Compartmental Ligands. Part 5.[1] Copper(II) Complexes of Schiff Bases derived from 1-(Pyrrol-2-yl)butane-1,3-dione: Crystal and Molecular Structure of [3,11-Dimethyl-1,13-bis(pyrrol-2-yl)-7-oxa-4,10-diazatrideca-2,11-diene-1,13-dionato(2–)-*N,N′,O,O′*]copper(II) †

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Mononuclear copper(II) complexes of acyclic, compartmental Schiff bases derived from 1-(pyrrol-2-yl)butane-1,3-dione and alkane-α,ω-diamines have been synthesised. The metal site occupancy has been shown to depend on the length of the alkane bridge. A three-dimensional *X*-ray crystal structure has been carried out on [3,11-dimethyl-1,13-bis(pyrrol-2-yl)-7-oxa-4,10-diazatrideca-2,11-diene-1,13-dionato(2–)-*N,N′,O,O′*]copper(II)–chloroform (1/0.5). The complex has $Z = 4$ in a triclinic cell with space group $P\bar{1}$ and dimensions $a = 12.144(4)$, $b = 12.315(7)$, $c = 16.063(8)$ Å, $\alpha = 97.13(4)$, $\beta = 106.92(4)$, $\gamma = 100.01(4)°$; $R = 0.058$ for 2 189 reflections.

The reaction of *o*-acetoacetylphenol with α,ω-diamines yields Schiff bases which provide adjacent, dissimilar donor sets, *e.g.* compound (1).[2] Such ligands are capable of selectively incorporating one metal ion to provide a mononuclear positional isomer which may then act as a precursor for the formation of homo- and hetero-binuclear complexes.[2,3]

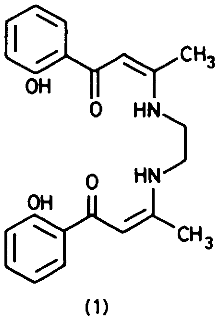
We have sought to modify the functionality of such ligand systems by preparing Schiff bases derived from the reaction of α,ω-diamines with 1-(pyrrol-2-yl)butane-1,3-dione (2). The introduction of pyrrole into the compartmental ligand leads to framework modification through change of both the donor environment and the spatiality of the outer compartment. Further modifications are then made by incorporating bridges of various lengths, and in certain cases, having additional potential donor atoms available. This gave new potentially binucleating ligands (3) with dissimilar donor sets.

This paper reports the synthesis of the pyrrole-containing Schiff bases and of their mononuclear copper(II) complexes, and the crystal and molecular structure of the mononuclear copper(II) complex of (3e).

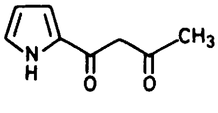
Results and Discussion

Acyclic Schiff Bases.—1-(Pyrrol-2-yl)butane-1,3-dione (2-acetoacetylpyrrole) (2) was prepared by the method of Treibs and Michl[4] and treated, in 2 : 1 ratio in ethanol, with the appropriate alkane-α,ω-diamine to give the acyclic Schiff bases (3a)—(3f).

The i.r. spectra of the bases show a sharp, medium to strong band in the 3 200—3 240 cm^{-1} region assigned to the pyrrolic NH stretch, and a band centred on 1 600 cm^{-1} attributed to the carbonyl group. The mass spectra of the compounds show peaks of low relative abundance corresponding to the molecular ion. The ^{1}H n.m.r. spectra (Table 1) show that compounds (3) exist as the ene-amine tautomers in solution. The Schiff bases were not very soluble in the normal n.m.r. solvents and, even at 220 MHz, poorly resolved spectra were recorded for several species: as a consequence the spectrum of (3c) was recorded at 400 MHz in order to be certain of assignments.



(1)



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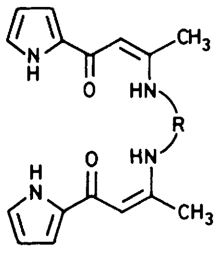

(3)

a; R = $[CH_2]_2$
b; R = $[CH_2]_3$
c; R = $[CH_2]_4$
d; R = $[CH_2]_5$
e; R = $[CH_2]_2O[CH_2]_2$
f; R = $[CH_2]_2S[CH_2]_2$

Mononuclear Metal Complexes.—Previous work with compartmental ligands such as (1) has shown that there is a site preference for metal complexation, depending on the metal used.[3] The ligands (3) present two dissimilar 'N_2O_2' donor sites for complexation, and mononuclear copper(II) complexes were prepared in order to determine selectivity preferences and to see if the bridge extension affected the choice of site occupancy.

Pure mononuclear complexes of (3) were recovered from the reaction of (3) with copper(II) ethanoate in alcoholic solvents, and the site occupancy was monitored by the use of i.r. spectra, showing the presence, or absence, of pyrrolic NH stretching. In the spectra of the complexes (4) derived from ligands containing short bridges, this stretch was present,

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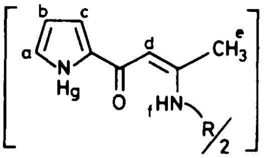
† *Supplementary data available* (No. SUP 23577, 30 pp.): bond lengths and angles, mean planes and torsion angles, thermal parameters, hydrogen co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

Table 1. ^{1}H N.m.r. spectra of Schiff bases



Base	Bridge R	Solvent (field)	δ
(3a)	CH_2CH_2 h h	$CDCl_3$-$(CD_3)_2SO$ (220 MHz)	2.05 (6 H, s, H_e), 3.55 (4 H, m, H_h), 5.45 (2 H, s, H_d), 6.09 (2 H, s, H_b), 6.60 (2 H, s, H_c), 6.80 (2 H, s, H_a), 10.85 (2 H, br, $H_{g/f}$), 11.2 (2 H, br, $H_{f/g}$)
(3b)	$CH_2CH_2CH_2$	Insoluble	
(3c)	$CH_2CH_2CH_2CH_2$ h j j h	$CDCl_3$-CD_3OD (400 MHz)	1.77 (4 H, m, H_j), 2.07 (6 H, s, H_e), 3.35 (2 H, m, H_h), 3.39 (2 H, m, H_h), 5.56 (2 H, s, H_d), 6.20 (2 H, dd, H_b), 6.70 (2 H, dd, H_c), 6.93 (2 H, dd, H_a)
(3d)	$CH_2[CH_2]_3CH_2$ h j h	CD_2Cl_2 (220 MHz)	1.65 (6 H, m, H_j), 2.02 (6 H, s, H_e), 3.30 (4 H, m, H_h), 5.55 (2 H, s, H_d), 6.18 (2 H, s, H_b), 6.62 (2 H, s, H_e), 6.85 (2 H, s, H_a), 9.7 (2 H, br, $H_{g/f}$), 10.8 (2 H, br, $H_{f/g}$)
(3e)	CH_2CH_2-O-CH_2CH_2 h j j h	$CDCl_3$-$(CD_3)_2SO$ (220 MHz)	2.10 (6 H, s, H_e), 3.55 (4 H, m, H_h), 3.70 (4 H, m, H_j), 5.50 (2 H, s, H_d), 6.15 (2 H, s, H_b), 6.66 (2 H, s, H_c), 6.90 (2 H, s, H_a), 14.2 (2 H, br, $H_{g/f}$), 14.4 (2 H, br, $H_{f/g}$)
(3f)	CH_2CH_2-S-CH_2CH_2 h j j h	$CDCl_3$ (220 MHz)	2.00 (6 H, s, H_e), 2.80 (4 H, t, H_g), 3.50 (4 H, q, H_h), 5.45 (2 H, s, H_d), 6.20 (2 H, s, H_b), 6.66 (2 H, s, H_c), 6.75 (2 H, s, H_a), 9.95 (2 H, br, $H_{g/f}$), 10.90 (2 H, br, $H_{f/g}$)

Table 2. Principal i.r. bands (cm^{-1}; KBr disc) and diffuse reflectance bands (nm) for the copper complexes

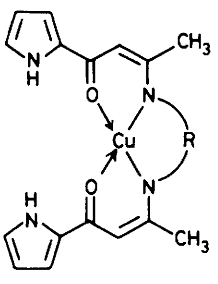
Complex	ν_{NH} (pyrrole)	ν_{NH} (amine)	ν_{C-O}	$\nu_{C\underline{\cdots}O}$, $\nu_{C\underline{\cdots}C}$	$\nu_{C\underline{\cdots}C}$, $\nu_{C\underline{\cdots}N}$	Diffuse reflectance
(4a)	3 345m		1 585m	1 545s	1 500vs	518 (sh), 373
(4b)	3 350m		1 590m	1 545s	1 500vs	526, 357br
(5a)		3 220w	1 610s	1 550s	1 510m	512 (sh), 370, 322 (sh)
(5b)		3 210w	1 600s	1 545s	1 510w	510 (sh), 370, 318 (sh)
(5c)		3 200w	1 600s	1 545s	1 510w	505 (sh), 377, 322 (sh)
(5d)		3 200w	1 600s	1 545s	1 500w	500 (sh), 370, 317 (sh)

indicating an inner site occupancy. A movement to higher wavenumber showed a loss of hydrogen bonding as compared with the free ligand. On lengthening the bridge to give complexes (5) the NH stretch was lost, thus indicating an outer site occupancy.

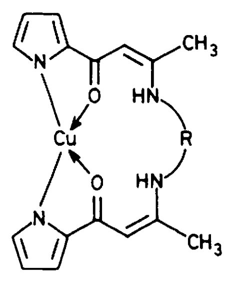
The diffuse reflectance spectra of all of the mononuclear copper(II) complexes indicated that the metal is present in an essentially square-planar geometry.

The complex (5c) was subjected to an *X*-ray molecular structure determination. The structures of the two independent complexes are illustrated in Figures 1 and 2; in the case of molecule 1, the conformation of the disorder component of higher occupancy is shown; atom labels shown are those used in the Tables and in the discussion. Bond lengths and angles (together with estimated standard deviations) are given in Table 3.

The asymmetric unit comprises one molecule each of two crystallographically independent copper complexes, and one



(4) a; R = $[CH_2]_2$
b; R = $[CH_2]_3$



(5) a; R = $[CH_2]_4$
b; R = $[CH_2]_5$
c; R = $[CH_2]_2O[CH_2]_2$
d; R = $[CH_2]_2S[CH_2]_2$

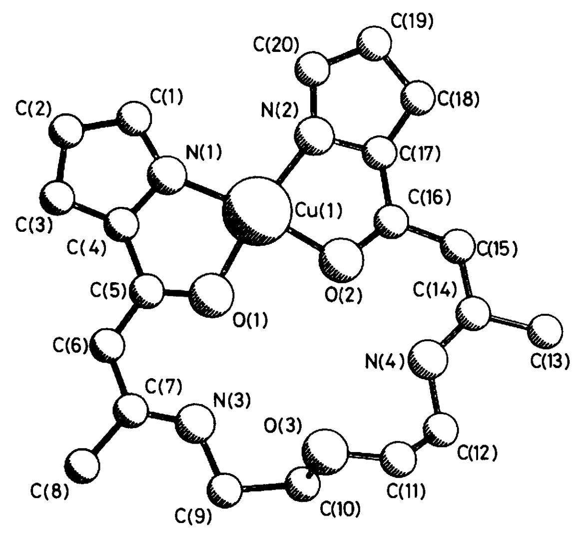


Figure 1. The molecular geometry and atom labelling of molecule 1: the atoms illustrated for the ether function correspond to the disorder component of higher occupancy; those of the component of lower occupancy are labelled C(10′), O(3′), and C(11′)

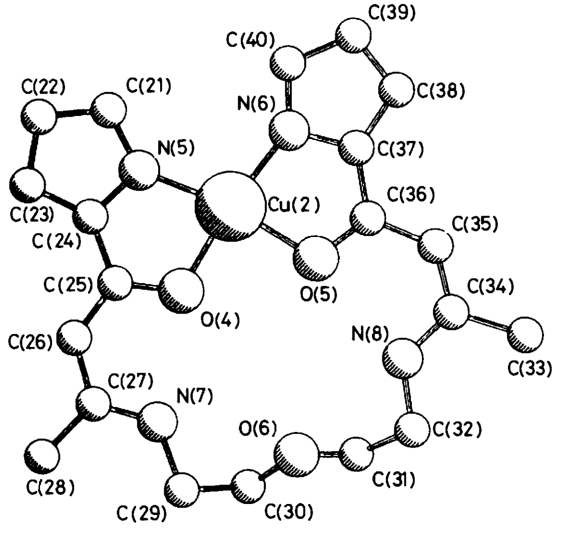


Figure 2. The molecular geometry and atom labelling of molecule 2

chloroform molecule of crystallisation; the two complexes are chemically very similar, differing only in conformational details. In each molecule, the copper(II) ion is bonded in an approximately square-planar environment in the outer compartment of the Schiff base ligand, which has two possible binding sites; the donor atoms are two pyrrole nitrogen and two ketonic oxygen atoms. Each of the two imino-nitrogen atoms carries a hydrogen atom (placed in optimum positions from a difference-Fourier synthesis) and two intramolecular hydrogen bonds are formed to the ketonic oxygen atoms. The oxygen atom of the ether function does not seem to take significant part in this hydrogen bonding despite its proximity to the imino-nitrogen atoms. In each molecule, the co-ordination plane of the copper shows some degree of non-coplanarity; in molecule 2 this is best seen as a deviation of O(4) from a perfect plane defined by the metal and the other three co-ordinated atoms. The pyrrole rings are essentially planar (r.m.s. deviations 0.007, 0.001, 0.006, and 0.019 Å) as are the β-oxoimine fragments which define the inner compartment (r.m.s. deviations 0.006, 0.018, 0.011, and 0.022 Å). Molecule 1 shows disorder of the ether function in two conformations; the minor component has a conformation which is almost identical with that shown by the ordered molecule 2, but the major component of molecule 1 adopts a distinctly different conformation (see Figures 1 and 2). Presumably these conformations are determined by slightly preferential intermolecular packing. The unoccupied inner compartment has a pentagonal shape of mean edge length 2.75 ±0.15 Å; for the minor component of molecule 1 and for molecule 2, the pentagons are fairly planar (r.m.s. deviations 0.08 and 0.04 Å, respectively), but the different conformation adopted by the ether function for the major component of molecule 1

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations

Lengths

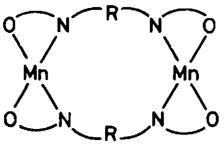
Cu(1)–N(1)	1.953(13)	Cu(2)–N(5)	1.929(13)
Cu(1)–N(2)	1.931(12)	Cu(2)–N(6)	1.898(13)
Cu(1)–O(1)	1.949(10)	Cu(2)–O(4)	1.959(10)
Cu(1)–O(2)	1.970(10)	Cu(2)–O(5)	1.976(10)
O(1)–C(5)	1.302(18)	O(4)–C(25)	1.322(19)
O(2)–C(16)	1.290(18)	O(5)–C(36)	1.300(17)
N(1)–C(1)	1.349(20)	N(5)–C(21)	1.327(20)
N(1)–C(4)	1.363(19)	N(5)–C(24)	1.355(20)
C(1)–C(2)	1.40(2)	C(21)–C(22)	1.39(2)
C(2)–C(3)	1.39(2)	C(22)–C(23)	1.38(3)
C(3)–C(4)	1.40(2)	C(23)–C(24)	1.39(2)
C(4)–C(5)	1.45(2)	C(24)–C(25)	1.42(2)
C(16)–C(17)	1.43(2)	C(36)–C(37)	1.42(2)
C(17)–C(18)	1.36(2)	C(37)–C(38)	1.38(2)
C(18)–C(19)	1.41(3)	C(38)–C(39)	1.38(2)
C(19)–C(20)	1.34(2)	C(39)–C(40)	1.39(2)
N(2)–C(20)	1.357(20)	N(6)–C(40)	1.327(20)
N(2)–C(17)	1.369(20)	N(6)–C(37)	1.374(20)

Angles

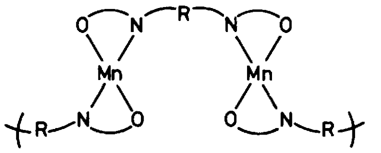
N(1)–Cu(1)–N(2)	104.9(5)	N(5)–Cu(2)–N(6)	105.8(5)
N(1)–Cu(1)–O(1)	83.8(5)	N(5)–Cu(2)–O(4)	81.8(5)
N(1)–Cu(1)–O(2)	171.6(5)	N(5)–Cu(2)–O(5)	170.1(5)
N(2)–Cu(1)–O(1)	170.8(5)	N(6)–Cu(2)–O(4)	170.5(5)
N(2)–Cu(1)–O(2)	83.4(5)	N(6)–Cu(2)–O(5)	84.1(5)
O(1)–Cu(1)–O(2)	87.9(4)	O(4)–Cu(2)–O(5)	88.3(4)
Cu(1)–O(1)–C(5)	113.9(9)	Cu(2)–O(4)–C(25)	113.6(9)
Cu(1)–N(1)–C(1)	141.5(11)	Cu(2)–N(5)–C(21)	137.9(11)
Cu(1)–N(1)–C(4)	110.7(10)	Cu(2)–N(5)–C(24)	114.7(10)
C(1)–N(1)–C(4)	107.8(13)	C(21)–N(5)–C(24)	107.3(13)
N(1)–C(1)–C(2)	108.8(14)	N(5)–C(21)–C(22)	110.4(14)
C(1)–C(2)–C(3)	108.4(15)	C(21)–C(22)–C(23)	106.3(16)
C(2)–C(3)–C(4)	104.9(15)	C(22)–C(23)–C(24)	106.3(15)
N(1)–C(4)–C(3)	110.1(14)	N(5)–C(24)–C(23)	109.7(14)
N(1)–C(4)–C(5)	116.3(13)	N(5)–C(24)–C(25)	113.5(14)
C(3)–C(4)–C(5)	133.6(15)	C(23)–C(24)–C(25)	136.7(15)
O(1)–C(5)–C(4)	115.0(13)	O(4)–C(25)–C(24)	116.1(14)
O(1)–C(5)–C(6)	122.0(14)	O(4)–C(25)–C(26)	120.6(14)
C(4)–C(5)–C(6)	123.0(14)	C(24)–C(25)–C(26)	123.2(15)
O(2)–C(16)–C(15)	121.9(14)	O(5)–C(36)–C(35)	119.7(13)
O(2)–C(16)–C(17)	118.3(14)	O(5)–C(36)–C(37)	118.6(13)
C(15)–C(16)–C(17)	119.9(14)	C(35)–C(36)–C(37)	121.7(14)
N(2)–C(17)–C(16)	113.7(14)	N(6)–C(37)–C(36)	113.9(13)
N(2)–C(17)–C(18)	110.1(14)	N(6)–C(37)–C(38)	109.6(14)
C(16)–C(17)–C(18)	135.8(15)	C(36)–C(37)–C(38)	136.5(15)
C(17)–C(18)–C(19)	106.2(15)	C(37)–C(38)–C(39)	107.8(15)
C(18)–C(19)–C(20)	106.7(16)	C(38)–C(39)–C(40)	104.4(15)
N(2)–C(20)–C(19)	111.2(15)	N(6)–C(40)–C(39)	112.6(15)
Cu(1)–N(2)–C(17)	112.6(10)	Cu(2)–N(6)–C(37)	112.7(10)
Cu(1)–N(2)–C(20)	141.4(11)	Cu(2)–N(6)–C(40)	141.9(11)
C(17)–N(2)–C(20)	105.8(12)	C(37)–N(6)–C(40)	105.4(13)
Cu(1)–O(2)–C(16)	112.0(9)	Cu(2)–O(5)–C(36)	110.6(9)

leads to a markedly less planar pentagon (r.m.s. deviation 0.31 Å). The approximate mean radius of the potential inner co-ordination site (2.34 Å) would be appropriate to accommodate a large cation such as Pb^{II}, and the conformation of the ether function shown by molecule 2 would be expected to be preferred to that shown by the major component of molecule 1. The chloroform molecule does not seem to interact with either complex. Attempts to incorporate other metals into the inner compartment have so far been unsuccessful.

In studies on related tetradentate Schiff base complexes, changing the length of the bridging moiety has led either to geometrical changes or to the generation of homobinuclear complexes. Using ligands derived from salicylaldehyde and alkane-α,ω-diamines, NH$_2$[CH$_2$]$_n$NH$_2$, Holm,[5] and later Hoyt and Everett,[6] showed that nickel(II) complexes remained square planar and diamagnetic up to $n = 5$. Weber[7] reached a similar conclusion using pyrrole-2-carbaldehyde and the corresponding diamines. In contrast, copper(II),[8] manganese(II),[9] and cobalt(III)[10] complexes derived from the salicylaldehyde Schiff bases were found to have an increased tetrahedral distortion as the bridging chain length increased. An alternative interpretation was presented for the manganese(II) complexes by Titus *et al.*,[11] who commented that increasing the length of the polymethylene chain gave the possibility for the ligand to bind two metal ions. This could result in discrete homobinuclear complexes of structure type (I),* or more extensively polymeric structures [type (II)].

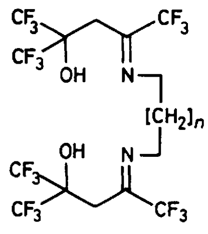


(I)

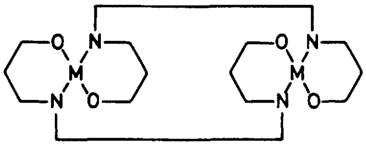


(II)

Recently Willis and co-workers[13,14] have reported that for copper(II) and nickel(II) complexes of the tetradentate, fluorinated Schiff base (6), small bridges lead to monomeric square-planar species, whereas for $n = 5$ or 6 association occurs to give dimeric *trans* species (7).



(6)



(7)

In our compounds the monomeric square-planar form is maintained with ligands having bridges containing up to five units. However, the metal can move from the increasingly strained inner site into the adjacent outer site with the flexible bridge helping to maintain the square-planar environment. The consequences of moving to a longer chain will be discussed later in this series of papers.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were recorded for KBr discs using a Perkin-Elmer 297 spectrophotometer. Mass spectra were obtained using a KRATOS MS 25 spectrometer. ^{1}H N.m.r. spectra were recorded at 220 MHz using a Perkin-Elmer R34 spectrometer at ambient temperature, and at 400 MHz using a Bruker 400-MHz spectrometer. Diffuse reflectance spectra were recorded using a Cary 14 spectrometer.

1-(Pyrrol-2-yl)butane-1,3-dione was synthesised according to the method of Treibs and Michl.[4] The alkane-α,ω-diamines were used as obtained commercially.

The Schiff bases were prepared by the following general procedure. 1-(Pyrrol-2-yl)butane-1,3-dione (0.01 mol) was dissolved in hot absolute ethanol (30 cm^3) and the required alkane-α,ω-diamine (0.005 mol) dissolved in chloroform (10 cm^3) was added. The colour changed to dark yellow and after heating for 15—30 min on a steam-bath the solution was left to cool. On evaporation, the pale cream, or yellow, Schiff bases precipitated. These were filtered off and dried, over silica gel, under vacuum. When necessary, light petroleum (b.p. 40—60 °C) was used as a precipitant. Analytical figures were as follows: compound (3a) (Found: C, 65.3; H, 7.2; N, 16.8%; $M^{\cdot+}$, 326. $C_{18}H_{22}N_4O_2\cdot0.5H_2O$ requires C, 64.5; H, 6.9; N, 16.7%; $M - 0.5H_2O$, 326); compound (3b) (Found: C, 65.6; H, 7.2; N, 16.9%; $M^{\cdot+}$, 340. $C_{19}H_{24}N_4O_2\cdot0.5H_2O$ requires C, 65.3; H, 7.2; N, 16.1%; $M - 0.5H_2O$, 340); compound (3c) (Found: C, 66.2; H, 7.3; N, 15.3%; $M^{\cdot+}$, 354. $C_{20}H_{26}N_4O_2\cdot0.5H_2O$ requires C, 66.1; H, 7.4; N, 15.4%; $M - 0.5H_2O$, 354); compound (3d) (Found: C, 66.7; H, 7.5; N, 14.6%; $M^{\cdot+}$, 368. $C_{21}H_{28}N_4O_2\cdot0.5H_2O$ requires C, 66.8; H, 7.7; N, 14.8%; $M - 0.5H_2O$, 368); compound (3e) (Found: C, 63.4; H, 7.2; N, 15.1%; $M^{\cdot+}$, 370. $C_{20}H_{26}N_4O_3\cdot0.5H_2O$ requires C, 63.3; H, 7.1; N, 14.8%; $M - 0.5H_2O$, 370); compound (3f) (Found: C, 62.3; H, 6.7; N, 14.3; S, 8.4%; M^+, 386. $C_{20}H_{26}N_4O_2S$ requires C, 62.2; H, 6.7; N, 14.5; S, 8.3%; M, 386).

The copper(II) complexes of the Schiff bases were synthesised using the following general procedure. Copper(II) ethanoate monohydrate (0.01 mol) was dissolved in hot ethanol (*ca.* 20 cm^3) and added dropwise to the required Schiff base (0.01 mol) dissolved in hot chloroform, or dichloromethane (20 cm^3). The colour of the solution changed to deep red-brown on complete addition of the copper(II) salt. The mixture was heated for 15—30 min on a steam-bath and the solution filtered. The filtrate was allowed to cool and the copper(II) complexes precipitated out. (The complexes were generally recovered as chloroform solvates, 0.1—1 mol equiv. of solvent being present.) Analytical figures were as follows: compound (4a) [Found: C, 54.5; H, 5.6; N, 13.6%; $M^{\cdot+}$, 387. $C_{18}H_{20}CuN_4O_2\cdot0.1CHCl_3$ requires C, 54.4; H, 5.0; N, 14.0%; $M - 0.1CHCl_3$, 387 (based on ^{63}Cu)]; compound (4b) (Found: C, 55.5; H, 5.6; N, 13.0%; $M^{\cdot+}$, 401. $C_{19}H_{22}CuN_4O_2\cdot0.1CHCl_3$ requires C, 55.5; H, 5.4; N, 13.5%; $M - 0.1CHCl_3$, 401); compound (5a) (Found: C, 57.5; H, 5.8; N, 13.6%; $M^{\cdot+}$, 415. $C_{20}H_{24}CuN_4O_2$ requires C, 57.8; H, 5.8; N, 13.5%; M, 415); compound (5b) (Found: C, 54.3; H, 5.7; N, 11.8%; $M^{\cdot+}$, 429. $C_{21}H_{26}CuN_4O_2\cdot0.3CHCl_3$ requires C, 54.6; H, 5.6; N, 11.9; $M - 0.3CHCl_3$, 429); compound (5c) (Found: C, 49.8; H, 5.1; Cl, 10.9; N, 11.3%; $M^{\cdot+}$, 431. $C_{20}H_{24}CuN_4O_3\cdot0.5CHCl_3$ requires C, 50.1; H, 5.0; Cl, 10.9; N, 11.4%; $M - 0.5CHCl_3$, 431; compound (5d) (Found: C, 44.5; H, 4.7; Cl, 15.7; N, 9.8; S, 4.9%; $M^{\cdot+}$, 447. $C_{20}H_{24}CuN_4O_2S\cdot CHCl_3$ requires C, 44.4; H, 4.6; Cl, 15.8; N, 9.8; S, 5.6%; $M - CHCl_3$, 447).

Structure Determination for the Complex (5c).—*Crystal data.* $Cu(C_{20}H_{24}N_4O_3)\cdot0.5CHCl_3(C_{20.5}H_{24.5}Cl_{1.5}CuN_4O_3)$, $M =$

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* This structure type was proposed by Pfeiffer and Pfitzer[12] for copper(II) complexes of Schiff bases derived from salicylaldehyde and having constrained amines, such as 1,3-diaminobenzene and 4,4′-diaminobiphenyl, as bridges.

Table 4. Atomic positional parameters with estimated standard deviations in parentheses *

Atom	X/a	Y/b	Z/c
Cu(1)	0.422 06(17)	0.123 60(15)	0.100 84(13)
Cu(2)	0.040 58(17)	0.420 63(16)	0.352 90(13)
Cl(1)	0.359 3(6)	−0.214 2(5)	0.257 0(5)
Cl(2)	0.397 7(6)	0.019 0(5)	0.314 8(5)
Cl(3)	0.566 4(6)	−0.100 0(5)	0.395 9(5)
O(1)	0.261 1(8)	0.070 6(7)	0.020 3(6)
O(2)	0.444 5(8)	−0.030 4(7)	0.076 2(6)
O(3)	0.143 3(25)	−0.260 3(18)	−0.031 8(12)
O(4)	−0.103 5(8)	0.464 7(8)	0.362 2(7)
O(5)	0.030 3(8)	0.325 7(8)	0.442 1(7)
O(6)	−0.256 1(9)	0.310 0(9)	0.521 5(8)
N(1)	0.378 0(10)	0.268 6(10)	0.111 0(8)
N(2)	0.581 1(10)	0.151 1(9)	0.181 4(8)
N(3)	0.075 9(11)	−0.067 1(10)	−0.095 9(9)
N(4)	0.396 8(13)	−0.250 6(10)	0.017 5(9)
N(5)	0.027 8(11)	0.522 0(9)	0.269 8(9)
N(6)	0.168 3(10)	0.354 2(10)	0.346 1(8)
N(7)	−0.294 1(10)	0.476 2(10)	0.413 3(9)
N(8)	−0.048 7(11)	0.215 5(11)	0.551 6(9)
C(1)	0.421 8(14)	0.376 6(11)	0.152 1(10)
C(2)	0.336 0(15)	0.438 0(13)	0.123 7(11)
C(3)	0.237 6(15)	0.366 3(12)	0.061 3(12)
C(4)	0.266 8(13)	0.260 8(12)	0.055 6(9)
C(5)	0.204 0(13)	0.150 1(12)	0.004 7(10)
C(6)	0.093 0(14)	0.129 7(12)	−0.055 9(12)
C(7)	0.029 9(13)	0.023 0(14)	−0.105 9(11)
C(8)	−0.092 4(16)	0.010 2(17)	−0.167 9(14)
C(9)	0.016 1(18)	−0.182 3(15)	−0.142 6(12)
C(10)	0.106 6(28)	−0.261 1(22)	−0.124 9(14)
C(11)	0.202 2(28)	−0.349 6(22)	−0.012 9(14)
C(12)	0.315 3(18)	−0.350 8(14)	−0.038 1(12)
C(13)	0.555 6(15)	−0.347 7(13)	0.067 0(13)
C(14)	0.508 1(16)	−0.244 7(12)	0.063 6(11)
C(15)	0.585 6(14)	−0.144 3(12)	0.112 8(11)
C(16)	0.548 8(13)	−0.039 4(12)	0.120 4(10)
C(17)	0.628 7(13)	0.058 3(12)	0.178 7(10)
C(18)	0.737 5(14)	0.080 2(13)	0.240 8(11)
C(19)	0.758 0(15)	0.191 9(14)	0.284 3(12)
C(20)	0.662 6(14)	0.230 7(12)	0.246 5(11)
C(21)	0.087 4(12)	0.561 4(12)	0.218 5(11)
C(22)	0.028 9(15)	0.631 5(15)	0.169 2(12)
C(23)	−0.070 4(14)	0.635 4(13)	0.193 7(12)
C(24)	−0.069 7(13)	0.565 5(12)	0.255 2(11)
C(25)	−0.141 0(14)	0.532 7(12)	0.308 1(11)
C(26)	−0.244 3(13)	0.568 8(12)	0.304 7(11)
C(27)	−0.315 4(13)	0.544 8(13)	0.355 9(12)
C(28)	−0.419 4(16)	0.596 9(14)	0.348 5(13)
C(29)	−0.367 3(13)	0.444 3(15)	0.468 4(13)
C(30)	−0.370 3(14)	0.322 8(15)	0.477 1(13)
C(31)	−0.258 7(15)	0.199 2(17)	0.532 6(12)
C(32)	−0.139 9(16)	0.193 4(15)	0.593 9(12)
C(33)	0.064 5(18)	0.090 3(16)	0.626 6(14)
C(34)	0.044 6(14)	0.169 2(13)	0.562 0(11)
C(35)	0.121 4(15)	0.194 8(14)	0.516 9(10)
C(36)	0.112 6(11)	0.268 9(11)	0.454 2(10)
C(37)	0.191 6(12)	0.282 4(12)	0.404 7(10)
C(38)	0.285 9(15)	0.238 1(13)	0.396 8(11)
C(39)	0.321 0(14)	0.280 3(15)	0.330 9(11)
C(40)	0.249 3(13)	0.355 3(13)	0.305 7(11)
C(41)	0.466 1(17)	−0.090 3(16)	0.299 0(12)
O(3′)	0.165 1(29)	−0.264 3(26)	−0.076 1(30)
C(10′)	0.044 3(32)	−0.261 3(34)	−0.088 5(36)
C(11′)	0.188 0(32)	−0.367 0(34)	−0.049 5(36)

* Atoms carrying a prime (′) superscript are those of the disordered ether component of lower occupancy. The e.s.d.s for the atoms of the groups of constrained geometry were derived from the e.s.d.s of the refined group parameters. Atoms Cl(1), Cl(2), Cl(3), and C(41) constitute the chloroform molecule of crystallisation.

491.66; crystallises from chloroform–methanol as green-brown plates; crystal dimensions 0.375 × 0.04 × 0.30 mm; triclinic, a = 12.144(4), b = 12.315(7), c = 16.063(8) Å, α = 97.13(4), β = 106.92(4), γ = 100.01(4)°, U = 2 224(2) Å^3, D_m = 1.44, Z = 4, D_c = 1.468 g cm^{-3}, $F(000)$ = 1 016, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 11.93 cm^{-1}.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the omega-scan method. 2 189 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 methods and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.98 Å, Cl–C–H 109, C–C–H 110°); their contributions were included in structure factor calculations (B = 7.0 Å^2); limited optimisation of the positional parameters of hydrogen atoms attached to nitrogen atoms was permitted. The disordered ether fragment of molecule 1 was refined, for both components, with constrained geometry (C–O 1.43 Å, C–O–C 110°) and the occupancy factor refined to 68.7 : 31.3%. Refinement converged at R = 0.0580 with allowance for anisotropic thermal motion of all non-hydrogen atoms, except for the carbon and oxygen atoms of the disordered ether fragment of lower occupancy, for which a common isotropic thermal parameter was refined. Allowance was also made 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. 15; unit weights were used throughout the refinement; computer programs formed part of the Sheffield X-ray system.

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