Copper Complexes of 1,1-Di(2-pyridyl)ethyl Methyl Ether: X-Ray Crystal Structures and Reactions with Dioxygen†

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The mixed-valence complexes $[Cu^{II}L^1_3][Cu^I_2I_4]$ (L^1 = di-2-pyridyl ketone), $[Cu^{II}(HL^2)_2][Cu^I_2I_4]$ [HL^2 = 1,1-di(2-pyridyl)ethanol] and $[Cu^{II}L^3_2][Cu^I_2I_4]$ [L^3 = 1,1-di(2-pyridyl)ethyl methyl ether] have been isolated from the reactions of CuI with the respective ligands. On interactions with dioxygen the last two complexes are oxidised to $[Cu^{II}_2L^2_2I_2]$ and $[Cu^{II}_2L^3_2(OH)_2][Cu^II_3]$ respectively. The X-ray crystal structures of $[Cu^{II}L^3_2][Cu^I_2I_4]$ and $[Cu^{II}_2L^3_2(OH)_2][Cu^II_3]$ are reported.

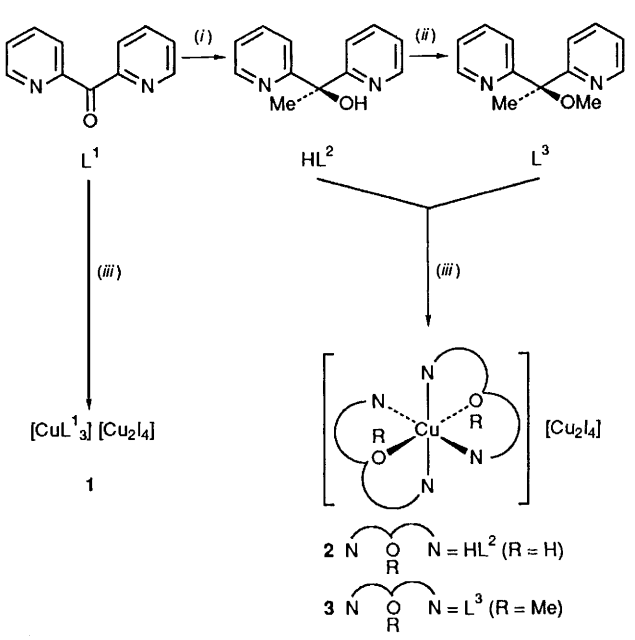
Notable advances have been made in copper–dioxygen chemistry in recent years.[1] The impetus for research in this area has come from the knowledge that a number of copper proteins such as haemocyanin, tyrosinase, and ascorbic acid oxidase contain di- or multi-nuclear copper sites, which, in the lower oxidation states, interact with dioxygen.[2] A number of ligands capable of co-ordinating through two or more nitrogens and an endogenous oxygen bridge have been proposed as models for the active sites of some of these copper proteins.[1,3] Here, we report the potential of di-2-pyridyl ketone, L^1, and related ligands HL^2 and L^3 as chelating agents for dinuclear copper centres.

X-Ray structures of a mixed-valence and a fully oxidised copper complex with L^3 as the ligand are also described. Some of the observed reactions are similar to oxidase activities of some of the copper proteins. Part of this work has been communicated earlier.[4]

Results and Discussion

(*a*) *Syntheses and Reactions.*—Ligands HL^2 and L^3 were synthesised from L^1 according to the reactions shown in Scheme 1. Attempts to couple two ligands by treating HL^2 with NaH followed by 1,2-dichloroethane or α,α′-dichloro-*p*-xylene were unsuccessful. With these substrates proton abstraction and halide elimination, rather than nucleophilic displacement of the halogen atoms, leads to the reformation of HL^2.

Reactions of CuI with these ligands produce mixed-valence complexes (Table 1) with ligated Cu^{2+} as the cation and $[Cu_2I_4]^{2-}$ as the counter ion. While L^1 acts as a bidentate ligand in complex **1**, tridentate chelation by HL^2 or L^3 is observed in **2** and **3** respectively (see Scheme 1). Characterisation of **2** by X-ray methods has been reported earlier;[4] in this work we report the X-ray structure of **3**. The formulation of **1** is based on analytical and spectroscopic data and is consistent with the known[5] modes of co-ordination of L^1. On co-ordination, in the IR spectrum of complex **1**, a shift of about 20 cm^{-1} is observed for the ketone function of L^1. This probably indicates that co-ordination takes place through the oxygen and one nitrogen atom. The mononuclearity of Cu^{2+} in the cations of **2** and **3** is unusual, since only bridged dinuclear copper cores have so far been observed in structurally characterised copper(II) complexes with bi- or tri-dentate ligands of the type HL^2 and L^3.



Scheme 1 (*i*) MgMeI; (*ii*) NaH, MeI; (*iii*) CuI

Complexes **2** and **3** are more sensitive to dioxygen than is **1**, as indicated by the rate of colour change. In all cases the acetonitrile solutions change from red-brown to green on exposure to dioxygen. In the case of **1**, the time required for this change is more than 1 h and analytically pure compounds could not be isolated from this reaction.

Exposure of an acetonitrile solution of complex **2** to dry dioxygen leads to the deposition of crystals of $[Cu_2L^2_2I_2]$ **4** suitable for X-ray structure determination.[4] However, although an acetonitrile solution of **3** turns green on contact with dioxygen, crystals of $[Cu_2L^3_2(OH)_2][CuI_3]$ **5** could be obtained only when the acetonitrile solution was allowed to evaporate in the presence of atmospheric moisture. Removal of solvent under reduced pressure yielded an amorphous green powder that was not further studied. Thus the presence of moisture appears to be necessary for the formation of **5**. Volumetric studies show the ratios of dioxygen absorption by complexes **2**

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† *Supplementary data available:* Complete bond lengths and angles, H-atom coordinates, structure factors, and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft fur Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, FRG. Any request for this material should quote a full literature citation and the reference number CSD 55228.

Table 1 Analytical and spectroscopic data for the new complexes

Complex	IR (cm^{-1})[a]	Analysis[b] (%) C	H	N	EPR[c]
1	1670vs, 1580s, 1565m	31.80	2.05	6.85	Active
		(31.65)	(1.90)	(6.70)	
2	3440(br)w, 1600vs, 1570m, 1145m	26.20	2.15	5.15	Active
		(26.20)	(2.20)	(5.10)	
3	1600s, 1570m, 1145m	27.80	2.60	5.00	Active
		(27.70)	(2.50)	(4.95)	
4	1600vs, 1580m	37.15	2.85	7.25	g_{iso} 2.062
		(36.55)	(2.80)	(7.20)	
5	3440(br)m, 1600s, 1575m	30.25	3.05	5.50	g_{iso} 2.0598
		(30.20)	(2.90)	(5.00)	

[a] Recorded in Nujol mull for complexes **2** and **5** and as KBr discs for the others. [b] Calculated values are given in parentheses. [c] To avoid the possibility of oxidation in solution, the spectra of powdered samples were recorded for complexes **1**–**3**. For **4** and **5** the spectra were recorded at 20 °C in acetonitrile.

Table 2 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
I(1)	1483.4(4)	2457.0(4)	8053.4(4)
I(2)	−2475.7(4)	324.6(4)	9487.3(4)
Cu(1)	5000	5000	5000
Cu(2)	479.2(8)	856.7(8)	9312.3(7)
C(1)	3299(5)	5670(5)	2786(5)
C(2)	2753(7)	5929(6)	1474(5)
C(3)	5106(7)	4049(7)	1574(6)
O	4861(4)	5182(3)	2776(3)
N(1)	4319(4)	6954(4)	5148(4)
C(12)	3508(5)	7043(5)	4022(5)
C(13)	2873(6)	8301(5)	4039(6)
C(14)	3076(6)	9466(5)	5251(6)
C(15)	3898(6)	9370(5)	6391(6)
C(16)	4537(6)	8093(5)	6297(5)
N(2)	2792(4)	4177(4)	4159(4)
C(22)	2191(5)	4569(5)	3122(5)
C(23)	682(6)	4044(6)	2491(6)
C(24)	−205(6)	3118(7)	2941(7)
C(25)	402(7)	2732(6)	4019(7)
C(26)	1908(6)	3280(5)	4610(6)

Table 3 Bond lengths (Å) and angles (°) for complex **3**

I(1)–Cu(2)	2.510(1)	I(2)–Cu(2)	2.581(1)
I(2)–Cu(2i)	2.598(1)	Cu(2) ⋯ Cu(2i)	2.677(2)
Cu(1)–O	2.380(4)	Cu(1)–N(1)	2.018(4)
Cu(1)–N(2)	2.003(3)	C(1)–C(2)	1.516(8)
C(1)–O	1.458(6)	C(1)–C(12)	1.519(6)
C(1)–C(22)	1.532(7)	C(3)–O	1.426(6)
N(1)–C(12)	1.344(6)	N(1)–C(16)	1.335(5)
C(12)–C(13)	1.389(7)	C(13)–C(14)	1.390(7)
C(14)–C(15)	1.364(8)	C(15)–C(16)	1.391(8)
N(2)–C(22)	1.339(7)	N(2)–C(26)	1.345(7)
C(22)–C(23)	1.377(6)	C(23)–C(24)	1.366(10)
C(24)–C(25)	1.375(11)	C(25)–C(26)	1.368(7)
Cu(2)–I(2)–Cu(2i)	62.2(1)	I(1)–Cu(2)–I(2)	123.0(1)
I(1)–Cu(2)–I(2i)	119.3(1)	I(2)–Cu(2)–I(2i)	117.8(1)
O–Cu(1)–N(1)	72.8(1)	O–Cu(1)–N(2)	75.7(1)
N(1)–Cu(1)–N(2)	86.7(1)	O–Cu(1)–O(ii)	180.0
N(1)–Cu(1)–O(ii)	107.2(1)	N(2)–Cu(1)–O(ii)	104.3(1)
N(1)–Cu(1)–N(1ii)	180.0	N(2)–Cu(1)–N(1ii)	93.3(1)
N(2)–Cu(1)–N(2ii)	180.0	C(2)–C(1)–O	112.2(4)
C(2)–C(1)–C(12)	112.6(4)	O–C(1)–C(12)	103.2(3)
C(2)–C(1)–C(22)	114.1(4)	O–C(1)–C(22)	107.3(4)
C(12)–C(1)–C(22)	106.6(4)	Cu(1)–O–C(1)	95.6(3)
Cu(1)–O–C(3)	124.7(4)	C(1)–O–C(3)	115.8(4)
Cu(1)–N(1)–C(12)	116.0(3)	Cu(1)–N(1)–C(16)	124.1(4)
C(12)–N(1)–C(16)	119.8(4)	C(1)–C(12)–N(1)	115.2(4)
C(1)–C(12)–C(13)	123.8(4)	N(1)–C(12)–C(13)	121.0(4)
C(12)–C(13)–C(14)	118.6(5)	C(13)–C(14)–C(15)	120.2(5)
C(14)–C(15)–C(16)	118.3(4)	N(1)–C(16)–C(15)	122.1(5)
Cu(1)–N(2)–C(22)	117.6(3)	Cu(1)–N(2)–C(26)	122.5(3)
C(22)–N(2)–C(26)	119.9(4)	C(1)–C(22)–N(2)	113.8(4)
C(1)–C(22)–C(23)	125.3(5)	N(2)–C(22)–C(23)	120.8(5)
C(22)–C(23)–C(24)	119.1(6)	C(23)–C(24)–C(25)	120.1(5)
C(24)–C(25)–C(26)	118.6(6)	N(2)–C(26)–C(25)	121.4(6)

Symmetry operators: i, − *x*, − *y*, 2 − *z*; ii, 1 − *x*, 1 − *y*, 1 − *z*.

and **3** to be 4:1 and 2:1 respectively. The probable stoichiometries are described by equations (1) and (2). In the oxidation

$$4\,\mathbf{2} + O_2 \longrightarrow 4\,\mathbf{4} + CuI + 4HI + 2H_2O \tag{1}$$

$$2\,\mathbf{3} + O_2 + 2H_2O \longrightarrow 2\,\mathbf{5} + I_2 \tag{2}$$

of **2** to **4** by dioxygen the required protons are supplied by the co-ordinated ligand. This reaction is similar to the oxidase activities of some of the copper proteins. Formation of dihydroxo-bridged binuclear copper(II) complexes, as seen in the conversion of **3** into **5**, have been reported with other tridentate ligands. Karlin *et al.*[6] have established the exact role of moisture in the formation of a similar dihydroxo-bridged complex.

The mixed-valence complexes **2** and **3** react with PPh_3 to yield the well known[7] tetrameric complex $[\{CuI(PPh_3)\}_4]$. We propose that these reactions proceed according to equation (3) ($L = HL^2$ or L^3).

$$4[CuL_2][Cu_2I_4] + 12PPh_3 \longrightarrow 3[\{CuI(PPh_3)\}_4] + 2I_2 + 8L \tag{3}$$

(*b*) *Crystal Structures of Complexes* **3** *and* **5**.—The atomic coordinates, bond lengths and bond angles for complexes **3** and **5** are given in Tables 2–5. The cation and anion of **3** are exactly centrosymmetric. The mixed-valence complexes **2** and **3** (Fig. 1) have very similar structures. Thus the Cu–N distances in **2** and **3** are 2.011(4), 1.998(4) and 2.018(4), 2.003(3) Å respectively. The Cu–O distances are also very similar, 2.410(3) and 2.380(4) Å respectively. These rather long Cu–O bonds are associated with the presence of H or Me on the oxygen atoms.

The Cu–O distances in complex **4** are 1.939 and 2.004(3) Å. This substantial shortening results mainly from the loss of the proton from the ligand and is also associated with a change in the C–O distance, from 1.448(6) to 1.411(5) Å. In contrast (Fig. 2) the Cu–O(Me) distances in **5**, 2.419(4) and 2.460(4) Å, are very close to those in **3**.

The two copper(II) centres in complex **5** adopt square-pyramidal geometries. The overall co-ordination around the dinuclear copper site is best described as two edge-sharing square pyramids. This should be contrasted with the distorted trigonal-bipyramidal geometries[4] observed in **4**. The base of the co-ordination pyramid for Cu(2) in **5** consists of the atoms N(1), N(2), O(3) and O(4); the mean deviation of these four atoms from their least-squares plane is 0.13 Å, and Cu(2) lies only 0.03 Å above the base plane. For Cu(3) the corresponding nitrogen atoms are N(3) and N(4); the mean deviation of the basal atoms is 0.11 Å, and Cu(3) lies 0.05 Å above the plane. The Cu(2)···Cu(3) distance is 2.842(2) Å. The structure contains an approximate (non-crystallographic) mirror plane through the anion and the atoms O(3) and O(4). The anions in **3** and **5**, $[Cu_2I_4]^{2-}$ and $[CuI_3]^{2-}$, contain trigonal-planar copper atoms and are documented in the literature.[8] Although in **5** one iodine atom I(2) of the anion occupies a bridging position between the two copper(II) atoms of the cation, the average $Cu^{II}\cdots I(2)$ distance 3.454(4) Å is much larger than the average Cu–I distance [2.546(2) Å] in $[CuI_3]^{2-}$. The interactions between I(2) and the two copper centres may therefore be considered as weak.

Table 4 Atomic coordinates (× 10^4) for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	2086.5(5)	6152.2(3)	8873.3(2)	C(25)	1122(9)	8223(5)	4868(3)
I(2)	896.1(5)	6204.1(2)	6713.6(2)	C(26)	1780(7)	7656(4)	5258(3)
I(3)	−2511.1(5)	6116.8(3)	8066.5(2)	N(3)	4416(5)	4619(3)	7028(2)
Cu(1)	166.0(9)	6167.0(4)	7911.3(4)	N(4)	3225(6)	4480(3)	5731(2)
Cu(2)	3977.2(8)	6974.6(4)	6205.8(3)	O(2)	6037(5)	4458(3)	5973(2)
Cu(3)	4117.5(8)	5346.4(4)	6258.5(3)	C(4)	5305(7)	3781(3)	6193(3)
N(1)	4156(5)	7764(3)	6936(2)	C(5)	6154(9)	3057(4)	6111(4)
N(2)	3025(6)	7776(3)	5625(2)	C(6)	7420(8)	4613(5)	6313(4)
O(1)	5840(5)	7860(2)	5919(2)	C(32)	4908(6)	3908(3)	6907(3)
C(1)	5049(7)	8538(3)	6064(3)	C(33)	4977(7)	3355(3)	7395(3)
C(2)	5907(9)	9257(4)	5934(4)	C(34)	4543(7)	3528(4)	8006(3)
C(3)	7178(8)	7754(4)	6318(4)	C(35)	4083(7)	4255(4)	8134(3)
C(12)	4634(6)	8464(3)	6787(3)	C(36)	4046(6)	4797(3)	7637(3)
C(13)	4703(7)	9057(3)	7239(3)	C(42)	3894(7)	3797(3)	5757(3)
C(14)	4314(7)	8913(4)	7870(3)	C(43)	3309(10)	3171(4)	5411(3)
C(15)	3879(7)	8192(4)	8030(3)	C(44)	2013(11)	3260(5)	5051(4)
C(16)	3810(6)	7627(4)	7553(3)	C(45)	1326(10)	3952(5)	5021(4)
C(22)	3667(7)	8458(3)	5620(3)	C(46)	1961(9)	4561(4)	5378(3)
C(23)	3043(10)	9064(4)	5243(3)	O(3)	3568(4)	6118(2)	5590(2)
C(24)	1765(11)	8931(5)	4867(3)	O(4)	5039(5)	6200(2)	6681(2)

Table 5 Bond lengths (Å) and angles (°) for complex **5**

I(1)–Cu(1)	2.543(2)	I(2)–Cu(1)	2.567(2)	C(13)–C(14)	1.376(9)	C(14)–C(15)	1.366(10)
I(3)–Cu(1)	2.527(2)	Cu(2) ··· Cu(3)	2.842(2)	C(15)–C(16)	1.377(9)	C(22)–C(23)	1.403(9)
I(2) ··· Cu(2)	3.385(3)	I(2) ··· Cu(3)	3.523(3)	C(23)–C(24)	1.381(12)	C(24)–C(25)	1.371(12)
Cu(2)–N(1)	2.017(5)	Cu(2)–N(2)	1.991(5)	C(25)–C(26)	1.380(10)	N(3)–C(32)	1.350(7)
Cu(2)–O(1)	2.419(4)	Cu(2)–O(3)	1.965(4)	N(3)–C(36)	1.340(7)	N(4)–C(42)	1.342(8)
Cu(2)–O(4)	1.892(4)	Cu(3)–N(3)	2.013(4)	N(4)–C(46)	1.336(9)	O(2)–C(4)	1.448(8)
Cu(3)–N(4)	1.994(5)	Cu(3)–O(2)	2.460(4)	O(2)–C(6)	1.437(8)	C(4)–C(5)	1.503(10)
Cu(3)–O(3)	1.950(4)	Cu(3)–O(4)	1.890(4)	C(4)–C(32)	1.535(8)	C(4)–C(42)	1.525(9)
N(1)–C(12)	1.341(7)	N(1)–C(16)	1.335(7)	C(32)–C(33)	1.378(8)	C(33)–C(34)	1.362(9)
N(2)–C(22)	1.330(8)	N(2)–C(26)	1.343(8)	C(34)–C(35)	1.368(10)	C(35)–C(36)	1.379(9)
O(1)–C(1)	1.433(7)	O(1)–C(3)	1.442(8)	C(42)–C(43)	1.387(9)	C(43)–C(44)	1.369(12)
C(1)–C(2)	1.517(10)	C(1)–C(12)	1.548(9)	C(44)–C(45)	1.363(12)	C(45)–C(46)	1.392(10)
C(1)–C(22)	1.518(9)	C(12)–C(13)	1.379(8)				
I(1)–Cu(1)–I(2)	120.4(1)	I(1)–Cu(1)–I(3)	123.0(1)	C(13)–C(14)–C(15)	119.3(6)	C(14)–C(15)–C(16)	119.5(6)
I(2)–Cu(1)–I(3)	116.6(1)	N(1)–Cu(2)–N(2)	87.9(2)	N(1)–C(16)–C(15)	121.8(6)	N(2)–C(22)–C(1)	115.9(5)
N(1)–Cu(2)–O(1)	73.7(2)	N(2)–Cu(2)–O(1)	72.8(2)	N(2)–C(22)–C(23)	120.6(6)	C(1)–C(22)–C(23)	123.4(6)
N(1)–Cu(2)–O(3)	170.1(2)	N(2)–Cu(2)–O(3)	95.8(2)	C(22)–C(23)–C(24)	118.6(7)	C(23)–C(24)–C(25)	120.4(7)
O(1)–Cu(2)–O(3)	116.2(2)	N(1)–Cu(2)–O(4)	95.8(2)	C(24)–C(25)–C(26)	118.2(7)	N(2)–C(26)–C(25)	122.1(6)
N(2)–Cu(2)–O(4)	173.3(2)	O(1)–Cu(2)–O(4)	102.9(2)	Cu(3)–N(3)–C(32)	117.8(4)	Cu(3)–N(3)–C(36)	122.5(4)
O(3)–Cu(2)–O(4)	81.4(2)	N(3)–Cu(3)–O(2)	74.0(2)	C(32)–N(3)–C(36)	119.5(5)	Cu(3)–N(4)–C(42)	118.5(4)
N(4)–Cu(3)–O(2)	71.2(2)	O(3)–Cu(3)–O(2)	115.3(2)	Cu(3)–N(4)–C(46)	121.4(4)	C(42)–N(4)–C(46)	120.0(5)
O(4)–Cu(3)–O(2)	106.9(2)	N(3)–Cu(3)–N(4)	88.1(2)	C(4)–O(2)–C(6)	115.4(5)	O(2)–C(4)–C(5)	112.9(6)
N(3)–Cu(3)–O(3)	170.6(2)	N(4)–Cu(3)–O(3)	94.1(2)	O(2)–C(4)–C(32)	108.7(5)	C(5)–C(4)–C(32)	112.9(5)
N(3)–Cu(3)–O(4)	96.5(2)	N(4)–Cu(3)–O(4)	174.4(2)	O(2)–C(4)–C(42)	102.0(5)	C(5)–C(4)–C(42)	112.8(5)
O(3)–Cu(3)–O(4)	81.9(2)	Cu(2)–N(1)–C(12)	117.9(4)	C(32)–C(4)–C(42)	106.7(5)	N(3)–C(32)–C(4)	114.3(5)
Cu(2)–N(1)–C(16)	123.5(4)	C(12)–N(1)–C(16)	118.6(5)	N(3)–C(32)–C(33)	120.7(5)	C(4)–C(32)–C(33)	124.9(5)
Cu(2)–N(2)–C(22)	116.9(4)	Cu(2)–N(2)–C(26)	122.9(4)	C(32)–C(33)–C(34)	119.7(6)	C(33)–C(34)–C(35)	119.6(6)
C(22)–N(2)–C(26)	120.2(5)	Cu(2)–O(1)–C(1)	95.3(3)	C(34)–C(35)–C(36)	119.2(6)	N(3)–C(36)–C(35)	121.2(6)
Cu(2)–O(1)–C(3)	112.6(4)	C(1)–O(1)–C(3)	115.1(5)	N(4)–C(42)–C(4)	114.5(5)	N(4)–C(42)–C(43)	121.0(6)
O(1)–C(1)–C(2)	111.3(6)	O(1)–C(1)–C(12)	106.9(5)	C(4)–C(42)–C(43)	124.4(6)	C(42)–C(43)–C(44)	118.5(7)
C(2)–C(1)–C(12)	113.7(5)	O(1)–C(1)–C(22)	103.1(5)	C(43)–C(44)–C(45)	120.9(7)	C(44)–C(45)–C(46)	118.3(8)
C(2)–C(1)–C(22)	113.9(5)	C(12)–C(1)–C(22)	107.2(5)	N(4)–C(46)–C(45)	121.3(7)	Cu(2)–O(3)–Cu(3)	93.1(2)
N(1)–C(12)–C(1)	113.4(5)	N(1)–C(12)–C(13)	122.3(5)	Cu(2)–O(4)–Cu(3)	97.4(2)		
C(1)–C(12)–C(13)	124.3(5)	C(12)–C(13)–C(14)	118.5(6)				

Experimental

General Comments.—Unless stated otherwise all manipulations were carried out under a dry dinitrogen atmosphere. Solvents were distilled from the appropriate drying agents before use. Infrared and NMR spectra were recorded on Perkin-Elmer 781 and Bruker 80 MHz Fourier-transform instruments. A Carlo–Erba 1106 and a Varian E-112 instrument were used for microanalyses and ESR experiments respectively. The oxygenation studies were carried out with P_2O_5-dried dioxygen.

X-Ray Structure Determination of Compound **3**.—*Crystal data.* $C_{26}H_{28}Cu_3I_4N_4O_2$, $M_r = 1126.7$, triclinic, space group $P\bar{1}$, $a = 8.574(2)$, $b = 9.860(3)$, $c = 10.441(3)$ Å, $\alpha = 109.10(2)$, $\beta = 95.04(2)$, $\gamma = 94.54(2)^\circ$, $U = 825.4$ Å^3, $Z = 1$, $D_c = 2.27$ Mg m^{-3}, $F(000) = 527$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 5.7$ mm^{-1}, $T = 293$ K.

Data collection and reduction. A brown tablet 0.35 × 0.3 × 0.1 mm was mounted on a glass fibre. 5464 Intensities were measured to $2\theta_{max}$ 50° on a Siemens R3 diffractometer using monochromated Mo-Kα radiation. An absorption correction based on ψ scans was applied, with transmission factors 0.52–0.99. Merging equivalents gave 2899 unique reflections (R_{int}

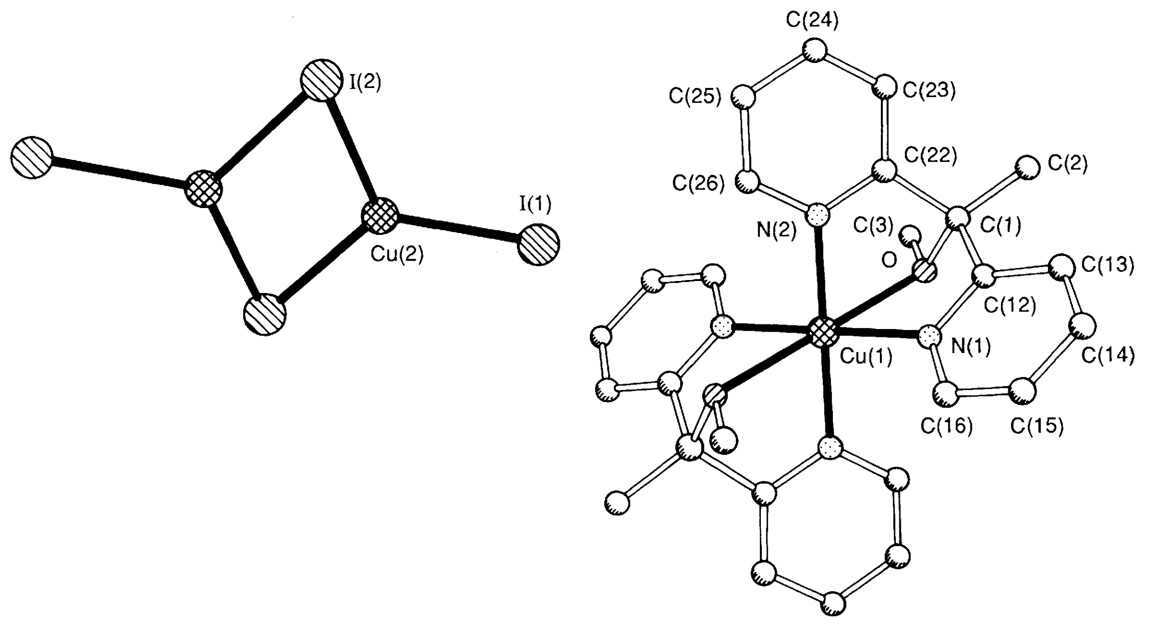
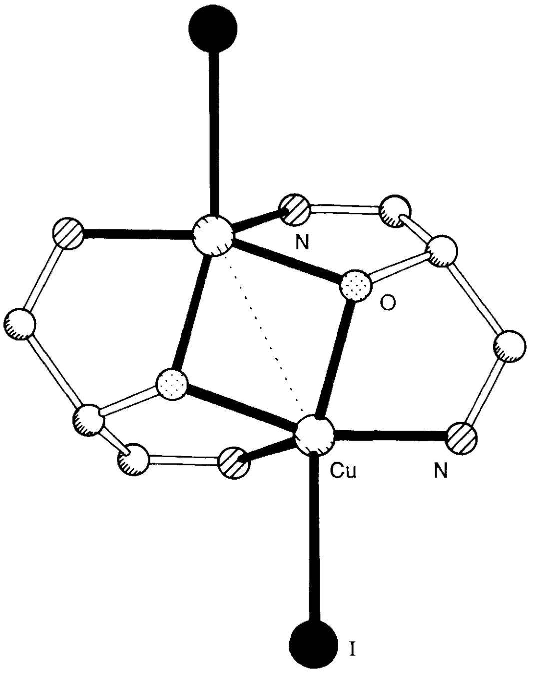


Fig. 1 Crystal structure of complex **3**



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0.017), of which 2393 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–24°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix anisotropic least-squares refinement on F. Hydrogen atoms were included using a riding model. Refinement proceeded to R 0.030, R' 0.036 for 184 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$; $S = 1.6$; maximum $\Delta/\sigma = 0.001$; maximum $\Delta\rho = 0.9$ e Å^{-3}.

X-Ray Structure Determination of Compound **5**.—*Crystal data.* $C_{26}H_{30}Cu_3I_3N_4O_4$, $M_r = 1033.9$, monoclinic, space group $P2_1/n$, $a = 9.276(2)$, $b = 17.428(4)$, $c = 20.257(4)$ Å, $\beta = 94.16(2)°$, $U = 3266$ Å^3, $Z = 4$, $D_c = 2.10$ Mg m^{-3}, $F(000) = 1968$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 4.8$ mm^{-1}, $T = 293$ K.

Data collection and reduction. As for complex **3**, with the following differences. Greenish blue prism 0.8 × 0.3 × 0.2 mm, 6677 reflections, 5722 unique (R_{int} 0.012), 3753 with $F > 4\sigma(F)$, transmission factors 0.64–0.99.

Structure solution and refinement. As for complex **3**, with the following differences. The hydroxyl H atoms could not be located unambiguously and were therefore not included in the refinement. R 0.032, R' 0.033 for 367 parameters; $S = 1.3$; maximum $\Delta/\sigma = 0.003$; maximum $\Delta\rho = 0.6$ e Å^{-3}.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Preparations.—HL^2. Di-2-pyridyl ketone (1.38 g, 8 mmol) was added to a Et_2O solution (40 cm^3) containing MgMeI (2.55 g, 15.35 mmol) over 3 h. The excess of Grignard reagent was quenched with 20% NH_4Cl solution. Ether extraction followed by solvent removal gave 1,1-di(2-pyridyl)ethanol HL^2 (1.5 g, yield 99%) as a viscous liquid. IR (neat): 3380(br)m, 1595vs, 1575s and 1150(br)s cm^{-1}. ^1H NMR: δ 1.95 (s, 3 H), 7.15 (m, 2 H), 7.7 (m, 4 H) and 8.5 (m, 2 H).

L^3. Sodium hydride (0.36 g, 15 mmol) was added to a tetrahydrofuran (thf) solution of HL^2 (2 g, 10.6 mmol) at 20 °C and stirred vigorously for 2.5 h. Methyl iodide (1.56 g, 11 mmol) in thf was added dropwise to the resultant blue solution. The excess of NaH was quenched with saturated NH_4Cl solution. The organic layer was removed and dried over Na_2SO_4. Solvent removal gave L^3 (2 g, yield 93%) as a viscous liquid. IR: 1600vs and 1580s cm^{-1}. ^1H NMR: δ 2.05 (s, 3 H), 3.25 (m, 3 H), 7.15 (m, 2 H), 7.60 (m, 4 H) and 8.58 (m, 2 H).

Complex **1**. Copper(I) iodide (0.190 g, 1 mmol) was heated with di-2-pyridyl ketone (0.73 g, 4 mmol) in rigorously dried MeCN for 1 h. The solution turned dark brown and was filtered, reduced in volume and kept at 10 °C for 2 d to give analytically pure crystals of complex **1**. Complexes **2** and **3** were synthesised in a similar fashion.

Complex **4**. An acetonitrile solution (1.1 g, 1 mmol) of complex **2** was exposed with stirring to dry dioxygen. Dioxygen absorption as measured by volumetry was in the molar ratio of 4 : 1 and was complete within 10 min. The solution was cooled at 10 °C for 5 d to yield green crystals of complex **4**.

The synthesis of complex **5** was carried out in a similar fashion. However, cooling the green solution at 10 °C did not yield crystals. Crystals suitable for X-ray work were grown by slow evaporation of an acetonitrile solution at ambient atmos-

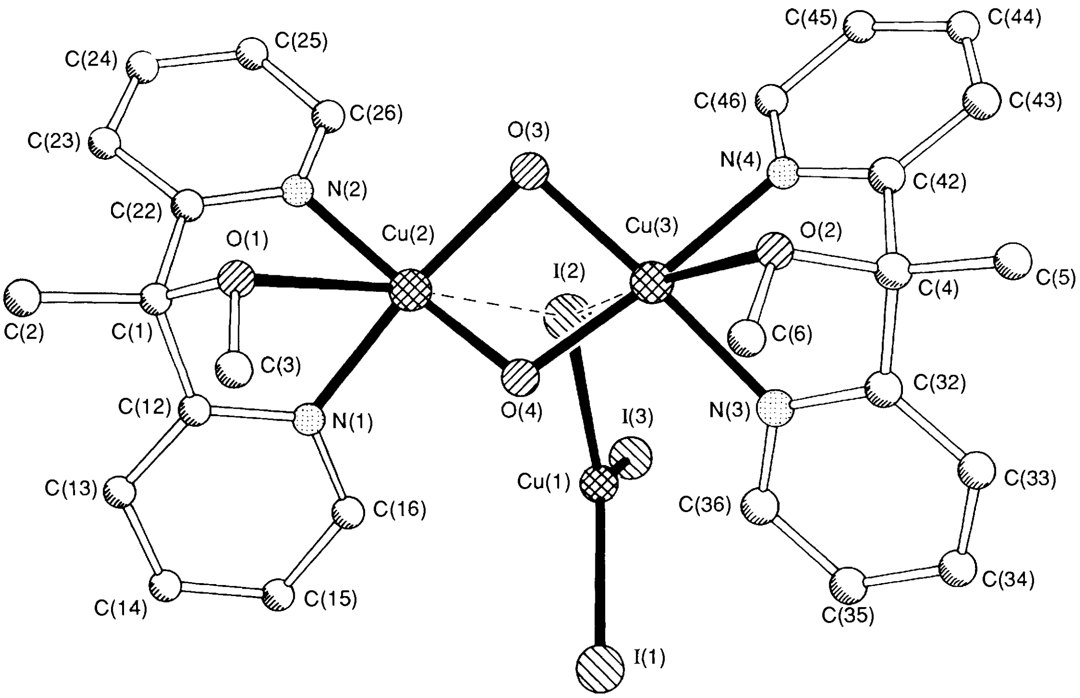

Fig. 2 Crystal structure of complex **5**

phere. Microanalytical, IR and EPR data for complexes **1**–**5** are given in Table 1.

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