Copper(I) Schiff-base Complexes: Reversible Carbon Monoxide Binding, Reactions with Dioxygen, and the Structure of a Dinuclear Complex containing Co-ordinated and Unco-ordinated Alkene Groups†

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Copper(I) complexes of a series of acyclic Schiff-base ligands (L^1—L^5) derived from the condensation of 2,6-diacetylpyridine with 2 mol of 4-aminobut-1-ene (L^1), allylamine (L^2), 1-aminobutane (L^3), 1-aminopropane (L^4), and 2-(ethylthio)ethylamine (L^5), have been prepared. Crystals of the dinuclear complex $[Cu_2L^1_2][BPh_4]_2$ are orthorhombic with a = 17.74(1), b = 17.78(1), c = 21.90(1) Å, Z = 4, and space group $Pb2_1a$ (no. 29). In the dimeric cation each Cu^I atom is bonded to the pyridine nitrogen and one imino nitrogen of one ligand molecule and to one imino nitrogen and one alkene group of the second ligand molecule in a distorted tetrahedral geometry. The second alkene group of each ligand remains unco-ordinated. In order to accommodate to this unusual co-ordination mode one imino group is severely twisted (by 83, 86° in the two ligand molecules) out of the plane of the pyridine ring, leading to two distinct ν(C=N) vibrations in the i.r. spectrum. On the basis of i.r. and other properties, it is proposed that the complexes of L^2—L^5, as well as $[Cu_2L^1_2][BPh_4]_2$ in MeCN solution, have mononuclear structures in which the trimethine pyridyldi-imine group retains its customary planarity and acts as a tridentate ligand. For $[CuL^3][ClO_4]$ and $[CuL^4][ClO_4]$ having no side-arm donor groups, and for $[CuL^2][ClO_4]\cdot H_2O$ having propene side chains, a T-shaped three-co-ordinated structure is suggested. For $[CuL^5][ClO_4]$, as well as for $[Cu_2L^1_2][BPh_4]_2$ and $[CuL^2][ClO_4]\cdot H_2O$ in solution, spectroscopic evidence indicates at least partial side-arm donor group co-ordination leading to four-co-ordinate species. All the complexes bind CO reversibly in MeCN solution to an extent dependent on the competition exercised by the pendant side-arm donor groups, where present. The complexes also bind O_2 in solution in a 0.25:1 O_2:Cu stoicheiometry at rates which parallel the CO affinities. The O_2 binding is partially reversible in some cases as evidenced by electronic spectral and O_2-uptake measurements on successive oxygenation/deoxygenation treatments. Among the ultimate products of the accompanying irreversible oxidation are the bis(ligand) Cu^{II} complexes $[CuL_2]^{2+}$.

We have previously described the preparation, properties, and reactions of some palladium(II)[1] and rhodium(I)[2] complexes of the Schiff-base ligands L^1 and L^2 derived from the condensation of one molecule of 2,6-diacetylpyridine with two molecules of, respectively, 4-aminobut-1-ene and allylamine. Both ligands contain a trimethine (pyridyldi-imine) group together with terminal alkene functions in the side arms. Since the planar conjugated trimethine group is well suited to co-ordinate at three corners of an approximate square plane our initial interest was to see whether a terminal olefinic group would occupy the fourth co-ordination site with possible concomitant activation to reaction by nucleophiles. For the case of the Pd^{II} complexes it was shown that the (pendant) olefinic groups interact intermolecularly with other Pd^{II} ions present in solution with accompanying activation to nucleophilic attack by H_2O leading to complexes of the corresponding ketones.[1] With Rh^I, on the other hand, no alkene co-ordination was observed, the reaction products being binuclear complexes of the pyridyldiaza ligands formed by solvent ethanol-to-ligand hydrogen transfer.[2]

In this paper we describe the products of reaction of Cu^I with L^1, L^2, and the related ligands L^3, L^4, and L^5, all containing the pyridyldi-imine moiety but differing in the nature of the side arms. Unlike Pd^{II} and Rh^I the d^{10} ion Cu^I is not well adapted to the formation of square-planar complexes[3] so it was of interest to determine the response of the planar trimethine co-ordinating group to this metal ion. In an earlier study[4] of the Cu^I complex of the related ligand L^6 it was shown that the trimethine group adopts a non-planar conformation so as to use two nitrogen atoms in bonding to one Cu^I atom in a dinuclear structure, the third nitrogen donor being co-ordinated to the second metal atom. It was also of interest, in the present study, to determine the role, if any, of the side-arm donor groups in L^1, L^2, and L^5.

Results and Discussion

The preparations of the ligands and complexes are described in the Experimental section. The ligands were characterised by elemental analysis, mass and i.r. spectra (Table 1), and ^1H and ^{13}C n.m.r. spectra (Tables 2 and 3). Characteristic features of all the i.r. spectra are a medium-to-strong intensity absorption band between 1 620 and 1 650 cm^{-1} attributable to the ν(C=N) vibration together with bands between 1 400 and 1 600 cm^{-1} due to pyridine ring vibrations. No distinct absorption due to ν(C=C) was apparent in the spectra of L^1 or L^2, this vibration

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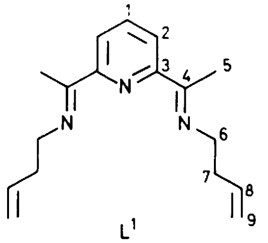
† *Supplementary data available* (No. SUP 56413, 16 pp.): thermal parameters, H-atom co-ordinates, dimensions in ligands and anions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

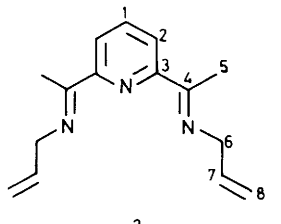
Non-S.I. units employed: atm = 101 325 Pa, Torr = (101 325/760) Pa, B.M. = 0.927 × 10^{-23} A m^2.

Table 1. Analytical, i.r., mass spectral and electrical conductance data for the ligands and complexes

		Analysis (%)							I.r. bands (cm^{-1})			
		Found			Calc.							
Compound	Colour	C	H	N	C	H	N	P^+	ν(C=N)	ν(C=C)	$\mu_{eff.}$/B.M.	Λ/S cm^2 mol^{-1}
L^1	Yellow	75.4	8.6	15.2	75.7	8.6	15.6	269	1 636	1 636		
L^2·H$_2$O	Yellow	69.9	7.9	15.6	69.5	8.2	16.2	241	1 638	1 638		
L^3	Yellow	74.3	9.8	14.7	74.7	10.0	15.4	273	1 636			
L^4	Yellow	73.0	9.0	16.3	73.4	9.4	17.1	245	1 640			
L^5	Yellow	59.4	7.9	11.1	60.4	8.1	12.4	337	1 636			
[CuL^1][ClO$_4$]	Yellow-brown	45.4	5.1	8.3	45.3	5.6	9.3		1 638	1 638, 1 585		156
[Cu$_2$L$^1{}_2$][BPh$_4$]$_2$	Yellow	75.5	6.7	6.4	75.5	6.7	6.4		1 656, 1 626	1 638, 1 565		296
[CuL^2][ClO$_4$]·H$_2$O	Dark brown	42.7	4.6	9.9	42.7	5.0	10.0		1 645	1 610		161
[CuL^3][ClO$_4$]	Dark brown	46.0	6.0	9.4	46.8	6.2	9.6		1 615			161
[CuL^4][ClO$_4$]	Dark brown	44.2	4.6	10.2	44.1	4.7	10.3		1 610			142
[CuL^5][ClO$_4$]	Yellow	39.1	5.3	7.6	39.4	5.6	8.1		1 620			125
[CuL$^1{}_2$][ClO$_4$]$_2$·2H$_2$O	Green	48.7	5.4	9.5	48.8	6.0	10.0		1 625	1 638		262
[CuL$^1{}_2$][BPh$_4$]$_2$	Green	78.1	7.0	6.6	78.3	6.9	6.7		1 625	1 625	1.92	224
[CuL$^2{}_2$][ClO$_4$]$_2$·EtOH	Green	45.8	5.3	10.4	46.1	4.9	10.8		1 640	1 640	1.94	249
[CuL$^3{}_2$][ClO$_4$]$_2$	Green	50.1	6.9	10.2	50.5	6.7	10.4		1 620		1.97	253
[CuL$^4{}_2$][ClO$_4$]$_2$	Green	47.7	6.2	11.0	47.8	6.2	11.2		1 630		1.96	271



L^1



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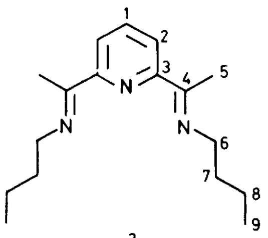

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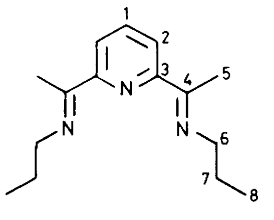

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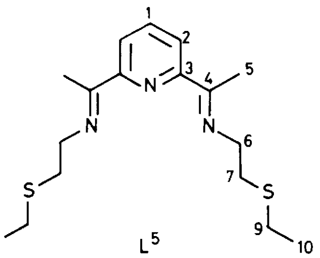
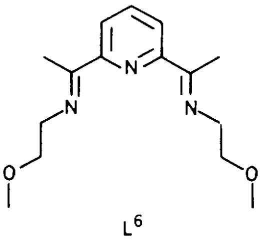


L^5



L^6

apparently occurring at the same energy as ν(C=N). Significantly, the 1 635—1 640 cm^{-1} band in the spectra of these two compounds is notably more intense than in the case of the other ligands.

The i.r. spectra of the Cu^I complexes, all of which have a CuL(X) (X = ClO$_4{}^-$ or BPh$_4{}^-$) stoicheiometry, are similar in important respects to those of the free ligands. All showed absorption between 1 610 and 1 660 cm^{-1} attributable to ν(C=N). However, the complex CuL^1(BPh$_4$) was unique in displaying three bands in this region (Table 1). Surprisingly, the spectrum of the ClO$_4{}^-$ salt displayed only one band between 1 600 and 1 650 cm^{-1} indicating some structural differences in the two compounds (see later). Both salts of the CuL^1 complex also showed a band of moderate intensity at 1 560—1 590 cm^{-1} which we assign to co-ordinated ν(C=C). No such band was apparent in the spectrum of CuL^2(ClO$_4$)·H$_2$O or of any of the other complexes. Initial conclusions to be drawn from the i.r. spectra of the L^1 and L^2 complexes are that at least one of the side-arm olefinic groups of L^1 is co-ordinated to the metal ion but not in the case of L^2, and that there are structural differences between the two L^1 complexes depending on the nature of the counter ion. It seemed possible that this difference in structure, might be due to anion co-ordination in the case of X = ClO$_4{}^-$ but not in the case of X = BPh$_4{}^-$. However, no clear conclusions on this question were apparent from an inspection of the profiles of the ν_3 and ν_4 vibrations of the ClO$_4{}^-$ group;[4] no splitting was observed though some slight broadening of the bands was apparent. No splitting or broadening of ν_3 or ν_4 was observed in the spectra of any of the other complexes containing ClO$_4{}^-$ anions.

Initial indications of structural variations among the complexes gained from the solid-state i.r. spectra were reinforced by differences in colour. Thus, the L^1 complexes, for which i.r. spectra suggest olefinic side-arm co-ordination, are yellow or yellow-brown. The L^5 complex, containing thioether groups in the side arms, is also yellow. All the complexes of the remaining ligands, including L^2 (containing propene side chains), are dark brown. A more detailed discussion of the electronic spectra (Table 4) is deferred until after a description of the structure of the complex CuL^1(BPh$_4$), hereafter formulated as the dimeric complex [Cu$_2$L$^1{}_2$][BPh$_4$]$_2$, as determined by the single-crystal *X*-ray analysis.

Crystal Structure of [Cu$_2$L$^1{}_2$][BPh$_4$]$_2$.—The structure comprises discrete dimeric [Cu$_2$L$^1{}_2$]$^{2+}$ cations (illustrated in Figure 1 together with the atomic numbering scheme) and [BPh$_4$]$^-$ anions. The structure of the dimeric cation is also

Table 2. Proton n.m.r. spectral data for the ligands and Cu^I complexes in CD_3CN at 20 °C*

Compound	δ/p.p.m. H^1	H^2	H^5	H^6	H^7	H^8	H^9	H^{10}
L^1	7.60 (t)	8.02 (d)	2.32 (s)	3.50 (t)	2.46 (q)	5.96 (m)	5.09 (m)	
L^2	7.55 (m)	8.10 (d)	2.30 (s)	4.11 (t)	5.99 (m)	5.18 (m)		
L^3	7.60 (m)	7.81 (m)	2.54 (s)	3.47 (t)	2.54 (m)	1.40 (m)	0.90 (t)	
L^4	7.12 (m)	7.63 (d)	1.83 (s)	2.92 (t)	1.30 (m)	0.52 (t)		
L^5	7.72 (m)	7.94 (m)	2.24 (s)	3.58 (t)	2.77 (m)		2.50 (m)	1.58 (t)
$[CuL^1][ClO_4]$	7.80 (m)	8.10 (m)	2.29 (s)	3.69 (t)	2.38 (m)	5.63 (m)	4.75 (m)	
$[Cu_2L^1{}_2][BPh_4]_2$	7.70 (m)	8.05 (m)	2.21 (s)	3.60 (t)	2.34 (m)	5.62 (m)	4.70 (m)	
$[CuL^2][ClO_4]\cdot H_2O$	7.90 (m)	8.21 (m)	2.40 (s)	4.05 (m)	5.81 (m)	5.10 (m)		
$[CuL^3][ClO_4]$	7.82 (m)	8.23 (d)	2.54 (s)	3.47 (t)	2.54 (m)	1.39 (m)	0.89 (t)	
$[CuL^4][ClO_4]$	8.18 (m)	8.18 (m)	2.45 (s)	3.24 (m)	1.1 (m)	0.49 (t)		
$[CuL^5][ClO_4]$	7.66 (m)	7.66 (m)	2.35 (s)	3.25 (m)	2.15 (m)		1.63 (m)	0.85 (t)

* s = Singlet, d = doublet, t = triplet, m = multiplet.

Table 3. Carbon-13 n.m.r. spectral data for the ligands L^1 and L^4 and their respective Cu^I complexes in CD_3CN at 20 °C

Complex	δ/p.p.m. C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
L^1	120.0	137.3	156.6	166.4	13.5	52.4	35.7	137.0	115.7
$[CuL^1][ClO_4]$	124.7	139.6	153.8	169.9	17.3	53.7	34.0	125.0	106.1
L^4	120.9	136.3	156.4	166.1	13.5	54.3	24.2	12.2	
$[CuL^4][ClO_4]$	126.9	140.6	154.5	170.5	16.6	55.8	23.9	10.7	

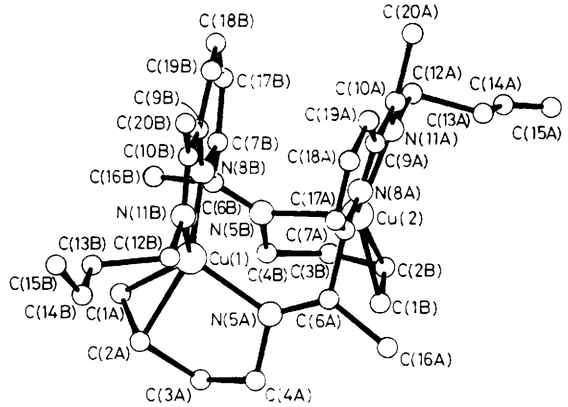


Figure 1. Structure of the dinuclear cation in $[Cu_2L^1{}_2][BPh_4]_2$ with the atomic numbering scheme

depicted schematically in Figure 2 in order to illustrate more clearly how each ligand molecule is co-ordinated to the Cu^I ions.

The co-ordination geometries of the two copper atoms are similar. Bond distances and angles are given in Table 5, torsion angles in Table 6, and least-squares planes in Table 7. Each copper atom is bonded to two nitrogen atoms (the pyridine nitrogen and one imino nitrogen) of one ligand molecule and to one imino nitrogen atom and to two olefinic carbon atoms of the second ligand molecule. Thus, Cu^I is bonded to C(1A) [2.06(3) Å], C(2A) [2.13(4) Å], and N(5A) [2.20(2)Å] of ligand A, and to N(8B) [1.93(3) Å] and N(11B) [1.98(3) Å] of ligand B. For Cu(2) bond lengths to C(1B), C(2B), N(5B), N(8A), and N(11A) are 2.31(6), 2.07(5), 2.11(3), 1.94(3), and 1.97(4) Å, respectively. Considering that the metal atoms each form one co-ordinate bond with the mid-point of the olefinic C(1)—C(2) bonds, defined as C(0), the geometry around each Cu^I atom is a very distorted tetrahedron, the six angles around the metal ranging from 78 to 141° [Cu(1)] and 77 to 131° [Cu(2)]. Despite the distortion the two planes Cu, C(0), N(5) and Cu, N(8), N(11) are nearly perpendicular in the two co-ordination spheres; for Cu(1) the angle is 82° while for Cu(2) it is 83°. There are some differences in the conformations of the bonded and non-bonded hydrocarbon side chains. Particularly notable are the differences in the C(1)–C(2)–C(3)–C(4) torsion angles (Table 6) at 38 and 132° in ligands A and B, respectively. This is rather surprising given that in both ligand molecules C(1) and C(2) are co-ordinated to a Cu atom. As might be expected the geometries of the unattached side chains are also different in the two ligands. The dimensions of the hydrocarbon side chains were not determined sufficiently accurately to permit meaningful discussion of changes in, *e.g.* C(1)–C(2), bond length on co-ordination.

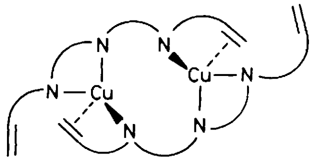


Figure 2. Diagrammatic representation of the structure of the dinuclear cation $[Cu_2L^1{}_2]^{2+}$ showing the co-ordinated and unco-ordinated alkene groups

The structure of the $[Cu_2L^1{}_2]^{2+}$ cation is similar in some respects to that found[4] for the dimeric cation in $[Cu_2L^6{}_2][ClO_4]_2$, where L^6 is the related acyclic Schiff-base ligand containing ether groups in the side arms. In both complexes each Cu^I atom is bonded to only two nitrogen atoms of the trimethine moiety of each ligand molecule (the pyridine nitrogen and one imino nitrogen) and to one imino nitrogen of the second ligand molecule. In order to accommodate to this

Table 4. Electronic spectra of the complexes*

	$10^{-3}\ \tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})	
Complex	Solid state	MeCN solution
$[CuL^1][ClO_4]$	28.2, 20.6	29.6 (sh), 28.2 (1 500)
$[Cu_2L^1{}_2][BPh_4]_2$	27.0	29.8 (sh), 28.1 (1 350)
$[CuL^2][ClO_4]\cdot H_2O$	30.1, 22.3, 17.6	29.3 (1 250), 23.0 (sh), 20.0 (sh)
$[CuL^3][ClO_4]$	28.4, 22.0, 17.6	
$[CuL^4][ClO_4]$	28.4, 22.4, 18.2	28.2 (970), 20.4 (sh)
$[CuL^5][ClO_4]$	28.2	28.2 (1 020), 21.4 (sh)
$[CuL^1{}_2][ClO_4]_2\cdot 2H_2O$	27.0, 13.6	28.6 (1 520)
$[CuL^1{}_2][BPh_4]_2$	30.0, 14.4	27.4 (sh), 14.2 (110)
$[CuL^2{}_2][ClO_4]_2\cdot EtOH$	28.0, 13.2	30.0 (1 050), 14.4 (130)
$[CuL^3{}_2][ClO_4]_2$	29.0, 27.2, 14.0	28.3 (sh), 14.4 (96)
$[CuL^4{}_2][ClO_4]_2$	28.0, 13.6	28.7 (460), 26.8 (sh), 13.6 (70)
		27.6 (sh), 14.3 (95)

* sh = Shoulder.

Table 5. Molecular dimensions in the metal co-ordination spheres of $[Cu_2L^1{}_2][BPh_4]_2$; distances (Å) and angles (°)

Cu(1)–C(1A)	2.06(3)	Cu(2)–N(8A)	1.94(3)
Cu(1)–C(2A)	2.13(4)	Cu(2)–N(11A)	1.97(4)
Cu(1)–N(5A)	2.20(2)	Cu(2)–C(1B)	2.31(6)
Cu(1)–N(8B)	1.93(3)	Cu(2)–C(2B)	2.07(5)
Cu(1)–N(11B)	1.98(3)	Cu(2)–N(5B)	2.11(3)
Cu(1)–C(0A)	1.99(4)	Cu(2)–C(0B)	2.06(5)
C(1A)–Cu(1)–C(2A)	35.9(14)	N(8A)–Cu(2)–N(11A)	77.0(13)
C(1A)–Cu(1)–N(5A)	92.7(12)	N(8A)–Cu(2)–C(1B)	106.7(17)
C(2A)–Cu(1)–N(5A)	84.9(11)	N(11A)–Cu(2)–C(1B)	133.9(20)
C(1A)–Cu(1)–N(8B)	124.0(13)	N(8A)–Cu(2)–C(2B)	145.8(15)
C(2A)–Cu(1)–N(8B)	155.1(13)	N(11A)–Cu(2)–C(2B)	123.1(17)
N(5A)–Cu(1)–N(8B)	115.5(10)	C(1B)–Cu(2)–C(2B)	39.1(21)
C(1A)–Cu(1)–N(11B)	141.3(13)	N(8A)–Cu(2)–N(5B)	115.6(11)
C(2A)–Cu(1)–N(11B)	111.5(13)	N(11A)–Cu(2)–N(5B)	104.9(13)
N(5A)–Cu(1)–N(11B)	106.7(9)	C(1B)–Cu(2)–N(5B)	113.5(18)
N(8B)–Cu(1)–N(11B)	77.6(11)	C(2B)–Cu(2)–N(5B)	87.6(16)
C(0A)–Cu(1)–N(11B)	126.8(14)	C(0B)–Cu(2)–N(5B)	101.6(16)
C(0A)–Cu(1)–N(5A)	88.7(12)	C(0B)–Cu(2)–N(8A)	125.2(15)
C(0A)–Cu(1)–N(8B)	140.7(14)	C(0B)–Cu(2)–N(11A)	131.4(18)

Table 6. Torsion angles (°) in $[Cu_2L^1{}_2][BPh_4]_2$

	Ligand A	Ligand B
N(5)–C(6)–C(7)–N(8)	−83	−86
N(8)–C(9)–C(10)–N(11)	−5	4
C(6)–N(5)–C(4)–C(3)	142	−154
C(4)–C(3)–C(2)–C(1)	38	132
C(10)–N(11)–C(12)–C(13)	92	92
N(11)–C(12)–C(13)–C(14)	−172	160
C(12)–C(13)–C(14)–C(15)	109	171

Table 7. Least-squares planes in $[Cu_2L^1{}_2][BPh_4]_2$. Deviations from planes are given in Å. Atoms not contributing to the planes are marked by an asterisk

Plane 1

N(5A)* −0.98, C(6A)* 0.07, C(7A) −0.03, C(17A) −0.02, C(18A) 0.06, N(8A) −0.01, C(9A) 0.06, C(10A)* 0.00, N(11A)* 0.01, C(19A) −0.07, C(12A) −0.02, C(20A)* −0.08, C(4A)* −0.97, Cu(2) 0.02

Plane 2

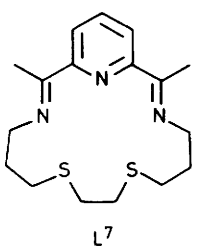
N(5B)* −0.95, C(6B)* 0.15, C(7B) −0.03, C(17B) −0.02, C(18B) −0.08, N(8B) 0.03, C(9B) 0.00, C(10A)* 0.00, N(11A)* −0.03, C(19A) −0.04, C(12B) 0.07, C(20B)* −0.07, C(4B)* −0.91, Cu(1) 0.13

unusual co-ordination mode there is a distortion of the trimethine group from planarity. In $[Cu_2L^6{}_2]^{2+}$ both imino groups of both ligand molecules are twisted out of the plane with their respective pyridine rings. In $[Cu_2L^1{}_2]^{2+}$ one imino nitrogen atom, N(11), remains co-planar with the pyridine ring but the other, N(5), lies out of the plane by −0.98 Å for N(5A) and −0.95 Å for N(5B). The N(5)–C(6)–C(7)–N(8) torsion angles are thus −83 for ligand A and −86° for ligand B. In analogous fashion to the situation in the present structure, in $[Cu_2L^6{}_2]^{2+}$ one side-arm donor (the ether oxygen) of each ligand molecule is co-ordinated while the other is not. However, in this case both ether oxygen atoms are co-ordinated to the same Cu^{I} atom while in $[Cu_2L^1{}_2]^{2+}$ the two co-ordinated alkene groups are bound to different Cu^{I} atoms. A further major distinction between the two dimeric structures is the occurrence of a Cu–Cu bond [2.627(1) Å] in $[Cu_2L^6{}_2]^{2+}$ but not in $[Cu_2L^1{}_2]^{2+}$ in which the Cu ··· Cu separation is 4.25 Å.

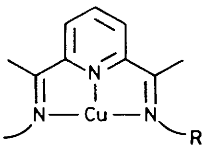
With the knowledge of the structure of the $[Cu_2L^1{}_2]^{2+}$ cation it is now possible to assign the three bands occurring between 1 600 and 1 660 cm^{-1} in the i.r. spectrum. The band at 1 638 cm^{-1} is assigned to unco-ordinated ν(C=C) since its position is virtually the same as that in the free ligand. The two remaining bands at 1 656 and 1 626 cm^{-1} are attributed to the two inequivalent C=N groups, the higher frequency absorption being associated with C(6)=N(5) since this group is no longer in conjugation with the pyridine ring.

A probable reason for the trimethine group distortion in $[Cu_2L^1{}_2]^{2+}$, as in $[Cu_2L^6{}_2]^{2+}$, is a disinclination of the filled *d* shell Cu^{I} ion to accommodate to the planar tridentate pyridyldi-imine group. It is well known that Cu^{I}, at least in its four-co-ordinate complexes, prefers a tetrahedral disposition of donor atoms.[3] However, as pointed out previously,[4] there is no evidence that trimethine group distortion in Cu^{I} complexes is a general phenomenon. It does not occur in the five-co-ordinate Cu^{I} complex $[CuL^7]^+$ in which L^7 is a macrocyclic ligand having an 'N_3S_2' donor set.[5] Here, trimethine group co-ordination, with retention of planarity, is virtually forced upon the Cu^{I} ion because of the cyclic array of donor atoms within a relatively small ring. The response of the Cu^{I} ion to the planar trimethine group is, in this case, to lengthen (to 2.519 Å) one of the Cu–N(imino) bonds. Moreover, as we discuss below, no evidence for trimethine group distortion, or for dimerization, has been found for the Cu^{I} complexes of the other ligands (L^2—L^5) which are also the subject of this paper.

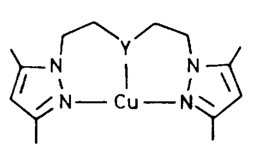
Structure of $[CuL^1][ClO_4]$ *and the* L^2—L^5 *Complexes.*— Since only $[Cu_2L^1{}_2][BPh_4]_2$ displayed more than one i.r. absorption band in the 1 600—1 660 cm^{-1} region it may reasonably be argued that in none of the remaining complexes is there any serious trimethine group distortion, *i.e.* that the trimethine group retains its planarity on complexation and that it is therefore functioning as a tridentate chelating group to a single Cu^{I} ion. In all these cases the i.r. spectra are closely similar to those of other metal complexes where trimethine group planarity has been proven by *X*-ray analysis.[6] These considerations lead us to propose that in the L^3 and L^4 complexes, in which there are no donor functions in the side arms, the metal ions are mononuclear and three-co-ordinate [structure (I); R = Bu^n or Pr^n]. Three-co-ordination is well established for Cu^{I}, but usually in situations where the co-ordination geometry is trigonal planar, or approximately so.[7] In the present case the disposition of donor atoms in L^3 and L^4 is such that the metal



L^7



(I)

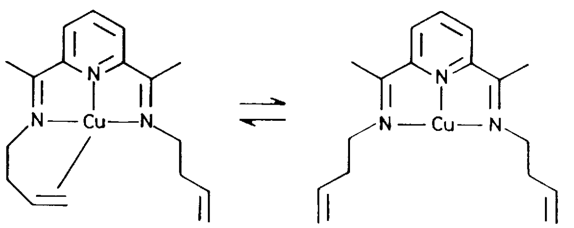


(II)

ion would have a T-shaped geometry. While such a geometry is unusual it has, in fact, recently been observed[8] in a few Cu^I complexes, structure (**II**), of the ligand bis[2-(3′,5′-dimethylpyrazol-1′-yl)ethyl] ether (pze; Y = O) and the corresponding sulphide (Y = S) and amine (Y = NH) derivatives. In [Cu(pze)][BF_4] the short Cu-N bonds [1.877(5), 1.874(5) Å] are comparable to the distances found in two-co-cordinate Cu^I complexes.[9] There is also a weaker interaction to the ether oxygen atom [Cu-O 2.197(4) Å] to give an overall T-shaped structure [N(1)-Cu-N(2) 169, N(1)-Cu-O 94, N(2)-Cu-O 96°] with the Cu^I atom sitting slightly (0.067 Å) out of the N_2O plane. The structure could thus be thought of as essentially two-co-ordinate with a (relatively) weak perturbation by the oxygen atom. Similar considerations may apply to the L^3 and L^4 complexes described here.

The complex $[CuL^2][ClO_4]{\cdot}H_2O$ probably has a similar structure. No evidence for co-ordination of the olefinic groups in the propene side arms in the solid state is apparent in the i.r. spectra though weak co-ordination may occur in solution (see later). In contrast to the remaining complexes the colours of the L^2, L^3, and L^4 complexes are dark brown as a result of multi-component absorption in the solid-state electronic spectra between 30 000 and 17 000 cm^{-1} (Table 4). The other complexes are either yellow ($[Cu_2L^1{}_2][BPh_4]_2$ and $[CuL^5][ClO_4]$) or yellow-brown ($[CuL^1][ClO_4]$), the solid-state electronic spectra in the same region showing no resolved features below 20 000 cm^{-1}. We interpret the differences in the spectra as arising from differences in the energies of the Cu^I-to-trimethine group $p_{\pi}{}^{*}$ charge-transfer transitions, these occurring at lower energy in cases where there is no side-arm donor co-ordination. It is proposed, therefore, that $[CuL^5][ClO_4]$ has a four-co-ordinate structure in the solid state in which one side-arm donor group is co-ordinated. As will be seen these conclusions are consistent with n.m.r. data for solutions and measurements relating to relative affinities for carbon monoxide. It is not possible, without full *X*-ray structural analysis, to exclude a five-co-ordinate structure in which both side-arm donor groups are co-ordinated but this seems unlikely in view of the fact that the co-ordination number requirement of Cu^I is usually satisfied by four donor atoms or groups.

It remains to consider the solid-state structure of $[CuL^1][ClO_4]$. As already noted, this complex, unlike the $[BPh_4]^-$ salt, shows a single band in the i.r. spectrum at 1 638 cm^{-1} which we attribute to overlapping ν(C=N) and unco-ordinated ν(C=C) vibrations. A band at 1 585 cm^{-1} not present in the free ligand may be assigned to co-ordinated ν(C=C). The solid-state electronic spectrum (Table 4) is intermediate in character between that of the dimeric $[BPh_4]^-$ salt (no band below 27 000 cm^{-1}) and those of the complexes of L^2, L^3, and L^4 (showing two lower energy bands between 17 000 and 23 000 cm^{-1}) in having one lower energy band at 20 600 cm^{-1}. The structure of this complex in the solid state therefore remains unknown. It is clearly different from that of the $[BPh_4]^-$ salt in displaying no evidence of trimethine group distortion. Most likely it is mononuclear with weak intramolecular olefinic group co-ordination.



(III) (IV)

Nature of the Complexes in Solution.—Properties of the complexes in acetonitrile solution were investigated by means of electrical conductance measurements and electronic and ^1H and ^{13}C n.m.r. spectra. All the Cu^I complexes have conductances (calculated on a monomeric formula) in the range expected for uni-univalent electrolytes in this solvent (Table 1).

Solution electronic spectra in the range 30 000—10 000 cm^{-1} fall into two groups, those exhibiting only one intense band between 30 000 and 28 000 cm^{-1} and those exhibiting in addition, a second band appearing as a pronounced shoulder, at 20 000—23 000 cm^{-1} (Table 4). In the former group are the L^1 and L^5 complexes containing side-arm donors (alkene and thioether, respectively) believed to be involved in co-ordination in the solid state. In the second group are the L^2, L^3, and L^4 complexes which in the solid state are believed to have three-co-ordinate structures. The spectra of the $[BPh_4]^-$ and $[ClO_4]^-$ salts of the L^1 complexes, while clearly different in the solid state, are very similar in solution. It is therefore likely that the dimer $[Cu_2L^1{}_2]^{2+}$ has dissociated in the polar solvent (acetonitrile) to give a mononuclear species involving co-ordination of all three nitrogen atoms of the trimethine group together with one side-arm alkene group [structure (**III**)].

These conclusions are reinforced by consideration of the ^1H n.m.r. spectra of the free ligands and their complexes in CD_3CN solution. Figure 3 compares the spectra (δ 3—6 region) of L^1 and $[Cu_2L^1{}_2][BPh_4]_2$ (see also Table 2). It can be seen that the chemical shifts of the olefinic protons are shifted upfield by 0.34—0.36 p.p.m. in the complex relative to the free ligand. There are also marked changes in profile; the resonances of other protons are less affected. The fact that no separate signals for co-ordinated and unco-ordinated olefinic groups were seen could mean either that both alkene groups are co-ordinated or, much more likely, that there is a rapid exchange between bound and free alkene groups. The occurrence of an equilibrium (**III**)$\rightleftharpoons$(**IV**) in solutions of $[Cu_2L^1{}_2][BPh_4]_2$ is supported by the observation of a significant temperature dependence of the co-ordination chemical shifts (Δδ) for the olefinic protons H^8 and H^9, these ranging from −0.38 and −0.39 p.p.m., respectively, at 233 K to −0.28 and −0.29 p.p.m. at 333 K. Other resonances showed little or no temperature dependence in chemical shift.

As observed for the ^1H n.m.r. spectra of $[Cu_2L^1{}_2][BPh_4]_2$ and $[CuL^1][ClO_4]$ the ^{13}C n.m.r. spectrum (Table 3) of the latter complex in CD_3CN also indicates olefinic side-arm co-ordination, the olefinic protons C^8 and C^9 displaying upfield shifts of 12.0 and 9.6 p.p.m., respectively.

The proton spectrum of $[CuL^2][ClO_4]{\cdot}H_2O$ in CD_3CN

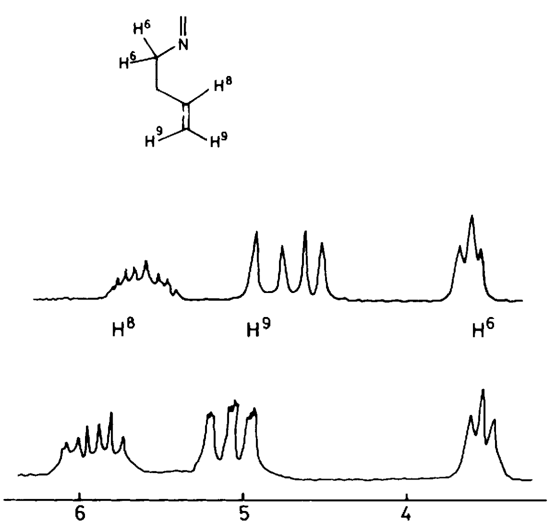


Figure 3. ^1H N.m.r. spectra (δ 3—6 region) of the free ligand L^1 (lower spectrum) and of the complex $[Cu_2L^1_2][BPh_4]_2$ (upper spectrum) in CD_3CN at 20 °C

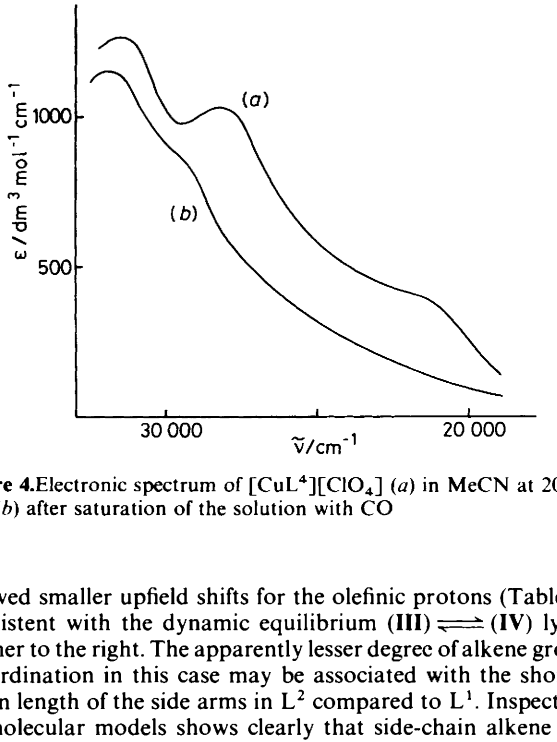


Figure 4. Electronic spectrum of $[CuL^4][ClO_4]$ (*a*) in MeCN at 20 °C and (*b*) after saturation of the solution with CO

showed smaller upfield shifts for the olefinic protons (Table 2) consistent with the dynamic equilibrium (**III**) $\rightleftharpoons$ (**IV**) lying further to the right. The apparently lesser degree of alkene group co-ordination in this case may be associated with the shorter chain length of the side arms in L^2 compared to L^1. Inspection of molecular models shows clearly that side-chain alkene co-ordination is more easily achieved in the case of L^1.

Similarly, the large upfield co-ordination shifts (Table 2) of the H^5 and H^7 protons of L^5 (in $[CuL^5][ClO_4]$) flanking the sulphur atoms indicate co-ordination of at least one of the thioether groups, the equilibrium (**III**) $\rightleftharpoons$ (**IV**) lying largely in favour of (**III**).

Reactions of the Cu^I *Complexes with Carbon Monoxide.*— In recent years a considerable number of Cu^I complexes have been shown to bind CO, often reversibly, providing, in certain cases, isolable complexes.[10] Usually, these CO adducts have distorted tetrahedral structures although a few five-co-ordinate CO adducts are also known.[11] It was observed that the Cu^I complexes in the present study underwent red or brown to yellow or yellow-brown colour changes in MeCN on passage of CO. Figure 4 shows the spectral change for the case of $[CuL^4][ClO_4]$. In all cases the spectral changes are reversible, the original spectrum being regenerated on passing argon through the solutions or on degassing under vacuum. Measurements of i.r. spectra of the carbonylated solutions established that the CO is terminally bonded[10] to the metal atom, ν(CO) being observed in all cases in the narrow range 2 080—2 100 cm⁻¹ (Table 8). The quantity of CO bound per Cu atom was measured at 0 °C by the method described in the Experimental section. The molar ratio CO:Cu never exceeded 0.6:1, being largest for $[CuL^4][ClO_4]$ and smallest for $[CuL^5][ClO_4]$, indicating that the carbonylation is incomplete even at 0 °C. On the assumption that the stoicheiometry of the reaction is that represented in equation (1), approximate equilibrium constants (K_{eq}) [equation (2)] were calculated (Experimental section) and are given in Table 8.

$$[CuL]^+ + CO \rightleftharpoons [CuL(CO)]^+ \qquad (1)$$

$$K_{eq} = \frac{[CuL(CO)^+]}{[CuL^+][CO]} \qquad (2)$$

Table 8. Association constants (K_{eq}) for CO adduct formation in MeCN at 0 °C and CO stretching frequencies at 20 °C

Complex	K_{eq}/dm³ mol⁻¹	ν(CO)/cm⁻¹
$[Cu_2L^1_2][BPh_4]_2$	1.6	2 083w
$[CuL^2][ClO_4]\cdot H_2O$	27.4	2 085s
$[CuL^3][ClO_4]$	24.1	2 085s
$[CuL^4][ClO_4]$	32.1	2 085s
$[CuL^5][ClO_4]$	*	2 095w

* Too low for measurement.

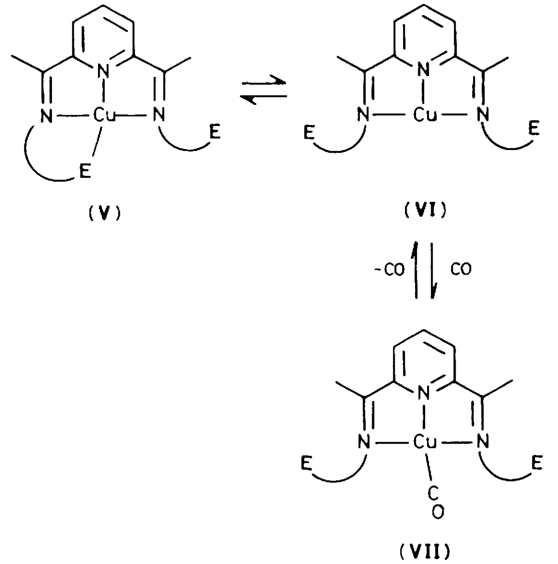
The variation in K_{eq} for the different complexes can be related to the degree of competition between CO and the side-arm donor groups, E, for the fourth co-ordination site on the Cu^I ion [equilibria (**V**) $\rightleftharpoons$ (**VI**) $\rightleftharpoons$ (**VII**)]. For $[CuL^3]^+$ and $[CuL^4]^+$ which contain alkyl side chains there is, of course, no competition. The complex $[CoL^4]^+$ binds CO somewhat more effectively than does $[CuL^3]^+$, the difference probably lying in a greater steric effect of the longer (butyl) side chain in L^3. $[CuL^2]^+$ having propene side chains binds CO almost as well as $[CuL^4]^+$ indicating only a minor degree of competition from the pendant alkene groups, a conclusion reached independently on the basis of ^1H n.m.r. spectra. For $[CuL^1]^+$ the competition is much greater, as previously concluded from both ^1H n.m.r. and electronic spectra in solution and consistent with the solid-state structure of $[Cu_2L^1_2][BPh_4]_2$ which reveals the attachment of one alkene group per Cu^I atom. The complex $[CuL^5]^+$ of the thioether ligand has the smallest affinity for CO, once again in agreement with conclusions reached independently from consideration of other solution properties already discussed and confirming that of all the side-arm donor groups the thioether group is co-ordinated mostly firmly.

Reactions of the Cu^I *Complexes with Dioxygen.*—All the complexes appear to have reasonable air stability over periods of days or weeks in the solid state. In solution, however, in the presence of air, they are oxidised to Cu^{II} species as judged by the development of green or green-brown colours at rates dependent on the nature of the complex and solvent. The rates of oxidation are greater in MeCN–MeOH mixed solvent than in MeCN itself. The susceptibility to oxidation of the different complexes qualitatively parallels the affinities for CO, the rates

Table 9. Observed stoicheiometries of the O_2 uptakes by three Cu^I complexes in MeCN at 30 °C

Complex	O_2:Cu mol ratio			
	O_2	Cu*		
$[Cu_2L^1{}_2][BPh_4]_2$	0.24	0.22	0.25	0.24
$[CuL^2][ClO_4]\cdot H_2O$	0.26	0.23	0.25	
$[CuL^4][ClO_4]$	0.24	0.23	0.23	

* The different entries refer to the ratios obtained in separate experiments.



following the ligand order $L^5 < L^1 < L^3 \sim L^2 < L^4$. The quantity of O_2 consumed was measured for three of the complexes in MeCN at 30 °C. The results (Table 9) indicate a stoicheiometry of 0.25 mol O_2 per mol Cu^I ion. End-points were sharp for $[CuL^2][ClO_4]\cdot H_2O$ and $[CuL^4][ClO_4]$, the reaction being complete in *ca.* 12 and 3 min, respectively. For $[Cu_2L^1{}_2][BPh_4]_2$, on the other hand, over 2 h was required to reach the 0.25:1 O_2:Cu molar ratio and there was some indication of a small further O_2 consumption at a very slow rate; this reaction, however, was complete (0.25:1 O_2:Cu molar ratio) in *ca.* 15 min when carried out in 1:1 MeCN–MeOH mixed solvent.

It was observed that for the case of the olefin-containing complexes $[Cu_2L^1{}_2][BPh_4]_2$ and $[CuL^2][ClO_4]\cdot H_2O$ in MeCN–MeOH the oxidations could apparently be partially reversed. Thus, after consumption of 0.25 mol O_2 at 30 °C passage of argon through the olive green solutions at 50 °C caused the colour to revert to dark brown. Readmission of O_2 regenerated the green colour with consumption of 0.15—0.20 mol O_2 per mol Cu, *i.e.* 60—80% of the original O_2 uptake. The spectral changes accompanying this cycle of operations are illustrated in Figure 5 for the case of $[Cu_2L^1{}_2][BPh_4]_2$. The loss of features in spectrum (*c*) in Figure 5, as well as the incomplete (*i.e.* 60—80%) reoxygenation, indicate the intervention of some irreversible oxidation process, possibly involving ligand and/or solvent. Further deoxygenations and oxygenations were noticeably sluggish and led finally to a brown solution which appeared unresponsive either to O_2 or to deoxygenation treatment. Attempts to isolate solution species in a pure solid form were unsuccessful, except following the first oxygenation. In these cases emerald green crystals $[CuL_2]X_2$ ($L = L^1$ or L^2, $X = ClO_4^-$ or BPh_4^-) separated on standing. The same complexes could be obtained by direct reaction of the free ligands with $Cu(ClO_4)_2\cdot 6H_2O$. As judged by physical properties (i.r. and electronic spectra and magnetic moments, Tables 1 and 4) these complexes have six-co-ordinate structures comprising two co-ordinated trimethine groups mutually at right angles, the pendant side-arm donors, where present, being unco-ordinated. This is the structure previously found,[12] and confirmed by *X*-ray structural analysis[13] for related complexes of Fe^{II} and Co^{II}.

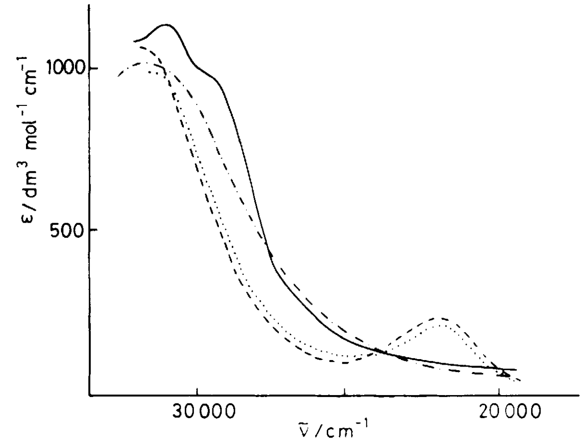
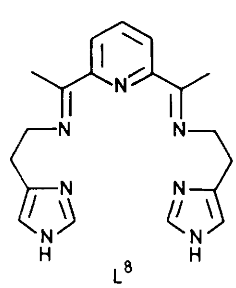


Figure 5. Electronic spectra of $[Cu_2L^1{}_2][BPh_4]_2$ (*a*) in 1:1 MeCN–MeOH (——); (*b*) after exposure to O_2 (– – –); (*c*) after heating solution (*b*) to 50 °C under vacuum (– • – • –); (*d*) after re-exposure of solution (*c*) to O_2 (• • • •)



L^8

The behaviour described above regarding the partially reversible oxygenation of $[Cu_2L^1{}_2][BPh_4]_2$ and $[CuL^2][ClO_4]$ is qualitatively similar to that reported for $[CuL^8]^+$ and related complexes by Wilson and co-workers,[14] where L^8 is the Schiff base formed by condensation of 2,6-diacetylpyridine with two equivalents of histamine. An important difference, however, is that MeCN or Me_2SO solutions of $[CuL^8]^+$ bind O_2 (with ~80% reversibility) in a O_2:Cu stoicheiometry of 0.50:1 compared to 0.25:1 in the present work. Wilson and co-workers[14] have suggested the formation of a μ-peroxo-dicopper(II) species, $[Cu_2L^8{}_2(O_2)]^{2+}$, in order to account for the 0.50:1 stoicheiometry [equation (3)]. For the systems described in the present work the observed 0.25:1 O_2:Cu ratio requires a further step [equation (4)] leading to a higher degree

$$2[CuL]^+ + O_2 \rightleftharpoons [Cu_2L_2(O_2)]^{2+} \quad (3)$$

$$[Cu_2L_2(O_2)]^{2+} + 2[CuL]^+ \rightleftharpoons [Cu_4L_4O_2]^{4+} \quad (4)$$

of aggregation. The observation of partial reversibility in O_2 binding implies some measure of reversibility in both reactions (3) and (4). Little can be said, on available information, regarding the nature of the tetranuclear aggregate $[Cu_4L_4O_2]^{4+}$. Possible formulations are a tetracopper(II) complex containing two bridging oxo groups. Such species have been described by Davies and El-Sayed,[15] though their formation might not be expected to be reversible. Alternately, species $[Cu_4L_4O_2]^{4+}$ could have a mixed valence (Cu^{I}_2, Cu^{II}_2) formulation containing co-ordinated peroxide, *i.e.* equation (4) does not involve O–O bond cleavage. Whatever the true nature of $[Cu_4L_4O_2]^{4+}$ it is clear that either $[Cu_2L_2(O_2)]^{2+}$ or $[Cu_4L_4O_2]^{4+}$ or both are unstable and decompose irreversibly to $[Cu^{II}L_2]^{2+}$ and other unidentified products. A possible reason for the apparent occurrence of reaction (4) in the present system but not in Wilson's system could be the absence of good donor (to Cu^{II}) groups in the pendant arms of L^1 and L^2 which would otherwise obviate the need for a higher degree of intermolecular association.

Conclusions

A series of Cu^{I} complexes of acyclic Schiff-base ligands all containing the pyridyldi-imine trimethine moiety together with, in some cases, potential donor groups in each of the two side arms originating in the imino nitrogens, has been prepared. I.r. spectra and other properties reveal that one of the complexes, $[Cu_2L^1{}_2][BPh_4]_2$, has a different solid-state structure from all the others. *X*-Ray analysis has shown this complex to contain dimeric cations in which each Cu^{I} ion is co-ordinated to two nitrogen atoms of the non-planar trimethine group of one ligand molecule and to the third nitrogen and one alkene group of the other ligand. While proof is lacking, the available evidence suggests that in all the other complexes, and in $[Cu_2L^1{}_2][BPh_4]_2$ in MeCN solution, the structures are monomeric in which the trimethine group acts, in the usual manner, as a tridentate ligand retaining its planarity. Where no potential donor atom is present in the side arms, or where these are propene groups as in L^2, it is proposed that the complexes contain three-co-ordinate Cu^{I} in an unusual but not unprecedented T-shaped structure. For the case of $[CuL^5][ClO_4]$ having thioether groups in the side arms there is clear evidence of co-ordination of at least one thioether group both in the solid state and in solution. The same is true of the solution species of $[Cu_2L^1{}_2][BPh_4]_2$ and $[CuL^2][ClO_4]{\cdot}H_2O$ where an equilibrium between co-ordinated and unco-ordinated alkene groups is thought to occur, this equilibrium lying mainly to the three-co-ordinate (dissociated) side in the case of L^2.

All the complexes in MeCN solution bind CO reversibly. The affinity for CO is low in all cases and corresponds to less than one CO per Cu atom even at 0 °C. The equilibrium constants for CO adduct formation depend on the degree of competition provided by the side-arm donor group where present, being largest for the three-co-ordinate complexes having no side-arm donor and smallest for the complex of the thioether ligand L^5.

The affinities for CO are paralleled by the susceptibilities of the complexes to aerobic oxidation as judged by the rates of O_2 uptake. The extent of O_2 uptake, measured for three of the complexes, was found to be 0.25 mol O_2 per mol Cu, a stoicheiometry corresponding formally to a four-electron reduction of O_2. Despite this, the binding of O_2 was found to be partially reversible in at least two of the systems examined as judged by the (partially) reversible regeneration of Cu^{I} species from oxidised solutions and the subsequent re-absorption of further O_2. A parallel irreversible oxidation leads to the formation of bis(ligand) Cu^{II} complexes as one of the final products.

Experimental

Preparation of the Ligands.—L^1—L^4 were prepared as described previously.[1] L^5 was prepared by a similar method starting from 2,6-diacetylpyridine and 2-(ethylthio)ethylamine. It was isolated as a yellow oil in >90% yield and characterised by elemental analysis, i.r., m.s. and ^1H n.m.r. spectra (Tables 1 and 2).

Preparation of the Complexes.—$[Cu_2L^1{}_2][BPh_4]_2$. A solution containing L^1 (0.54 g, mmol) and $Na[BPh_4]$ (1 g, 3 mmol) in dry EtOH (20 cm^3) and dry MeCN (110 cm^3) was heated to reflux under an atmosphere of N_2 and mixed with $[Cu(MeCN)_4][ClO_4]$ (0.66 g, 2 mmol) in 30 cm^3 of the same solvent mixture. The resulting deep red-brown solution was heated near to reflux for several minutes when the yellow product began to separate. After cooling the mixture to 0 °C the product was isolated in 72% yield. It was recrystallised from O_2-free MeCN.

$[CuL][ClO_4]$ ($L = L^1$—L^5). These complexes were all prepared by the same general method involving reaction of the ligand (2 mmol) with $[Cu(MeCN)_4][ClO_4]$ (2 mmol) in O_2-free EtOH or EtOH–MeCN mixtures (50—100 cm^3) at 70 °C. Products separated in 40—80% yield on cooling and/or concentration depending on solubility characteristics.

The Cu^{II} complexes $[CuL^2][ClO_4]_2$ (L^3—L^5), $[CuL^1{}_2][ClO_4]_2{\cdot}2H_2O$, and $[CuL^2{}_2][ClO_4]_2{\cdot}EtOH$ were prepared *via* reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.25 mmol) with the appropriate ligand (1.0 mmol) in ethanol (50 cm^3). The green crystalline products separated on standing. The complex $[CuL^5{}_2][ClO_4]_2$ is very hygroscopic and no reliable magnetic susceptibility measurements could be made. The complex $[CuL^1{}_2][BPh_4]_2$ was obtained by a similar method in which $Na[BPh_4]$ was added to the Cu^{II} solution before mixing with the L^1 solution.

Structure Determination of $[Cu_2L^1{}_2][BPh_4]_2$.—*Crystal data.* $C_{82}H_{86}B_2Cu_2N_6$, M = 1 304.3, orthorhombic, a = 17.74(1), b = 17.78(1), c = 21.90(1) Å, Z = 4, D_c = 1.24, D_m = 1.24 g cm^{-3}, $F(000)$ = 2 736, Mo-K_α radiation, λ = 0.710 7 Å, μ = 13.8 cm^{-1}, systematic absences $0kl$, $l = 2n + 1$, hkl, $k = 2n + 1$, space group $Pb2_1a$ (no. 29) determined by the successful structure determination. Equivalent positions x, y, z; $-x, \frac{1}{2} + y, -z$; $-x, y, \frac{1}{2} + z$; $x, \frac{1}{2} + y, \frac{1}{2} - z$.

A crystal (0.2 × 0.3 × 0.4 mm) prepared as described above was mounted on a Stoe STADI2 diffractometer and data were collected *via* variable ω scans. Background counts were 20 s and a scan rate of 0.33° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 3 419 Independent data were measured with a $2\theta_{max.}$ of 40° of which 1 519 with $I > 2.0\sigma$ were used in subsequent calculations. Standard reflections were measured throughout the data collection but no deterioration was observed. The data were of poor quality because the crystal diffracted weakly. An empirical absorption correction was applied.[16] The structure was determined with some difficulty from Patterson functions and Fourier methods were used to complete the structure determination. The structure was then refined by full-matrix least squares using SHELX76. The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. This was $w = 1/[\sigma^2(F) + 0.003\,F^2]$ with $\sigma(F)$ taken from counting statistics. Because of the poor quality of the data only the copper atoms were refined anisotropically; all other atoms were refined isotropically. The benzene rings in the anions were refined as rigid groups. Hydrogen atoms bonded to carbon were placed in tetrahedral or trigonal positions but the thermal parameters were not refined.

Four large blocks were used in the least-squares refinement consisting of the two ligands and two anions. In the final cycles of refinement no shift was greater than 0.03σ. The final difference Fourier map showed no significant features (maxi-

Table 10. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[Cu_2L^1{}_2][BPh_4]_2$*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	2 148(3)	2 500	230(2)	C(34)	599(13)	2 642(12)	5 554(9)
C(1A)	2 072(21)	2 806(21)	1 135(16)	C(35)	810(13)	2 506(12)	6 158(9)
C(2A)	2 300(20)	3 405(23)	855(16)	C(36)	531(13)	2 961(12)	6 625(9)
C(3A)	3 191(21)	3 572(24)	843(18)	C(41)	−1 017(10)	4 630(12)	6 827(10)
C(4A)	3 625(22)	2 862(22)	770(17)	C(42)	−936(10)	5 202(12)	6 396(10)
N(5A)	3 385(12)	2 394(14)	273(11)	C(43)	−1 567(10)	5 598(12)	6 194(10)
C(6A)	3 845(19)	2 031(21)	−51(15)	C(44)	−2 279(10)	5 423(12)	6 423(10)
C(7A)	3 552(15)	1 554(16)	−520(12)	C(45)	−2 360(10)	4 851(12)	6 854(10)
N(8A)	3 338(14)	881(15)	−321(11)	C(46)	−1 729(10)	4 454(12)	7 056(10)
C(9A)	3 157(23)	427(31)	−795(22)	C(51)	−508(11)	3 616(12)	7 636(8)
C(10A)	2 856(26)	−336(27)	−614(22)	C(52)	−458(11)	3 947(12)	8 212(8)
N(11A)	2 904(21)	−382(21)	−74(17)	C(53)	−662(11)	3 538(12)	8 730(8)
C(12A)	2 631(30)	−1 162(34)	232(24)	C(54)	−915(11)	2 799(12)	8 671(8)
C(13A)	3 442(39)	−1 735(40)	277(29)	C(55)	−966(11)	2 468(12)	8 095(8)
C(14A)	3 100(40)	−2 528(56)	484(33)	C(56)	−762(11)	2 878(12)	7 577(8)
C(15A)	3 081(45)	−3 039(51)	127(38)	C(61)	440(10)	4 705(13)	7 289(9)
C(16A)	4 762(23)	2 085(24)	−75(18)	C(62)	284(10)	5 446(13)	7 457(9)
C(17A)	3 564(16)	1 740(18)	−1 117(13)	C(63)	862(10)	5 912(13)	7 665(9)
C(18A)	3 370(19)	1 239(21)	−1 573(15)	C(64)	1 597(10)	5 637(13)	7 706(9)
C(19A)	3 075(23)	604(28)	−1 391(21)	C(65)	1 753(10)	4 896(13)	7 538(9)
C(20A)	2 531(19)	−918(21)	−1 096(15)	C(66)	1 175(10)	4 430(13)	7 330(9)
Cu(2)	3 274(3)	416(4)	478(2)	B(2)	4 676(23)	3 427(26)	7 426(20)
C(1B)	4 408(39)	638(40)	959(28)	C(71)	4 430(14)	3 874(15)	8 069(10)
C(2B)	3 832(28)	193(28)	1 289(21)	C(72)	4 687(14)	3 624(15)	8 636(10)
C(3B)	3 348(30)	757(33)	1 707(25)	C(73)	4 424(14)	3 961(15)	9 171(10)
C(4B)	2 512(24)	642(27)	1 638(17)	C(74)	3 904(14)	4 548(15)	9 138(10)
N(5B)	2 329(18)	722(18)	1 006(14)	C(75)	3 647(14)	4 798(15)	8 572(10)
C(6B)	1 664(26)	923(25)	858(20)	C(76)	3 910(14)	4 462(15)	8 037(10)
C(7B)	1 482(17)	1 009(21)	159(14)	C(81)	4 863(14)	4 114(15)	6 880(9)
N(8B)	1 625(15)	1 655(16)	−123(13)	C(82)	5 184(14)	4 816(15)	6 992(9)
C(9B)	1 464(20)	1 692(22)	−649(18)	C(83)	5 316(14)	5 311(15)	6 509(9)
C(10B)	1 602(20)	2 442(26)	−964(18)	C(84)	5 127(14)	5 103(15)	5 914(9)
N(11B)	1 902(15)	2 870(16)	−599(13)	C(85)	4 806(14)	4 400(15)	5 802(9)
C(12B)	2 037(23)	3 664(24)	−807(19)	C(86)	4 674(14)	3 906(15)	6 285(9)
C(13B)	1 351(32)	4 180(36)	−628(25)	C(91)	4 096(12)	2 841(15)	7 172(11)
C(14B)	1 494(56)	4 981(69)	−605(44)	C(92)	4 328(12)	2 261(15)	6 786(11)
C(15B)	1 166(48)	5 541(56)	−552(36)	C(93)	3 795(12)	1 793(15)	6 512(11)
C(16B)	910(27)	1 013(27)	1 292(20)	C(94)	3 029(12)	1 906(15)	6 624(11)
C(17B)	1 157(19)	318(24)	−72(17)	C(95)	2 796(12)	2 485(15)	7 010(11)
C(18B)	1 057(18)	389(26)	−673(16)	C(96)	3 330(12)	2 953(15)	7 283(11)
C(19B)	1 148(19)	1 057(22)	−969(18)	C(101)	5 563(10)	3 023(18)	7 514(12)
C(20B)	1 409(19)	2 474(23)	−1 641(15)	C(102)	5 534(10)	2 291(18)	7 742(12)
B(1)	−265(22)	4 105(24)	7 034(18)	C(103)	6 199(10)	1 920(18)	7 902(12)
C(31)	41(13)	3 551(12)	6 488(9)	C(104)	6 892(10)	2 282(18)	7 834(12)
C(32)	−170(13)	3 687(12)	5 884(9)	C(105)	6 920(10)	3 013(18)	7 606(12)
C(33)	109(13)	3 232(12)	5 417(9)	C(106)	6 256(10)	3 384(18)	7 445(12)

* The phenyl rings were refined as rigid groups.

mum height was 0.49 e Å^{-3} and the minimum was −0.38 e Å^{-3}). The final *R* value was 0.114 (*R'* 0.115). Scattering factors were taken from International Tables.[17] Calculations were made using SHELX76[18] on the CDC7600 computer at the University of Manchester Computer Centre. Atomic co-ordinates are given in Table 10.

Measurements of O_2 *and* CO *Uptake.*—Physical measurements of O_2 and CO gas uptakes were monitored by the pressure change (ΔP) in a thermostatted reaction vessel of volume 18.97 cm^3 containing 5—10 cm^{-3} of complex solution. The pressure in the reaction vessel was recorded automatically using a Langham–Thompson type UP4 transducer and referred to a standard reference pressure of 0.67 atm.

The equilibrium constant for the gas in the reaction vessel with the solvent is given by equation (i), where $V_{tot.}$ = total volume of reaction vessel and transducer (cm^3), V_l = volume of solvent (cm^3), and P_i = initial gas pressure in the reaction vessel (Torr).

$$K_{solvent} = \left(\frac{V_{tot.} - V_l}{V_l}\right)\left(\frac{\Delta P}{P_i - \Delta P}\right) \qquad \text{(i)}$$

The number of moles (N) of gas consumed was calculated from equation (ii), where T_{rv} = the temperature of the reaction vessel (K), T_r = room temperature (K), V = volume of the reaction vessel (cm^3), and K = partition function between gas and liquid phases. The term $2.22/T_r$ is a correction to take account of a small unthermostatted gas space.

$$N = \left(\frac{\Delta P}{6\,231 \times 10^4}\right)\left\{\left(\frac{V - V_l}{T_{rv}}\right) + \left(\frac{2.22}{T_r}\right) + \left(\frac{KV_l}{T_{rv}}\right)\right\} \qquad \text{(ii)}$$

Other Physical Measurements.—Infrared spectra were measured on KBr discs and Nujol mulls using a Perkin-Elmer 598 spectrometer. Proton and ^{13}C n.m.r. spectra were recorded at 250 and 62.9 MHz using a Bruker WM250 instrument. Mass spectra were obtained using either an A.E.I. MS30 or MS902 spectrometer. Magnetic susceptibilities were measured by the Gouy method.

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