cu(2)–N(3)–C(24)	115.0(9)
C(9)–N(1)–C(11)	124.1(12)	C(22)–N(3)–C(24)	119.0(12)
Cu(1)–N(2)–C(12)	106.4(9)	Cu(2)–N(4)–C(25)	106.6(10)
Cu(1)–O(5)–Cu(2)	101.3(4)	Cu(2)–O(7)–Cu(1)	103.0(4)
Cu(1)–O(5)–C(27)	115.2(10)	Cu(2)–O(7)–C(29)	113.5(9)
Cu(2)–O(5)–C(27)	138.9(10)	Cu(1)–O(7)–C(29)	135.2(10)
O(5)–C(27)–O(6)	120.3(15)	O(7)–C(29)–O(8)	124.5(15)
O(5)–C(27)–C(28)	117.5(15)	O(7)–C(29)–C(30)	113.4(14)
O(6)–C(27)–C(28)	122.1(16)	O(8)–C(29)–C(30)	122.0(15)
Cu(1)–O(6)–C(27)	73.9(10)	Cu(2)–O(8)–C(29)	71.5(10)
O(6) ··· O(10) ··· N(2)	67(4)	O(8) ··· O(9) ··· N(4)	65.1(5)
		O(8) ··· O(9) ··· O(6$^{\rm II}$)	141.3(8)
		N(4) ··· O(9) ··· O(6$^{\rm II}$)	123.6(7)

Symmetry operations: I, $1 - x, -\frac{1}{2} + y, -z$; II, $1 - x, \frac{1}{2} + y, -z$.

these latter are approximately planar (r.m.s. deviations 0.022 and 0.013 Å) with relatively small out-of-plane displacements (0.088 and 0.092 Å) of the copper atoms. The carbon–carbon torsion angles in the 1-imino-2-aminopropane chelate ligands are somewhat smaller (+41.3 and −39.5°) than would be expected in free 1,2-diaminopropane due to the steric constraints resulting from chelation: the methyl groups are equatorially sited. Bond lengths in the skeleton are generally satisfactory [with the exception of those involving atom C(21)] and in adequate agreement between the two approximately centrosymmetrically related fragments. There are two water molecules present in the lattice, one in only reduced population [O(10) set at 20%]. Each water is hydrogen bonded to both the primary amine and the weakly co-ordinated (non-bridging) acetate oxygen on the same copper atom. The water which is present in full occupancy, O(9), also forms a further hydrogen bond to a symmetry-related, weakly co-ordinated acetate oxygen, O(6); water O(10) does not fulfil a bridging role. Internal hydrogen bonds are found between the phenolic and ketonic oxygen atoms of each co-ordinated ligand.

In the majority of reported complexes containing acetate bridges, it is found that the acetate acts as a bidentate bridging

Table 3. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for $[Cu(HL^5)(O_2CMe)]$

Cu(1)–O(2)	1.898(2)	C(6)–C(7)	1.483(4)
Cu(1)–O(3)	1.988(2)	O(2)–C(7)	1.311(4)
Cu(1)–O(4)	2.547(3)	N(1)–C(9)	1.318(4)
Cu(1)–N(1)	1.960(3)	O(3)–C(18)	1.269(4)
Cu(1)–N(2)	1.989(3)	O(4)–C(18)	1.229(4)
O(1)–C(1)	1.352(4)	C(18)–C(19)	1.506(5)
		O(1) ··· O(2)	2.492(4)
O(2)–Cu(1)–O(3)	85.63(9)	Cu(1)–O(2)–C(7)	125.85(20)
O(2)–Cu(1)–O(4)	92.45(9)	Cu(1)–N(1)–C(9)	122.5(2)
O(2)–Cu(1)–N(1)	92.30(10)	Cu(1)–N(1)–C(11)	119.2(2)
O(2)–Cu(1)–N(2)	163.76(10)	C(9)–N(1)–C(11)	118.1(3)
O(3)–Cu(1)–O(4)	56.12(8)	Cu(1)–N(2)–C(13)	120.3(2)
O(3)–Cu(1)–N(1)	175.93(10)	Cu(1)–N(2)–C(17)	120.2(2)
O(3)–Cu(1)–N(2)	90.42(9)	C(13)–N(2)–C(17)	119.4(3)
O(4)–Cu(1)–N(1)	120.57(10)	Cu(1)–O(3)–C(18)	103.16(19)
O(4)–Cu(1)–N(2)	98.41(9)	O(3)–C(18)–O(4)	122.4(3)
N(1)–Cu(1)–N(2)	92.51(10)	O(3)–C(18)–C(19)	116.6(3)
		O(4)–C(18)–C(19)	120.9(3)

ligand, with each oxygen co-ordinated to a different metal ion. A common example of this is copper(II) acetate dihydrate. Numerous other examples are to be found in the literature.[5] There are few examples of complexes where monodentate acetate ligands form bridges. Recently, however, Sinn and co-workers[6] have reported such a complex, $[\{Cu(L)(O_2CMe)\}_2]\cdot H_2O\cdot C_2H_5OH$ [HL = *N*-(2-hydroxy-1,1-dimethylethyl)-salicylaldimine], which has a structure very like that of $[\{Cu(HL^1)(O_2CMe)\}_2]$. The unsymmetrical nature of Sinn's complex is ascribed to hydrogen bonding between lattice solvent molecules and the non-interacting oxygen of the bridging acetate. Although this is also possible in our molecule, the presence of a tridentate ligand in a meridional position leaves only one site for a ligand situated at normal (*ca.* 2.0 Å) distance from the copper; other ligands must therefore be more remotely sited as a consequence of Jahn–Teller tetragonal elongation. The similarity between the i.r. spectra and diffuse reflectance spectra of $[Cu(HL^1)(O_2CMe)]$ and the copper complexes of H_2L^2 and H_2L^4 leads to the conclusion that these compounds also possess a dimeric structure similar to that described above. All three compounds display bands at *ca.* 600 nm in their diffuse reflectance spectra.

The reaction of an ethanolic solution of copper(II) acetate with the ligand H_2L^5 in ethanol gave a deep green solution from which dark green platelets of $[Cu(HL^5)(O_2CMe)]$ crystallised. The i.r. spectrum showed bands at 1 580 and 1 500 cm^{-1}, assigned as previously, and a broad band centred on 3 400 cm^{-1} again indicated an inner N_2O site occupancy. This was confirmed by the crystal structure of the complex. Table 3 gives selected bond lengths and angles with estimated standard deviations.

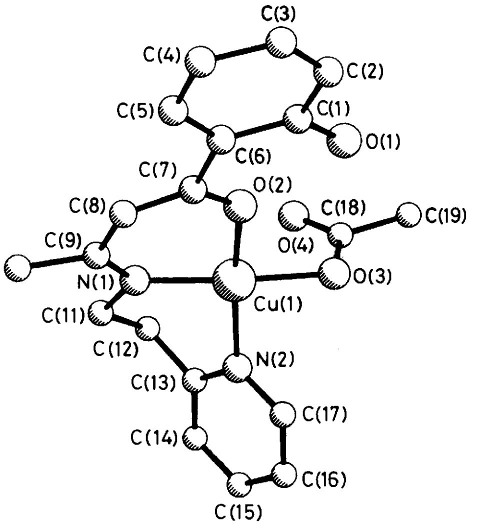
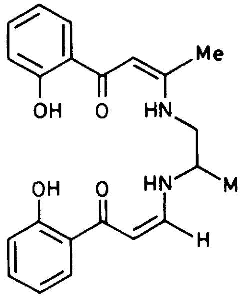


Figure 2. The molecular structure of $[Cu(HL^5)(O_2CMe)]$ with atom labelling



H_4L^6

The mononuclear copper complex $[Cu(HL^5)(O_2CMe)]$ (Figure 2) has a five-co-ordinate geometry with a significant (15°) tetrahedral distortion of the approximately square-planar arrangement of the closest atoms [both nitrogens, the ketonic oxygen, and O(3) of the acetate group]. The second acetate oxygen is much closer to the copper (2.55 Å) than are the comparable oxygen atoms in the related binuclear complex $[\{Cu(HL^1)(O_2CMe)\}_2]$ and the copper atom is displaced from the mean plane of atoms O(2), O(3), N(1), N(2) towards O(4) by 0.10 Å. The sixth metal co-ordination site, opposite to O(4), is blocked at 3.28 Å by atom H(2) of a symmetry related molecule. The phenyl and pyridyl rings are each closely planar (r.m.s. deviations 0.006 and 0.004 Å) and the former is twisted very little (4.6°) from the mean plane through the keto-imine fragment (r.m.s. deviation 0.022 Å) from which the copper deviates by 0.495 Å. The six-membered (1-pyridyl-2-iminoethane)copper chelate ring adopts a boat conformation. There are no water molecules of crystallisation and the only hydrogen bonding is internal between the phenolic and ketonic oxygen atoms. All ligand bond lengths are unexceptional.

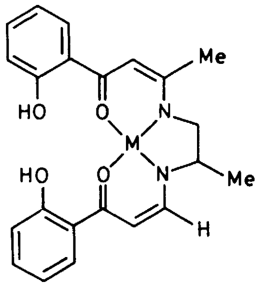
The formation of a mononuclear complex is regarded as resulting from a greater steric congestion at the copper caused by the increased ligand bulk. In $[\{Cu(HL^1)(O_2CMe)\}_2]$ the diamine–copper(II) interaction gives a five-membered ring whereas in the $[Cu(HL^5)(O_2CMe)]$ complex a six-membered ring is formed from the (1-pyridyl-2-iminoethane)copper(II) interaction.

The Use of H_2L^1 *as an Intermediate in the Preparation of Unsymmetrical 'Full-unit' Schiff Base Complexes.*—Reaction of the 'half-unit', H_2L^2, with 2-(formylacetyl)phenol (2,3-dihydro-2-hydroxy-4*H*-1-benzopyran-4-one) in equimolar ratio, followed by concentration of the resulting solution yields an orange-red oil. Attempts at solidifying the oil proved unsuccessful. The mass spectrum of the oil showed a parent peak at m/e = 370, corresponding to the unsymmetrical 'full-unit' H_4L^6.

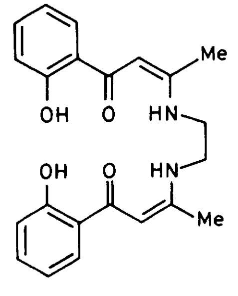
The reaction of the unsymmetrical ligand H_4L^6 with metal acetates in equimolar ratio produces mononuclear complexes of the type $[M^{II}(H_2L^6)]$. The reactions with copper(II) acetate dihydrate and nickel(II) acetate yield brown complexes, $[Cu(H_2L^6)]$ and $[Ni(H_2L^6)]$ respectively. The colour is characteristic of mononuclear copper and nickel complexes where the metal ion is co-ordinated in the inner, N_2O_2, site. The

Table 4. I.r. data (cm^{-1}) for complexes of the unsymmetrical, 'full-unit' Schiff bases

Complex	
$[Cu(H_2L^6)]$	3 400br, 1 620s, 1 595s, 1 505s, 1 470s, 1 440s, 1 315m, 1 127m, 760s, 680m
$[Ni(H_2L^6)]$	3 400br, 1 610m, 1 600m, 1 525s, 1 505m, 1 470m, 1 295m, 760m
$[UO_2(H_2L^6)]$	3 400br, 1 625s, 1 600s, 1 550m, 1 500s, 1 295m, 900s, 755m
$[Cu_2(L^6)]$	3 430br, 1 600s, 1 510s, 1 490s, 1 445s, 1 320m, 1 107m, 760s



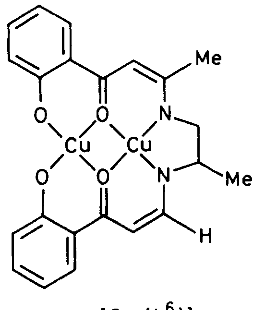
$[M^{II}(H_2L^6)]$; M=Cu or Ni



H_4L^7

reaction of the ligand with dioxouranium(VI) acetate yields an orange compound, $[UO_2(H_2L^6)]$. The i.r. spectral data for these complexes are shown in Table 4. Both the copper and nickel complexes display a double band in the region of 1 600 cm^{-1}, due to C=O stretching and a band at *ca.* 1 520 due to C=C, plus C–N vibrations. The two spectra are very similar in appearance, indicating similar structures for the two complexes. The spectrum of the dioxouranium(VI) complex displays the expected band at 900 cm^{-1} due to O=U=O vibration. Bands found at 1 600 and 1 550 cm^{-1} are ascribed to the C=O and C=C vibrations respectively, while the strong band at 1 625 cm^{-1} may be ascribed to C=N vibration, indicating that the molecule is almost entirely in the imine form. This implies the dioxouranium(VI) group is sited in the outer, O_2O_2 compartment of the ligand. This is in accord with results obtained from the symmetrical ligand H_4L^7.[3] It is probable that there is too much steric constraint put upon the ligand if the dioxouranium(VI) group co-ordinates in the inner N_2O_2 compartment.

Reaction of the unsymmetrical ligand H_4L^6 with two molar equivalents of copper(II) acetate dihydrate yields the green, binuclear complex $[Cu_2(L^6)]$. The i.r. spectrum displays one band at 1 600 cm^{-1} due to $C\overset{\cdots}{-}O$ vibrations, and a second rather broad band at 1 510 cm^{-1} assigned to $C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$ vibrations. The proposed structure of the binuclear complex $[Cu_2(L^6)]$ is based upon the known structure of binuclear complexes of H_4L^7.[7]



$[Cu_2(L^6)]$

Experimental

Details of physical measurements were given in ref. 2. 1-(2'-Hydroxyphenyl)butane-1,3-dione was prepared by the literature method,[8] as was the ligand H_2L^4.[2]

Preparation of 6-Amino-1-(2'-hydroxyphenyl)-3-methyl-4-azahept-2-en-1-one, H_2L^1.—1-(2'-Hydroxyphenyl)butane-1,3-dione (1.78 g, 0.01 mol) in absolute ethanol (100 cm^3) was added dropwise to a stirred solution of 1,2-diaminopropane (0.84 g, 0.01 mol) in absolute ethanol (50 cm^3) at room temperature. After addition was complete, the resulting yellow solution was stirred at room temperature for a further 30 min. The solvent was then removed on a rotary evaporator, leaving either a yellow solid, or an oil which solidified on standing (sometimes the oil required cooling). The solid was washed quickly with cold ethanol, then dried *in vacuo* over silica. Yield 1.6 g (70%). Mass spectrum: P^+ at m/e = 234, corresponding to $C_{13}H_{18}N_2O_2$ (Found: C, 66.0; H, 7.65; N, 11.75. $C_{13}H_{18}N_2O_2$ requires C, 66.6; H, 7.75; N, 11.95%).

The preparations of ligands H_2L^2, H_2L^3, and H_2L^5 were carried out using the above method.

The condensation of 1-(2'-hydroxyphenyl)butane-1,3,-dione with 1,2-diamino-2-methylpropane, at room temperature, yielded H_2L^2 as a yellow solid. Yield (57%). Mass spectrum: P^+ at m/e = 248, corresponding to $C_{14}H_{20}N_2O_2$ (Found: C, 67.75; H, 7.65; N, 10.70. $C_{14}H_{20}N_2O_2$ requires C, 67.7; H, 8.15; N, 11.3%).

The condensation of 1-(2'-hydroxyphenyl)butane-1,3-dione and *N*,*N*-dimethyl-1,2-diaminoethane, at room temperature, yielded H_2L^3 as a yellow solid. Yield (65%). Mass spectrum: P^+ at m/e = 248, corresponding to $C_{14}H_{20}N_2O_2$ (Found: C, 67.05; H, 7.90; N, 11.2. $C_{14}H_{20}N_2O_2$ requires C, 67.7; H, 8.15; N, 11.3%).

The condensation of 1-(2'-hydroxyphenyl)butane-1,3-dione and 2-(2'-aminoethyl)pyridine, at room temperature, yielded H_2L^5 as a yellow solid. Yield (57%). Mass spectrum = P^+ at m/e = 282, corresponding to $C_{17}H_{18}N_2O_2$ (Found: C, 72.35; H, 6.35; N, 10.05. $C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.45; N, 9.90%).

Preparation of the Complexes $[\{Cu(HL^n)(O_2CMe)\}_2]$.—The complexes were prepared using the same general method. Copper(II) acetate (1.0 g, 0.005 mol) in hot 95% ethanol (100 cm^3) was added to the ligand (0.005 mol) in hot chloroform (50 cm^3). The solution was heated for 15 min and the volume reduced to 50 cm^3. The resulting blue-green product was filtered off, washed with ethanol, and dried *in vacuo* over silica (Found for n = 1: C, 50.35; H, 5.90; N, 7.90. $C_{15}H_{20}CuN_2O_4$ requires C, 50.6; H, 6.00; N, 7.55%. Found for n = 2: C, 53.65; H, 6.30; N, 8.75. $C_{16}H_{22}CuN_2O_4$ requires C, 53.9; H, 6.50; N, 9.00%. Found for n = 4: C, 49.05; H, 5.30; N, 8.50. $C_{14}H_{17}CuN_2O_4$ requires C, 49.2; H, 5.30; N, 8.20%. Found for n = 5: C, 56.2; H, 5.20; N, 7.25. $C_{19}H_{20}CuN_2O_4$ requires C, 56.5; H, 5.00; N, 6.95%).

Table 5. Atomic positional parameters with estimated standard deviations for $[\{Cu(HL^1)(O_2CMe)\}_2]\cdot 1.2H_2O$*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.576 11(19)	−0.038 84(13)	0.238 12(18)	C(10)	0.943 4(19)	0.053 0(11)	0.471 4(17)
Cu(2)	0.221 38(19)	−0.001 30(13)	0.122 53(18)	C(11)	0.708 9(15)	−0.041 4(11)	0.512 4(14)
O(1)	0.597 8(11)	0.043 7(7)	−0.149 3(12)	C(12)	0.562 9(17)	−0.073 0(10)	0.517 6(14)
O(2)	0.647 1(10)	0.023 1(6)	0.098 4(10)	C(13)	0.548 3(19)	−0.122 6(12)	0.641 3(17)
O(3)	0.203 7(12)	−0.093 1(7)	0.500 1(11)	C(14)	0.092 7(17)	−0.140 4(9)	0.487 8(18)
O(4)	0.145 3(11)	−0.062 9(6)	0.258 9(10)	C(15)	0.068 9(22)	−0.185 9(10)	0.604 8(17)
O(5)	0.438 7(10)	−0.080 5(6)	0.097 3(10)	C(16)	−0.041 5(20)	−0.238 4(10)	0.603 1(20)
O(6)	0.583 8(13)	−0.172 5(6)	0.095 9(15)	C(17)	−0.125 7(20)	−0.242 6(10)	0.488 3(19)
O(7)	0.361 6(10)	0.036 9(6)	0.265 8(10)	C(18)	−0.104 8(16)	−0.196 9(9)	0.368 5(16)
O(8)	0.234 4(12)	0.138 0(8)	0.257 7(13)	C(19)	0.003 6(17)	−0.149 3(9)	0.366 4(16)
N(1)	0.722 9(12)	−0.005 9(8)	0.378 4(10)	C(20)	0.033 3(14)	−0.103 7(8)	0.244 1(16)
N(2)	0.519 7(13)	−0.107 2(7)	0.384 1(12)	C(21)	−0.049 5(14)	−0.111 0(9)	0.126 9(17)
N(3)	0.084 7(11)	−0.031 3(7)	−0.021 3(12)	C(22)	−0.025 9(16)	−0.073 8(8)	−0.005 9(14)
N(4)	0.292 1(15)	0.065 4(7)	−0.024 8(13)	C(23)	−0.139 1(19)	−0.090 7(10)	−0.119 8(20)
C(1)	0.701 0(15)	0.097 1(10)	−0.137 2(16)	C(24)	0.099 8(17)	0.002 9(11)	−0.155 7(14)
C(2)	0.719 7(18)	0.136 5(11)	−0.254 3(17)	C(25)	0.245 8(17)	0.032 6(10)	−0.160 8(18)
C(3)	0.823 3(20)	0.187 1(9)	−0.248 5(19)	C(26)	0.261 0(22)	0.083 8(11)	−0.281 7(20)
C(4)	0.915 8(21)	0.199 2(10)	−0.128 5(21)	C(27)	0.467 5(19)	−0.144 5(9)	0.059 0(17)
C(5)	0.892 1(19)	0.161 0(9)	−0.014 2(18)	C(28)	0.358 9(22)	−0.181 9(12)	−0.035 0(22)
C(6)	0.783 1(14)	0.107 1(8)	−0.017 2(14)	C(29)	0.339 7(16)	0.103 9(9)	0.296 8(16)
C(7)	0.753 9(16)	0.064 5(9)	0.112 4(14)	C(30)	0.467 1(20)	0.138 8(11)	0.381 0(22)
C(8)	0.847 5(16)	0.071 7(8)	0.231 1(15)	O(9)	0.250 3(18)	0.223 4(10)	0.016 0(18)
C(9)	0.828 4(13)	0.037 2(8)	0.351 9(16)	O(10)	0.535(16)	−0.264(9)	0.278(15)

* Atoms O(9) and O(10) are the oxygen atoms of the water molecules of crystallisation with occupancies of 1.0 and 0.2 respectively.

Table 6. Atomic positional parameters with estimated standard deviations for $[Cu(HL^5)(O_2CMe)]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	−0.005 86(4)	0.217 43(4)	0.225 74(4)	C(7)	0.034 0(4)	0.480 4(3)	0.264 4(3)
O(1)	0.306 9(3)	0.436 6(2)	0.414 1(3)	C(8)	−0.098 2(4)	0.500 1(3)	0.198 0(3)
O(2)	0.100 3(3)	0.378 0(2)	0.265 6(2)	C(9)	−0.177 9(4)	0.418 1(3)	0.121 1(3)
O(3)	0.148 6(2)	0.137 5(2)	0.333 3(2)	C(10)	−0.309 0(4)	0.469 5(4)	0.046 9(4)
O(4)	0.274 1(3)	0.178 3(3)	0.140 5(2)	C(11)	−0.226 1(4)	0.235 5(3)	0.020 8(3)
N(1)	−0.143 9(3)	0.304 4(3)	0.112 1(2)	C(12)	−0.159 0(4)	0.114 6(4)	0.010 8(3)
N(2)	−0.149 5(3)	0.040 1(2)	0.233 3(2)	C(13)	−0.209 1(4)	0.008 8(3)	0.129 0(3)
C(1)	0.242 8(4)	0.544 1(3)	0.413 4(3)	C(14)	−0.313 9(4)	−0.112 7(4)	0.132 8(3)
C(2)	0.309 4(4)	0.627 6(4)	0.490 1(3)	C(15)	−0.358 0(4)	−0.202 2(3)	0.247 0(4)
C(3)	0.253 0(4)	0.739 7(4)	0.492 6(4)	C(16)	−0.296 5(4)	−0.169 9(3)	0.353 6(3)
C(4)	0.130 9(5)	0.771 4(4)	0.419 2(4)	C(17)	−0.191 5(4)	−0.048 2(3)	0.343 6(3)
C(5)	0.063 5(4)	0.689 1(4)	0.344 3(4)	C(18)	0.272 9(4)	0.140 6(3)	0.254 7(3)
C(6)	0.114 9(3)	0.572 7(3)	0.339 3(3)	C(19)	0.422 4(4)	0.097 7(4)	0.308 4(4)

Preparation of Mononuclear Complexes of the Unsymmetrical 'Full-unit' Schiff Base 1,10-*Bis*(2′-*hydroxyphenyl*)-3,6-*dimethyl*-4,7-*diazadeca*-2,8-*diene*-1,10-*dione*, H_4L^6.—The ligand H_2L^1 (0.468 g, 0.002 mol) and 2-(formylacetyl)phenol (0.328 g, 0.002 mol) were refluxed in chloroform (100 cm^3) for 1 h. The solution was then evaporated down to an oil, which would not solidify. The oil was redissolved in chloroform (100 cm^3) and added to metal(II) acetate (0.002 mol) in 95% ethanol. The resulting solution was heated for 30 min, and the volume was reduced to *ca.* 50 cm^3. The resulting precipitate was filtered off, washed with ethanol, and dried *in vacuo* over silica giving $[M(H_2L^6)]$ (Found for M = Cu: C, 59.05; H, 5.10; N, 6.30. $C_{22}H_{22}CuN_2O_4$ requires C, 59.8; H, 5.05; N, 6.35%. Found for M = Ni: C, 60.75; H, 5.20, N, 6.25. $C_{22}H_{22}N_2NiO_4$ requires C, 60.4; H, 5.10; N, 6.40%. Found for M = UO_2: C, 39.1; H, 3.30; N, 4.25. $C_{22}H_{22}N_2O_6U\cdot H_2O$ requires C, 39.65; H, 3.65; N, 4.20%).

Preparation of $[Cu_2(L^6)]$.—The ligand solution was made up as above, then added to copper(II) acetate (0.8 g, 0.004 mol) in 95% ethanol (100 cm^3). The solution was heated for 30 min and the resulting green solid filtered off, washed with ethanol, then dried *in vacuo* over silica (Found: C, 52.95; H, 4.50; N, 5.80. $C_{22}H_{20}Cu_2N_2O_4$ requires C, 52.45; H, 4.00; N, 5.55%).

Crystal Data for $[Cu(HL^1)(O_2CMe)]\cdot 0.6H_2O$.—Crystallises from chloroform–ethanol as blue-green needles; crystal dimensions 0.475 × 0.055 × 0.075 mm, $C_{15}H_{21.2}CuN_2O_{4.6}$, M = 366.68, monoclinic, a = 9.380(3), b = 18.570(9), c = 9.725(8) Å, β = 93.99(5)°, U = 1 689.9(17) Å^3, D_m = 1.45 g cm^{-3}, Z = 4, D_c = 1.441 g cm^{-3}, $F(000)$ = 764, space group $P2_1$ (C_2^2, no. 4), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 13.15 cm^{-1}.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex *R*3*m* diffractometer by the omega-scan method. The 1 550 independent 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 were placed in calculated positions [C–H 0.96, O–H 0.98, N–H 0.92 Å; C–O–H 109, C–C–H(methyl) 111°]; their contributions were included in structure factor calculations (B = 10.0 Å^2) but no refinement of positional parameters was permitted. Two water molecules of crystallisation were detected and included in calculations with, respectively, 100% and 20% occupancy; their hydrogen atoms were not positioned. Refinement converged at R = 0.0476 with allowance for anisotropic thermal motion of all non-hydrogen atoms, with the exception of the oxygen atoms of the water molecules. Table 5 lists the atomic positional parameters with estimated standard deviations.

Crystal Data for $[Cu(HL^5)(O_2CMe)]$.—Crystallises from ethanol as dark green plates; crystal dimensions 0.138 × 0.338 × 0.570 mm, $C_{19}H_{20}CuN_2O_4$, $M = 403.92$, triclinic, $a = 8.157(7)$, $b = 10.651(7)$, $c = 10.900(7)$ Å, $\alpha = 78.62(7)$, $\beta = 85.814(14)$, $\gamma = 101.914(13)^\circ$, $U = 901.9(13)$ Å^3, $D_m = 1.48$ g cm^{-3}, $Z = 2$, $D_c = 1.487$ g cm^{-3}, $F(000) = 418$, space group $P\bar{1}$ (C_i, no. 2), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 12.37 cm^{-1}.

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 omega-scan method. The 2 529 independent 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 were placed in calculated positions [C–H 0.96, O–H 0.91 Å; C–O–H 109, 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. No water of crystallisation was present in the lattice. Refinement converged at $R = 0.0332$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper. Table 6 lists the atomic positional parameters with estimated standard deviations.

Scattering factors were taken from ref. 9; unit weights were used throughout both refinements. Computer programs formed part of the Sheffield *X*-ray system.

Acknowledgements

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