

Synthesis, spectra and crystal structures of complexes of ambidentate $C_6H_5C(O)C(NO)CN^{-\dagger}$

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Compounds of Ni^{II}, Cu^{II}, Pb^{II}, Ag^I, Tl^I, Sn^{IV} and Sb^V with the oxime $C_6H_5C(O)C(NO)CN$ (HL) were obtained from water, alcohol or acetonitrile solutions. The copper(II) complexes have been prepared in high yields using metallic copper powder. The compounds were characterized by IR, UV/VIS spectroscopy, magnetochemistry and X-ray analysis. The crystal and molecular structures of $[CuL_2(H_2O)]$ and $[CuL_2(4\text{-mpy})_2]$ (4-mpy = 4-methylpyridine) have been determined. In both complexes the anions adopt a *cis-anti* conformation, and the Cu^{II} is five-co-ordinated. The wide variety of co-ordination modes exhibited by the oximate are reviewed and discussed.

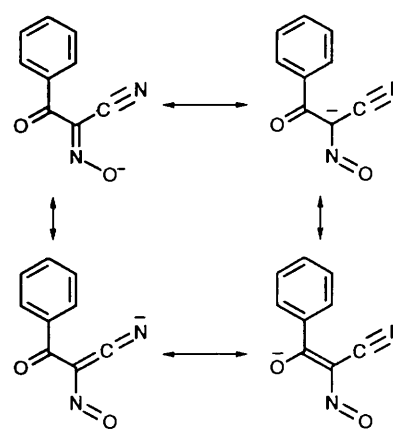
The co-ordination chemistry of cyanoximes has been intensively studied in the last decade due to their ability to act as ambidentate ligands.^{1,2} This ability to form stable metal complexes with different chemical properties in aqueous or non-aqueous media together with the variety of co-ordination modes makes cyanoximes especially interesting as building blocks for the design of new types of selective sorbents. This class of compounds, which has the general formula $RC(NO)CN$, contains donor groups R, such as amides,³ thioamides,⁴ keto groups⁵ and N-heterocycles.⁶ The different donor atom sets available to take part in co-ordination are N_2O_2 , N_2S_2 , $N_2N'_2$ and O_2S_2 . Cyanoximes themselves are relatively strong acids and can easily be deprotonated in water or alcoholic solution to form yellow stable anions. The acidity of free cyanoximes, as well as the solubility of their alkali-metal salts, is significantly greater than that for known simple oximes and dioximes. This makes them attractive potential ligands for co-ordination chemistry. In addition, some cyanoximes and their complexes have demonstrated strong antimicrobial,^{7,8} growth-regulating⁹ and antidote properties against some agricultural pesticides and herbicides.¹⁰

The ambidentate behaviour of cyanoximes toward various metal ions suggests that they can be considered as models for the different modes of metal binding in proteins and enzymes. It is well known that the inhibition of vital functions in biological systems by metal ions, such as in enzymes, is directly connected to two major factors which are the difference in binding constants of the ions and the irreversible change in the co-ordination mode of the active centre in the complex formed.¹¹⁻¹⁴

The present paper exemplifies the above-mentioned ambidentate properties of cyanoxime anions using the benzoyl-cyanoxime anion $^-ONC(CN)C(O)C_6H_5$ (L^-).

Results and Discussion

The oxime $C_6H_5C(O)C(NO)CN$ (HL) itself is a weak acid with a pK_a value of 4.53, which is significantly lower than that of common oximes or dimethylglyoxime which has a pK_a of 10.6.¹⁵ The pK_a value for HL was determined in water-methanol (30%) solutions by pH titration at 25 °C and constant



Scheme 1

ionic strength NaCl ($I = 0.1 \text{ mol dm}^{-3}$). The calculations were made using the PSEQUAD program package.¹⁶

The oxime deprotonates in water or polar organic solvents forming yellow solutions. The colour originates from $n \rightarrow \pi^*$ transitions in the visible region of the spectrum similar to the transitions^{17,18} of NO_2^- and $ONC(CN)_2^-$ anions. The anionic form, L^- has the possibility of charge delocalization which can be described by four main mesomeric forms² (Scheme 1). It can also exist in several conformations due to rotation around the C-C bond between the benzoyl group and cyanoxime fragment, and the presence of rotational isomers of the NO group (Scheme 2). Two of the four are found in the compounds that will be discussed below. The ability to adopt several conformations, together with the number of possible co-ordination modes of the anion, allow this particular compound, and cyanoximes in general, to be considered as models for ambidentate biological receptors capable of complexation of different metal ions.

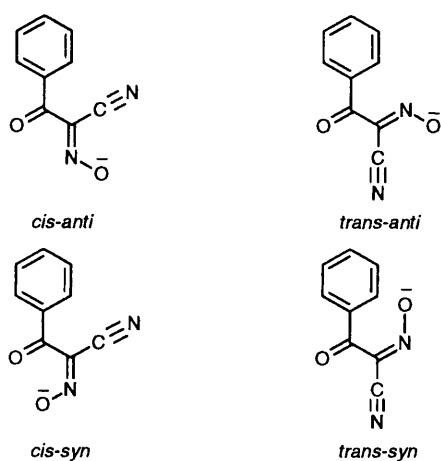
Some properties of co-ordination compounds which were prepared are shown in Table 1 and IR spectroscopic data are summarized in Table 2. The IR spectroscopic criteria for establishing the co-ordination modes for nitroso-containing anions have been developed previously by Kohler and Lampeka and co-workers.^{18,19} The exact assignment of vibrations including those of the $>C-N-O$ fragment in the L^-

[†] *Non-SI units employed: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T⁻¹.*

Table 1 Some properties of the synthesized compounds

Compound ^a	Colour	Yield (%)	Analysis (%) ^b				Electronic spectrum (cm ⁻¹)	Magnetic moment ^c $\mu_{\text{eff}}/\mu_{\text{B}}$
			M	C	H	N		
CsL	Red-orange	≈ 100		35.40 (35.30)	1.70 (1.65)	9.10 (9.15)	23 240 ^d	—
TiL	Orange	74	53.95 (54.15)	28.55 (28.60)	1.40 (1.30)	7.35 (7.40)	24 500 ^d	—
AgL	Violet	83	38.20 (38.40)	38.10 (38.45)	1.80 (1.80)	9.95 (9.95)	—	—
HgL ₂	Lemon-yellow	78	—	39.00 (39.50)	1.85 (1.85)	10.15 (10.25)	—	—
PbL ₂	Yellow	68	37.16 (37.45)	38.75 (39.05)	1.85 (1.80)	9.95 (10.10)	—	—
SnEt ₃ L	Colourless	92	30.95 (31.35)	47.10 (47.55)	5.30 (5.30)	7.30 (7.40)	—	—
SnMe ₂ L ₂	Colourless	90	23.50 (23.85)	48.15 (48.20)	3.30 (3.20)	11.15 (11.25)	—	—
SbPh ₄ L	Colourless	95	—	65.30 (65.70)	4.20 (4.15)	4.55 (4.65)	—	—
SbPh ₃ L(Cl)	Colourless	92	—	57.15 (57.72)	3.55 (3.55)	4.70 (5.00)	—	—
[NiL ₂]	Brown	65	14.40 (14.50)	53.10 (53.35)	2.55 (2.45)	13.50 (13.85)	16 100, ^e 20 900, 27 000	—
[NiL ₂ (H ₂ O) ₂]	Green	30	13.15 (13.30)	48.85 (49.00)	2.80 (2.70)	12.55 (12.70)	15 880, 20 000, 25 800	2.78
[NiL ₂ (py) ₂]	Yellow-orange	87	10.30 (10.45)	59.55 (59.70)	3.60 (3.55)	14.70 (14.95)	13 000, 20 560, 25 500	2.69
[NiL ₂ (2-mpy) ₂]	Yellow-brown	80	9.35 (9.45)	60.55 (60.95)	4.10 (4.05)	14.10 (14.20)	13 320, 20 600, 25 500	3.05
[NiL ₂ (3-mpy) ₂]	Orange	82	9.30	60.80	4.15	14.15	13 040, 20 600, 25 300	3.02
[NiL ₂ (4-mpy) ₂]	Red-brown	85	9.35	60.70	4.15	14.15	12 920, 20 400, 26 600	2.94
[CuL ₂ (H ₂ O)]	Black-blue	93	14.70 (14.85)	50.15 (50.50)	2.90 (2.80)	12.95 (13.10)	15 880	1.77
[CuL ₂ (py) ₂]	Deep green	93	10.95 (11.20)	59.05 (59.20)	3.55 (3.50)	14.60 (14.80)	15 080	1.68
[CuL ₂ (2-mpy) ₂]	Salad-green	86	10.70 (10.65)	60.40 (60.45)	4.10 (4.05)	13.95 (14.10)	14 400	—
[CuL ₂ (3-mpy) ₂]	Salad-green	92	10.45	60.25	4.05	13.85	13 600	—
[CuL ₂ (4-mpy) ₂]	Dark green	94	10.50	60.40	4.05	14.00	14 600	—
Cs[FeL ₃]	Dark blue	81	7.85 (7.90)	45.30 (45.75)	2.15 (2.10)	11.70 (11.85)	16 390	Diamagnetic

^a py = Pyridine; 2-, 3- or 4-mpy = 2-, 3- or 4-methylpyridine. ^b Calculated values in parentheses. ^c At 300 K. ^d Water solution. ^e Solid-state reflectance.



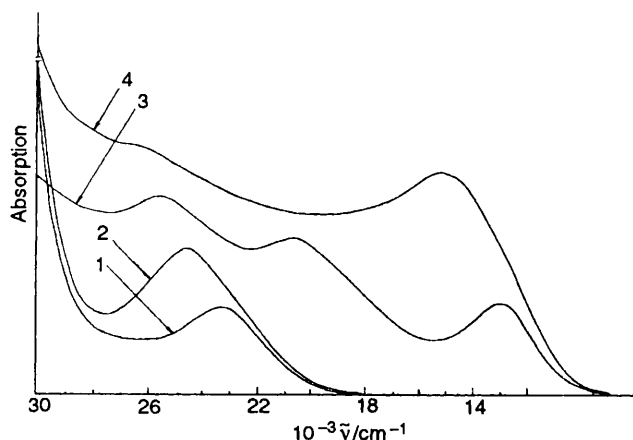
anion was carried out using ¹⁵N isotopic labelling. The high-frequency shift of the $\nu(\text{NO})$ vibrations in the IR spectra of 3d-metal complexes indicates that these metal ions are bonded to the L⁻ ligand by the nitrogen atom of the nitroso group. Several complexes of Cu^{II} and Ni^{II} exhibit a small low-frequency shift of the $\nu(\text{C}=\text{O})$ vibrations (Table 2). These observations support bidentate chelate co-ordination of the benzoylcyanoximato anion

to these 3d-metal ions. Similar behaviour was found previously for cyanoximates of other transition metals.^{21,22} In the organometallic derivatives of Sn^{IV}, such as SnEt₃L and SnMe₂L₂ the anions are co-ordinated *via* the oxygen atoms of the oxime group. Low-frequency shifts of the $\nu(\text{NO})$ and $\nu(\text{CNO})$ bands in the IR spectra of the organoantimony derivatives also indicate this co-ordination mode. In complexes of Tl^I, Ag^I and Hg^{II} it is difficult to determine the co-ordination mode of the anion using IR spectral data. The position of the $\nu(\text{C}\equiv\text{N})$ band in the IR spectrum of the silver(I) complex at 2240 cm⁻¹ (Table 2) definitely indicates participation of the CN group in co-ordination, which was confirmed by X-ray structural data. It should be noted that analysis of the shifts of the $\nu(\text{C}=\text{O})$ bands in the spectra of the complexes relative to the position of this vibration in the spectrum of the CsL salt cannot provide reliable information about the co-ordination modes of the anion. The IR spectra of the amine complexes Ni^{II} and Cu^{II} do not contain bands above 3050 cm⁻¹ which indicates the absence of co-ordinated water.

Iron(II) forms an intensely coloured stable tris(benzoylcyanoximato) anionic complex, which was characterized in aqueous solution using a spectrophotometric method. The ionic strength of the solution and its temperature were kept constant at 0.01 mol dm⁻³ (KCl) and 298 K. The starting materials, FeSO₄·7H₂O and KL, were obtained in the same way as that described for CsL. Both starting solutions and their mixtures were prepared and measurements on this system were

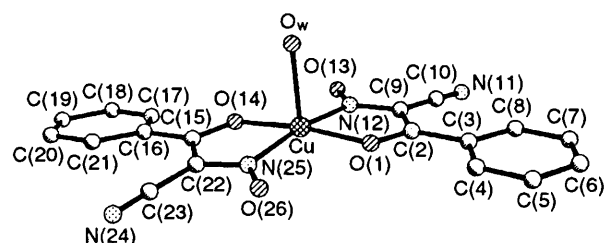
Table 2 Infrared spectroscopic data for the compounds

Compound	Anion band (cm ⁻¹)				
	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{N}-\text{O})$	$\nu(\text{N}-\text{O})$	$\delta(\text{C}-\text{N}-\text{O})$
HL	2232	1655	1315	1060 1045*	810
CsL	2205	1620	1355	1165	800
TiL	2205	1615	1330	1140	800
AgL	2240	1640	1330	1190 1320*	820
HgL ₂	2218	1623	1305	1190	833
SnEt ₃ L	2230	1635	1180	1148 1135*	810
SnMe ₂ L ₂	2220	1650	1170	1120	785
SbPh ₄ L	2210	1628	1335	1132 1120*	
SbPh ₃ L(Cl)	2220	1640		1055	
[NiL ₂]	2210	1595	1360	1185	810
[NiL ₂ (H ₂ O) ₂]	2215	1600	1350	1180	835
[NiL ₂ (py) ₂]	2210	1645	1355	1205	810
[NiL ₂ (2-mpy) ₂]	2210	1600	1365	1185	805
[NiL ₂ (3-mpy) ₂]	2210	1640	1355	1200	795
[NiL ₂ (4-mpy) ₂]	2210	1645	1355	1205	810
[CuL ₂ (H ₂ O)]	2218	1600	1360	1180	830
[CuL ₂ (py) ₂]	2215	1650	1340	1175	740
[CuL ₂ (2-mpy) ₂]	2215	1635	1345	1175	770
[CuL ₂ (3-mpy) ₂]	2220	1640	1340	1170	790
[CuL ₂ (4-mpy) ₂]	2210	1640	1345	1160	815
Cs[FeL ₃]	2205	1610	1360	1205	815

* Vibration of ¹⁵N isotopomer.**Fig. 1** Electronic absorption spectra of aqueous solutions of CsL (1), and TiL (2), and diffuse reflectance spectra of solid samples of [NiL₂(py)₂] (3), [CuL₂(4-mpy)₂] (4)

conducted under anaerobic conditions (Ar). Data obtained at 610 nm were used for the calculation of stability constants of the Fe²⁺-L⁻ system by means of the Bjerrum method. In aqueous solution three consecutive complexes FeL⁺ ($\epsilon = 900$; $\log \beta_1 = 0.85 \pm 0.05$), FeL₂ ($\epsilon = 2700$, $\log \beta_2 = 3.55 \pm 0.05$) and FeL₃⁻ ($\epsilon = 12\,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\log \beta_3 = 6.36 \pm 0.05$) are formed. It is interesting that the tris-complex becomes the dominant species in solution only in the presence of excess of HL. This differs from the behaviour of other cyanoximes in complex formation with iron(II).²³

Electronic spectral data and magnetic moments for several 3d-metal complexes indicate that they have distorted-octahedral structures. Typical electronic spectra for nickel(II) and copper(II) compounds are shown in Fig. 1. Assignment of the spectral bands was based on data in ref. 24. There are two bands in the spectra of the nickel complexes at 13 000–16 000 [³A_{2g} → ³T_{1g}(P)] and 20 000–20 900 cm⁻¹ (³A_{2g} → ³T_{1g}) corresponding to d-d transitions. The copper complexes show one expected band for ²T_{2g} → ²E_g d-d transitions at 13 600–

**Fig. 2** Molecular structure of [CuL₂(H₂O)] showing the atom numbering scheme. Hydrogen atoms are omitted for clarity

15 800 cm⁻¹ (Table 1, Fig. 1). These are typical positions for bands in the electronic spectra of divalent nickel and copper ions in five- or six-coordination. The charge-transfer band of the L anion in the spectrum of CsL is located at 23 240 cm⁻¹ (Fig. 1), while for other complexes this band shifts to 25 500–27 000 cm⁻¹ (Table 1). The magnetic moments for the copper(II) and nickel(II) complexes are in the range of expected spin-only values for the 3d-metal ions in five-co-ordinated and pseudo-octahedral surroundings (Table 1). Values of μ_{eff} can also provide information about the monomeric structures of the complexes studied. Since values of the magnetic moments were not unusual, no thermomagnetic studies were carried out. The Cs[FeL₃] complex contains iron(II) as the central atom in a diamagnetic ¹A₁ ground state (Table 1).

X-Ray structural data

Selected bond distances and angles for the complexes studied are given in Tables 3 and 4. The molecular structure of [CuL₂(H₂O)] is shown in Fig. 2. Both benzoylcyanoxime ligands present have *cis-anti* configurations and act as bidentate chelating ligands *via* the oxygen atoms of the carbonyl groups and the nitrogen atoms of the NO groups. The anions are in the nitroso form which can be clearly seen by an examination of the bond lengths C(9)–N(12), C(22)–N(25) and N(12)–O(13), N(25)–O(26) respectively (Table 3). Both ligands have a planar cyanoxime core NC–C(NO)–C(O) which is almost co-coplanar with their attached phenyl groups. The dihedral angle between

Table 3 Selected bond lengths (pm) and angles (°) for $[\text{CuL}_2(\text{H}_2\text{O})]$

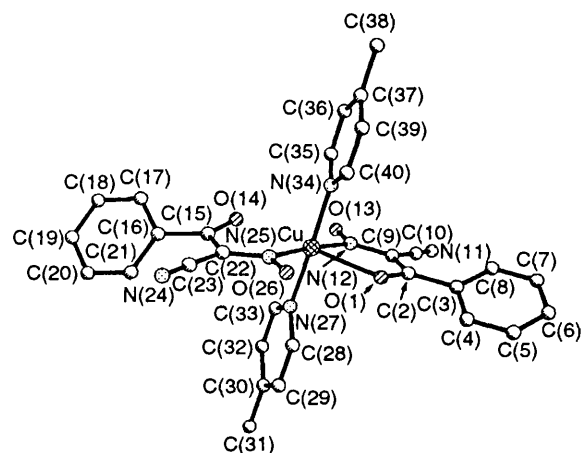
Co-ordination polyhedron			
Cu–O(1)	195.5(3)	Cu–O _w	220.6(3)
Cu–N(12)	199.5(3)	Cu–N(25)	198.0(3)
Cu–O(14)	195.6(3)		
O(1)–Cu–N(12)	81.1(1)	O(1)–Cu–O(14)	171.1(1)
N(12)–Cu–O(14)	97.6(1)	O(1)–Cu–N(25)	98.0(1)
O(14)–Cu–N(25)	81.6(1)	N(12)–Cu–N(25)	169.1(1)
O _w –Cu–O(1)	94.8(1)	N(12)–Cu–O _w	95.1(1)
N(25)–Cu–O _w	95.8(1)	O(14)–Cu–O _w	94.0(1)
Anions			
O(1)–C(2)	125.5(4)	O(1)–C(2)–C(3)	117.7(3)
C(3)–C(2)	147.8(6)	C(3)–C(2)–C(9)	125.0(3)
C(2)–C(9)	144.5(5)	C(2)–C(9)–C(10)	127.2(4)
C(10)–C(9)	142.9(5)	C(10)–C(9)–N(12)	118.5(3)
O(13)–N(12)	125.9(4)	O(13)–N(12)–Cu	127.2(2)
C(9)–N(12)	133.3(5)	C(9)–N(12)–O(13)	120.4(3)
O(14)–C(15)	125.3(4)	O(14)–C(15)–C(16)	117.6(3)
C(22)–C(15)	144.2(6)	C(22)–C(15)–O(14)	116.8(4)
C(15)–C(16)	146.8(6)	C(15)–C(16)–C(17)	117.5(3)
N(25)–C(22)	134.0(5)	N(25)–C(22)–C(15)	114.8(3)
C(23)–C(22)	144.9(5)	C(23)–C(22)–N(25)	117.9(4)
N(24)–C(23)	112.9(5)	N(24)–C(23)–C(22)	177.5(5)
O(26)–N(25)	124.9(4)	O(26)–N(25)–Cu	127.5(3)

the chelate ring Cu–N(12)–C(9)–C(2)–O(1) and the nearest phenyl group is 3.5°, while the dihedral angle between the chelate ring Cu–N(25)–C(22)–C(15)–O(14) and its neighbouring phenyl group is 11.1°. The average deviation of an atom from the least-squares plane of O(13)–N(12)–C(9)–C(10)–N(11) is 1.6 pm, while that from the plane O(26)–N(25)–C(22)–C(23)–N(24) is 0.2 pm. The copper(II) ion is co-ordinated by two atoms of each ligand forming two five-membered metalocycles which are essentially planar. The average deviations of the atoms from the planes Cu–O(1)–C(2)–C(9)–N(12) and Cu–O(14)–C(15)–C(22)–N(25) are 0.9 and 1.9 pm, respectively. The dihedral angle between these two planes is 10.6°. The co-ordination polyhedron of Cu^{II} in this complex can be described as a distorted square pyramid, with the central metal atom being 17 pm out of the plane [N(25)–O(1)–N(12)–O(14)] towards the water oxygen (Fig. 4). The angle between the line joining the Cu to O_w and the least-squares plane of the rectangular base is 89.4°.

The co-ordination of the copper ion in $[\text{CuL}_2(4\text{-mpy})_2]$ differs from that in $[\text{CuL}_2(\text{H}_2\text{O})]$ (see Figs. 2 and 3). One of the L[–] anions functions as a bidentate ligand, similar to the two in $[\text{CuL}_2(\text{H}_2\text{O})]$, while the second acts as a monodentate ligand interacting with the metal ion only through the nitrogen of the NO group. It is unusual when two identical ligands in the same complex have different co-ordination modes. Both benzoylcyanoxy ligands in the structure are essentially non-planar as the phenyl groups are rotated out of the plane of the cyanoxime core atoms (Fig. 3). The average deviation of an atom from the least-squares plane of the core atoms O(14)–C(15)–C(22)–C(23)–N(24)–O(26)–N(25) in the monodentate ligand is 4.2 pm, while that of an atom from the least-squares plane of the cyanoxime fragment O(13)–N(12)–C(9)–C(10)–N(11)–O(1)–C(2) of the bidentate ligand is 2.4 pm. The phenyl rings in the L[–] ligands form dihedral angles between the planar cyanoxime fragments of 27.3° in the chelating ligand and 51.3° in the monodentate anion. The chelating atoms of the bidentate ligand and Cu^{II} form a nearly planar group, Cu–O(1)–C(2)–C(9)–N(12), with an average deviation of an atom from the plane of 2 pm. The monodentate L[–] anion in turn forms a plane C(15)–C(22)–N(25)–O(26)–Cu with an average deviation from the plane of 8.6 pm. The dihedral angle between these two planes is 7.6°. Both ligands are in a *cis-anti* configuration and have nitroso character as shown by the bond lengths of the >CNO fragment (Table 4). The co-ordination polyhedron of

Table 4 Selected bond lengths (pm) and angles (°) for $[\text{CuL}_2(4\text{-mpy})_2]$

Co-ordination polyhedron			
Cu–O(1)	229.8(3)	Cu–N(34)	201.4(3)
Cu–N(12)	202.5(3)	Cu–N(27)	202.5(3)
Cu–N(25)	202.6(3)		
O(1)–Cu–N(12)	75.7(1)	O(1)–Cu–N(25)	102.4(1)
N(12)–Cu–N(25)	176.3(1)	O(1)–Cu–N(27)	91.9(1)
N(25)–Cu–N(27)	88.8(1)	O(1)–Cu–N(34)	91.4(1)
N(34)–Cu–N(25)	93.5(1)	N(12)–Cu–N(27)	88.2(1)
N(27)–Cu–N(34)	175.5(1)	N(12)–Cu–N(34)	89.7(1)
Chelating anion			
O(1)–C(2)	123.9(4)	N(11)–C(10)	113.6(6)
C(3)–C(2)	149.0(6)	O(13)–N(12)	126.0(4)
C(2)–C(9)	146.4(5)	C(9)–N(12)	134.2(5)
C(10)–C(9)	143.4(5)		
O(1)–C(2)–C(3)	118.4(3)	C(9)–N(12)–O(13)	120.5(3)
C(3)–C(2)–C(9)	122.4(3)	Cu–O(1)–C(2)	110.8(2)
C(2)–C(9)–C(10)	126.5(3)	Cu–N(12)–C(9)	118.0(2)
C(10)–C(9)–N(12)	117.4(3)	O(1)–C(2)–C(9)	119.2(3)
N(11)–C(10)–C(9)	176.1(5)	C(2)–C(9)–N(12)	116.1(3)
O(13)–N(12)–Cu	121.5(2)		
Monodentate anion			
O(14)–C(15)	123.5(4)	C(23)–C(22)	142.8(5)
C(16)–C(15)	149.5(6)	N(24)–C(23)	113.7(6)
C(15)–C(22)	145.0(5)	O(26)–N(25)	125.8(4)
N(25)–C(22)	133.6(5)		
O(14)–C(15)–C(16)	119.6(3)	N(24)–C(23)–C(22)	178.7(5)
C(16)–C(15)–C(22)	119.6(3)	O(26)–N(25)–C(22)	120.5(3)
C(15)–C(22)–C(23)	123.8(4)	Cu–N(25)–C(22)	119.7(2)
N(25)–C(22)–C(15)	117.9(3)	Cu–N(25)–O(26)	119.4(3)
C(23)–C(22)–N(25)	118.3(3)	O(14)–C(15)–C(22)	120.8(3)

**Fig. 3** Molecular structure of $[\text{CuL}_2(4\text{-mpy})_2]$ showing the atom numbering scheme. Hydrogen atoms are omitted for clarity

the Cu^{II} can best be described as a distorted square pyramid with the oxygen atom O(1) at its apex (Fig. 3). The Cu–O(1) bond length is long compared to the Cu–N bond distances (Table 4). The central atom is 1.8 pm out of the rectangular plane comprising N(25), N(34), N(12) and N(27) towards O(1), and the Cu–O(1) bond makes an angle of 76.7° with the base plane (Fig. 4). The interatomic distance between the copper ion and O(14) is 249 pm, which together with other structural differences in the ligands suggests that it is not included in the co-ordination sphere of the metal ion. The two 4-methylpyridine ligands have normal geometries and co-ordination for these species in complexes.

The DTA analysis data for $[\text{CuL}_2(4\text{-mpy})_2]$ are unusual (Fig. 5). There is an extremely sharp exothermic peak which can be assigned to the chelating effect as O(14) interacts with the copper ion to form a five-membered ring after the loss of two molecules of 4-mpy at 190 °C. The CuL₂ which forms is a

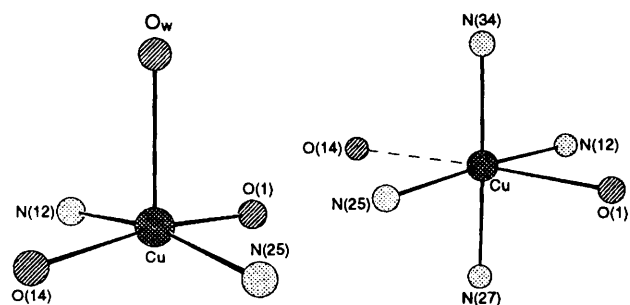


Fig. 4 Co-ordination polyhedrons of the copper(II) atoms in the structures of $[\text{CuL}_2(\text{H}_2\text{O})]$ and $[\text{CuL}_2(4\text{-mpy})_2]$

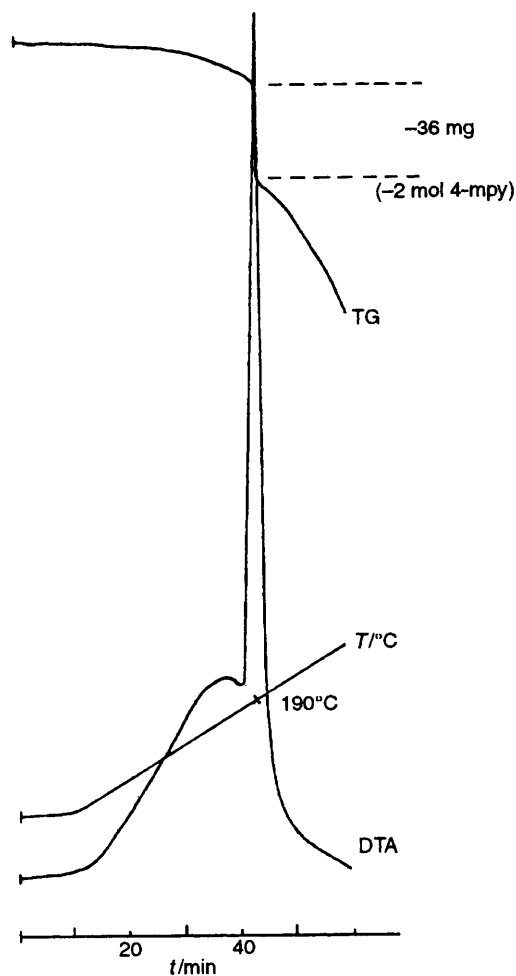


Fig. 5 Thermal analysis data for the $[\text{CuL}_2(4\text{-mpy})_2]$ complex. Sample weight: 120 mg

volatile compound which continuously sublimes after 200 °C causing a weight loss. Other complexes of Cu^{II} and Ni^{II} which have been examined demonstrate a common behaviour upon heating, showing the expected weight losses and thermal effects, but the copper salts all form volatile products which are similar to the respective copper β -diketonates.

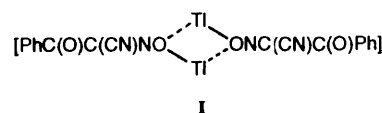
The different binding modes found for the L^- anion are summarized in Table 5. The benzoylcyanoxime anion in the complex SbPh_4L exhibits monodentate co-ordination *via* the oxygen atom of the oxime group.⁵ The $\text{O}(1)\text{-N}(1)$ bond length is slightly longer than that of $\text{N}(1)\text{-C}(25)$.⁵ The anion has a planar structure and has a *trans-anti* configuration of the $>\text{CNO}$ group relative to the carbonyl group. The compounds SbPh_4L and $\text{SbPh}_3\text{L}(\text{Cl})$ form molecular solutions in benzene, but ionize in dimethylsulfoxide and hot dimethylformamide according to equation (1) ($n = 0$ or 1; solv = solvent).



The antimony(v) atom has a distorted trigonal-bipyramidal co-ordination (SbC_4O) (Table 5). This is unexpected because of the ability of this element to form six, seven or eight-co-ordinated compounds. It is interesting that in this particular case the IR spectroscopic data had established that the L^- ligand shows a monodentate co-ordination mode prior to the crystal structure study.

In the complex $[\text{Tl}(18\text{-crown-6})\text{L}]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) the anion also exhibits monodentate co-ordination to the metal ion *via* the oxygen atom of the nitroso group (Table 5). It adopts the *trans-anti* non-planar configuration. The co-ordination number of the Tl^{I} in this complex is seven and the geometry can be described as a distorted hexagonal pyramid.²⁵

In the complex TlL the anion functions as a tridentate bridging ligand using oxygen atoms of the nitroso and carbonyl groups (Table 5). The anion is non-planar and also has a *trans-anti* configuration. The dihedral angle between the cyanoxime fragment and the plane of carbonyl group is 8°. ²⁶ The co-ordination polyhedron of the Tl^{I} having a stereoactive $6s^2$ lone pair can be described as a distorted tetrahedron. The packing mode in the crystal involves polymeric chains comprised of dimeric centrosymmetrical units **I**.



In the complex AgL the ligand acts as a bidentate anion and also as a bridge forming three additional bonds to the silver atoms of neighbouring molecules (Table 5). The anion is in the nitroso form and has a *cis-anti* configuration of the CNO and carbonyl groups. It is non-planar, with a torsion angle of 48° between the main plane $\text{N}(2)\text{-C}(2)\text{-C}(1)\text{-C}(3)\text{-O}(2)$ and the phenyl group.²⁶ This significant deviation from planarity is responsible for the unusual colour of this salt, which can be explained in terms of the diminishing conjugation in the anion. The two $\text{Ag}\text{-N}$ bonds are especially short which indicates the formation of covalent bonds, while the remaining three $\text{Ag}\text{-O}$ bonds are longer and have ionic character. The co-ordination polyhedron of the silver atom can be described as a distorted trigonal bipyramid.

The X-ray structural data for complexes of the ambidentate benzoylcyanoxime anion discussed in this paper clearly show the significant influence of certain central atoms on the co-ordination mode of the anion. Specific interactions between a given central metal ion and the ligand during bond formation are responsible for the choice of co-ordination mode in different complexes.

Experimental

Preparation of compounds

The co-ordination compounds were synthesized according to Scheme 3. Reaction (2) is generally the most convenient way to prepare thallium(I) complexes with oximes.¹ The best way to prepare copper compounds is shown in reaction (4). Thus, the copper(II) complexes were prepared from metallic copper powder (70 mesh) in methanol in the presence of a stoichiometric amount of the free cyanoxime and the respective amine. The reaction time is 25 min when am = pyridine, and 180 min when am = 2-methylpyridine. Crystals suitable for X-ray analysis were obtained from these reaction mixtures. Details for several key compounds are given below.

HL. Benzoylacetonitrile $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{CN}$ (Aldrich) (20 g, 0.138 mol) was dissolved in a mixture of glacial acetic acid (15.8

Table 5 Observed co-ordination modes for $C_6H_5C(O)C(NO)CN$

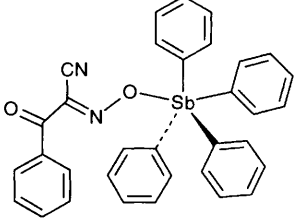
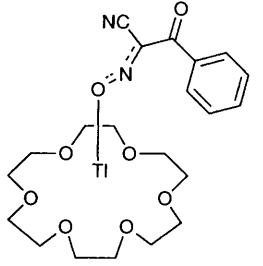
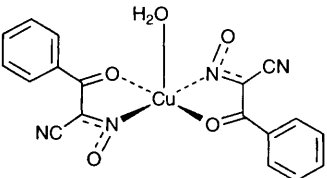
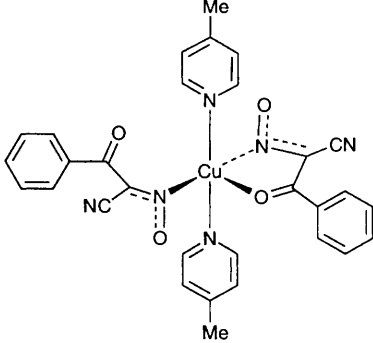
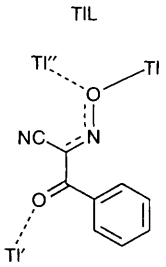
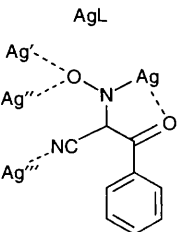
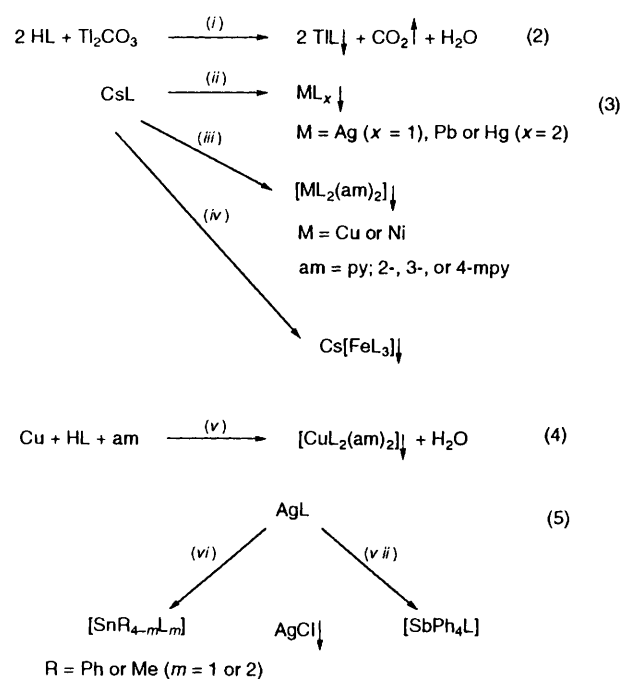
Compound	Comments	Ref.
<p style="text-align: center;">SbPh₄L</p>  <p style="text-align: center;">[Ti(18-crown 6)L]</p>	<p>Monodentate ligand, <i>trans-anti</i> planar configuration, oxime form Trigonal-bipyramidal co-ordination polyhedron (Sb^VC₄O)</p>	5
 <p style="text-align: center;">[CuL₂(H₂O)]</p>	<p>Monodentate anion, <i>trans-anti</i> non-planar configuration, nitroso form</p>	25
 <p style="text-align: center;">[CuL₂(4-mpy)₂]</p>	<p>Bidentate chelate ligand, planar <i>cis-anti</i> configuration, nitroso form</p>	This work
 <p style="text-align: center;">TIL</p>	<p>Both bidentate chelate and monodentate co-ordination of the anion, <i>cis-anti</i> configuration, nitroso form</p>	This work
 <p style="text-align: center;">AgL</p>	<p>Three-co-ordinated bridged ligand, non-planar <i>trans-anti</i> configuration, nitroso form Distorted TIO₃ tetrahedron counting the 6s lone pair</p>	26
	<p>Five-co-ordinated anion, both chelate and bridging, <i>cis-anti</i> configuration, nitroso form Distorted trigonal-bipyramidal AgN₂O₃ co-ordination</p>	26

Table 6 Crystal and refinement data *

	[CuL ₂ (H ₂ O)]	[CuL ₂ (4-mpy) ₂]
Formula	C ₁₈ H ₁₂ CuN ₄ O ₅	C ₃₀ H ₂₄ CuN ₆ O ₄
Crystal size/mm	0.1 × 0.2 × 0.4	0.14 × 0.30 × 0.32
<i>a</i> /pm	852.2(4)	1064.7(2)
<i>b</i> /pm	933.2(3)	1074.6(2)
<i>c</i> /pm	1143.7(5)	1267.9(2)
α /°	87.71(3)	87.47(1)
β /°	89.81(3)	86.51(2)
γ /°	70.70(3)	83.10(2)
<i>U</i>	0.8578(6)	1.4365(5)
<i>D_c</i> /kg m ⁻³	1.657	1.378
μ /mm	1.314	0.806
Total reflections	3265	5381
Number of independent reflections [<i>F</i> > 6.0σ(<i>F</i>)]	2362	3329
<i>F</i> (000)	434	614
Weighting scheme, <i>w</i> ⁻¹	σ ² (<i>F</i>) + 0.0067 <i>F</i> ²	Unit weights
<i>R</i>	0.042	0.036
<i>R</i> '	0.062	0.038

* Details in common: triclinic, space group *P* $\bar{1}$; *Z* = 2.



Scheme 3 (i) Heat, water; (ii) M(NO₃)_x, water; (iii) MCl₂, 4 am, water; (iv) FeCl₂·4H₂O, water; (v) O₂ (air), MeOH; (vi) SnR_{4-m}Cl_m, MeCN; (vii) SbPh₄Cl, MeCN

cm³, 0.276 mol) and PrⁱOH (400 cm³). The reaction mixture was cooled to -5 °C, and a solution of NaNO₂ (11.42 g, 0.165 mol) in water (20 cm³) was added dropwise over 20 min. The reaction flask was then cooled in an ice-bath for 2 h followed by evaporation on a Rotavap to form a viscous oil. This was extracted five times by 100 cm³ portions of diethyl ether. Charcoal (3 g) was added to the combined ether layers to decolourize the solution which was left for 2 d. The almost colourless solution was then filtered and dried over anhydrous Na₂SO₄ overnight. Evaporation of the ether solution gave 24 g of HL, which had a slightly yellow colour. Yield 96%, m.p. 119 °C (ether). This product can be further purified either through its Ag⁺ salt followed by the addition of 5% HCl and rapid extraction by diethyl ether, or by means of recrystallization from CHCl₃. NMR [(CD₃)₂SO]: ¹H, δ 7.56–7.91 (aromatic protons) and 15.12 (oxime); ¹³C, δ 108.7 (CN), 185.4 (carbonyl), 135.2, 134.1, 130.7 and 128.9 (phenyl).

CsL. The oxime (1 g, 5.8 mmol), was dissolved in PrⁱOH (50 cm³) and Cs₂CO₃ (0.94 g, 2.9 mmol) was added followed by

Table 7 Positional parameters (× 10⁴) for the non-hydrogen atoms of CuL₂(H₂O)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu	1352(1)	2085(1)	729(1)
O(1)	2496(3)	3294(3)	-131(2)
C(2)	3467(4)	2604(4)	-908(3)
C(3)	4342(5)	3469(4)	-1608(3)
C(4)	4088(5)	4947(5)	-1341(4)
C(5)	4850(6)	5834(5)	-1952(4)
C(6)	5858(6)	5248(5)	-2868(4)
C(7)	6161(8)	3792(6)	-3136(5)
C(8)	5393(8)	2882(6)	-2517(5)
C(9)	3658(4)	1024(4)	-1040(3)
C(10)	4788(5)	-14(4)	-1789(3)
N(11)	5720(5)	-912(4)	-2333(3)
N(12)	2738(4)	494(3)	-309(3)
O(13)	2827(3)	-880(3)	-311(2)
O(14)	517(3)	764(3)	1740(2)
C(15)	-304(4)	1395(4)	2600(3)
C(16)	-1072(5)	496(4)	3344(3)
C(17)	-631(6)	-1039(5)	3156(4)
C(18)	-1272(6)	-1977(5)	3824(4)
C(19)	-2388(6)	-1364(5)	4707(4)
C(20)	-2850(7)	156(6)	4890(4)
C(21)	-2206(6)	1095(5)	4219(4)
C(22)	-409(4)	2945(4)	2771(3)
C(23)	-1220(5)	3893(4)	3718(3)
N(24)	-1837(6)	4672(4)	4437(3)
N(25)	355(4)	3541(3)	1956(3)
O(26)	347(4)	4878(3)	2008(2)
O _w	-857(4)	2789(4)	-432(3)

vigorous stirring. The solution immediately turned bright orange, and after the liberation of CO₂, was evaporated to dryness. The extremely hygroscopic orange caesium salt was obtained in nearly 100% yield. The hygroscopic property of the salt made further work with it very inconvenient. A solution of CsL in MeCN or in alcohols was always used as the initial L⁻ carrier instead of the solid salt. Thus, a solution of L⁻ had to be prepared each time prior to the synthesis of the complexes of Cu^{II}, Ni^{II} or Fe^{II}.

AgL. A solution containing AgNO₃ (2.94 g) in water (10 cm³) was added rapidly to a solution containing CsL (5.28 g) in PrⁱOH (20 cm³) or MeCN with vigorous stirring at room temperature. A violet microcrystalline precipitate of AgL immediately formed. The solid was filtered off, washed with water and then methanol, and dried in a desiccator. This salt was widely used for the synthesis of benzoylcyanoximate derivatives of the organo-tin(IV) and -antimony(V).

Table 8 Positional parameters ($\times 10^4$) for the non-hydrogen atoms of $[\text{CuL}_2(4\text{-mpy})_2]$

Atom	x	y	z	Atom	x	y	z
Cu	1980(1)	2777(1)	2632(1)	C(21)	4959(4)	6342(4)	1688(3)
O(1)	1286(3)	1038(3)	1972(2)	C(22)	2654(3)	4963(3)	1359(3)
C(2)	1176(3)	219(3)	2679(3)	C(23)	2806(4)	5692(4)	400(3)
C(3)	622(3)	-932(3)	2420(3)	N(24)	2925(5)	6252(4)	-374(3)
C(4)	689(4)	-1246(4)	1374(3)	N(25)	2042(3)	3950(3)	1340(2)
C(5)	124(5)	-2235(5)	1050(4)	O(26)	1621(3)	3648(3)	494(2)
C(6)	-504(5)	-2943(4)	1784(4)	N(27)	3816(3)	2123(3)	2284(3)
C(7)	-597(5)	-2643(5)	2833(4)	C(28)	4191(4)	1698(4)	1322(3)
C(8)	-39(4)	-1644(4)	3155(3)	C(29)	5428(4)	1250(4)	1062(4)
C(9)	1581(3)	415(3)	3736(3)	C(30)	6333(4)	1212(4)	1806(4)
C(10)	1633(4)	-477(4)	4612(3)	C(31)	7692(5)	716(5)	1544(5)
N(11)	1701(4)	-1136(4)	5338(3)	C(32)	5935(4)	1640(4)	2791(4)
N(12)	1997(3)	1523(3)	3874(2)	C(33)	4686(4)	2089(4)	3007(3)
O(13)	2382(3)	1768(3)	4753(2)	N(34)	197(3)	3469(3)	3089(2)
O(14)	2761(3)	4731(3)	3194(2)	C(35)	-89(4)	3733(3)	4108(3)
C(15)	3075(3)	5290(3)	2366(3)	C(36)	-1283(4)	4177(3)	4478(3)
C(16)	3917(4)	6303(3)	2401(3)	C(37)	-2256(4)	4368(4)	3799(3)
C(17)	3724(4)	7140(4)	3203(4)	C(38)	-3576(4)	4857(4)	4178(4)
C(18)	4565(6)	8006(5)	3312(5)	C(39)	-1963(4)	4085(4)	2751(3)
C(19)	5609(6)	8023(5)	2611(6)	C(40)	-743(4)	3644(4)	2425(3)
C(20)	5803(5)	7208(6)	1811(5)				

The compounds synthesized were analysed for C, H, N composition using a Carlo Erba Strumentazione C1600 apparatus. The percentage Cu, Ni or Pb was determined by volumetric titration with ethylenediaminetetraacetate, while the silver(I) was determined using Folgard's titration with NCS^- ions. Thallium(I) and Fe were determined using atomic absorption. Tin was analysed by means of SnO_2 gravimetry. The analytical and spectroscopic data confirmed the proposed molecular formulae.

Physical methods

Proton and ^{13}C NMR spectra of benzoylcyanoxime were recorded at 298 K using a Bruker CXP-200 FT spectrometer with standard one-pulse sequences. The internal standard was SiMe_4 . The IR spectra were recorded on an IR-20 (Karl Zeiss, Jena) spectrometer using KBr pellets or Nujol for the complexes of Hg, Pb, Ag and Tl. The exact assignment of vibrations including the $>\text{C}-\text{N}-\text{O}$ fragment was done by means of a careful analysis of IR spectra of ^{15}N (50%) enriched compounds. Synthesis of isotopomeric complexes were carried out using $\text{Na}^{15}\text{NO}_2$ as the source of ^{15}N for the ligand, and were no different from that described above. Electronic absorption spectra of several compounds in the visible region ($30\,000\text{--}11\,000\text{ cm}^{-1}$) were obtained using a Specord M40 (Karl Zeiss, Jena) spectrometer. Those of CsL, TIL and NH_4L were recorded in water and EtOH, while for the remaining complexes solid-state diffuse reflectance spectra were recorded relative to MgO .

Magnetic moments for several 3d-metal complexes were determined using the Gouy method at room temperature. Diamagnetic corrections were calculated using Pascal constants.²⁷ The χ_g values²⁸ of $\text{Co}[\text{Hg}(\text{SCN})_4]$ and $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) as standard substances were used for the magnetic field (2400–4400 G) calibration. The thermomagnetic behaviour of the nickel(II) and copper(II) complexes was not studied since their measured magnetic moments at room temperature were not significantly different from the spin-only values for monomeric compounds.

Differential thermal analysis (DTA) using a derivatograph Q1500 (Karl Zeiss, Jena) was used to study the thermal behaviour of the amine complexes of Cu^{II} and Ni^{II} . Each sample (120 mg) was mixed with dried Al_2O_3 (100 mg) as the inert matrix.

Crystallography

Clear single crystals of $[\text{CuL}_2(\text{H}_2\text{O})]$ and $[\text{CuL}_2(4\text{-mpy})_2]$ were selected after slow evaporation of the solvent from the mother-liquors in a desiccator over concentrated sulfuric acid. Crystal and intensity data were collected using a Siemens R3m/V automated X-ray diffractometer at 293 K with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7107\text{ \AA}$). The crystal data and experimental details are summarized in Table 6. The intensity data were collected using the $\theta\text{--}2\theta$ mode and a variable scan rate. Three standard reflections were measured every 97 (about 1.5 h) for both sets of data. They showed no systematic changes, indicating both electronic and crystal stability.

Both structures were solved using direct methods and refined using full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically on F . With the exception of the water hydrogens in $[\text{CuL}_2(\text{H}_2\text{O})]$, the positions of the hydrogen atoms were calculated and these atoms were allowed to ride on their neighbouring heavy atoms during the final refinement procedures. The water hydrogens were located in a difference map and the riding model was also used for them. All hydrogen atoms were assigned isotropic thermal parameters which were not refined. Atomic scattering factors for the atoms were obtained from ref. 29. The program used was SHELXTL PLUS.³⁰ Atomic coordinates for $[\text{CuL}_2(\text{H}_2\text{O})]$ and $[\text{CuL}_2(4\text{-mpy})_2]$ are given in Tables 7 and 8.

Structure factors and hydrogen-atom parameters can be obtained from N. K. D. Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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