Partially Encapsulated Copper(I) Complexes of Mono(*o*-aryl)-substituted Derivatives of 2,2′-Bipyridine and 1,10-Phenanthroline†

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Copper(I) complexes of the potentially terdentate ligands 6-(2-dimethylaminophenyl)-2,2′-bipyridine (L^1) and 2-(2-dimethylaminophenyl)-1,10-phenanthroline (L^2), [CuL_2][PF_6] (L = L^1 **1** or L^2 **2**), have been prepared. Both complexes have highly distorted tetrahedral structures in which only the α,α′-diimine fragments are co-ordinated; the $C_6H_4NMe_2$ fragments are pendant, and are twisted with respect to the co-ordinated bipyridine and phenanthroline fragments such that the pendant aromatic ring of one ligand lies stacked with the co-ordinated fragment of the other ligand. This results in 'partial encapsulation' of the copper(I) centres which confers chemical stability (no autoxidation in the presence of O_2) and electrochemical stability (wide 'redox-existence ranges' for the Cu^I oxidation states) on the complexes. The inter-ligand stacking also results in distortion away from pseudo-tetrahedral geometry at the metal centres towards square planar (θ, the angle of intersection of the two CuN_2 planes, is 75° for **1** and 76° for **2**); ^1H NMR and electronic spectra show that this is maintained in solution. Neither complex is luminescent at room temperature, possibly due to intramolecular quenching *via* transient co-ordination of the pendant amine groups. Oxidation of **1** and **2** to the copper(II) complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ with ferrocenium affords stable solutions whose EPR spectra indicate that the metals now have geometries that are much more flattened towards square-planar geometry; this would not be possible with more highly encapsulated complexes of bipyridines or phenanthrolines with two pendant aryl substituents in the *ortho* positions.

Continuing our recent studies[1-3] on the co-ordination chemistry of new mixed-donor polydentate ligands, we describe in this paper the synthesis and co-ordination behaviour of copper(I) complexes of the potentially terdentate N-donor ligands 6-(2-dimethylaminophenyl)-2,2′-bipyridine (L^1) and 2-(2-dimethylaminophenyl)-1,10-phenanthroline (L^2). We showed in earlier papers how these ligands could act as conventional N_3-donor ligands to palladium(II)[2] and ruthenium(II)[3] and, somewhat unexpectedly, as N,N,C-cyclometallating ligands to Ru^{II} *via* a 'turned-around' co-ordination of the phenyl ring with the NMe_2 group pendant.[3] Both Pd^{II} and Ru^{II} have strong stereoelectronic requirements and the structures of the complexes obtained reflect this; we therefore decided to see how L^1 and L^2 behaved with a kinetically labile metal ion having no stereoelectronic requirements. Accordingly, the syntheses, crystal structures, electrochemical, spectroscopic and luminescence properties of [CuL_2][PF_6] (L = L^1 **1** or L^2 **2**) are described.

Experimental

Details of the equipment used for the spectroscopic and electrochemical studies are as described earlier.[1-3] The ligands L^1 and L^2 were prepared as previously described.[3] The compound [$Cu(MeCN)_4$][PF_6] was prepared according to a published method.[4]

Preparation of [$Cu(L^1)_2$][PF_6] **1** *and* [$Cu(L^2)_2$][PF_6] **2**.—To a stirred solution of L^1 (for **1**) or L^2 (for **2**) (1 mmol) in methanol (20 cm^3) was added [$Cu(MeCN)_4$][PF_6] (0.186 g, 0.5 mmol). The mixture immediately became dark brown. After stirring for 1 h the solution was concentrated *in vacuo* and cooled; in each case a brown microcrystalline solid precipitated which was filtered off, washed with diethyl ether and dried. The brown solids (yield: 80%) were crystallised from CH_2Cl_2–hexane. Data for **1**: FAB mass spectrum, *m/z* 613 [$\{Cu(L^1)_2\}^+$], 338 [$\{CuL^1\}^+$] (Found: C, 56.7; H, 4.4; N, 10.7. Calc. for $C_{36}H_{34}CuF_6N_6P$: C, 57.0; H, 4.5; N, 11.1%). Data for **2**: FAB mass spectrum, *m/z* 661 [$\{Cu(L^2)_2\}^+$], 362 [$\{CuL^2\}^+$] (Found: C, 59.5; H, 4.4; N, 10.0. Calc. for $C_{40}H_{34}CuF_6N_6P$: C, 59.5; H, 4.2; N, 10.4%).

Crystal-structure Determinations.—X-Ray quality crystals of complexes **1** and **2** were grown from CH_2Cl_2–hexane as brown blocks. The crystals selected were sealed in glass capillary tubes in an atmosphere saturated with the vapour of the recrystallisation solvent mixture, as a precaution against solvent loss. Data were collected using a Siemens R3m/V four-circle diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 73 Å). The data were corrected for Lorentz and polarization effects, and for absorption using an empirical method based on azimuthal scan data.[5] Details of the crystal data and intensity collection are summarised in Table 1.

Both structures were solved by conventional heavy-atom methods. Successive Fourier-difference syntheses were used to locate all non-hydrogen atoms; hydrogen atoms were included in calculated positions. All initial calculations were performed with a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[5] The final least-squares refinements on F^2 were carried out on a Silicon Graphics Indigo R4000 computer using SHELX 93.[5] Scattering factors with corrections for anomalous dispersion were taken from ref. 6.

Additional material available from the Cambridge Crystallographic Date Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp.xxv–xxx.

Results and Discussion

Preparation, Characterisation and Crystal structures of Complexes **1** *and* **2**.—Reaction of either ligand with $[Cu(MeCN)_4][PF_6]$ in methanol afforded brown precipitates; FAB mass spectra and elemental analyses suggested the formulations $[Cu(L^1)_2][PF_6]$ for **1** and $[Cu(L^2)_2][PF_6]$ for **2**. If L^1 and L^2 were behaving as terdentate donors, this would require six-co-ordinate Cu^I centres, which is unlikely.

The crystal structure of complex of **1** is shown in Fig. 1. Bond lengths and angles are given in Table 2, and atomic coordinates in Table 3. The complex is four-co-ordinate, with only the bipyridine fragments of L^1 co-ordinated and the $C_6H_4NMe_2$ groups pendant. The geometry is best described as distorted tetrahedral, with the two ligands non-equivalent; the co-ordinated bipyridine fragments are not planar, having torsion angles of *ca.* 3° between rings 2 and 3, and *ca.* 23° between rings 5 and 6. The Cu–N bond lengths vary from 1.983(2) Å [Cu–N(61)] to 2.090(2) Å [Cu–N(51)], which is a much wider range than observed in, for example, the more symmetrical complex $[Cu(dmbipy)_2][BF_4]$ (dmbipy = 6,6′-dimethyl-2,2′-bipyridine) where the Cu–N distances vary between 2.018 and 2.052 Å.[7] In many $[Cu(N\text{–}N)_2]^+$ complexes (where N–N signifies an α,α'-diimine) there is a distortion away from pseudo-tetrahedral (really D_{2d}) geometry towards planarity. This distortion is defined by the dihedral angle θ between the two CuN_2 planes: thus, θ is 0° for planar complexes and 90° for 'tetrahedral' complexes. In copper(I) complexes of substituted bipyridines and phenanthrolines, θ is typically 70–80°,[7–9] and the value of θ for **1** is therefore typical at 75°. The pendant aromatic rings are twisted with respect to the bipyridine fragments (torsion angles *ca.* 59° between rings 1 and 2, and *ca.* 61° between rings 3 and 4), so that they can overlap with a section of the other ligand resulting in π-stacking interactions with the average separation between overlapping segments

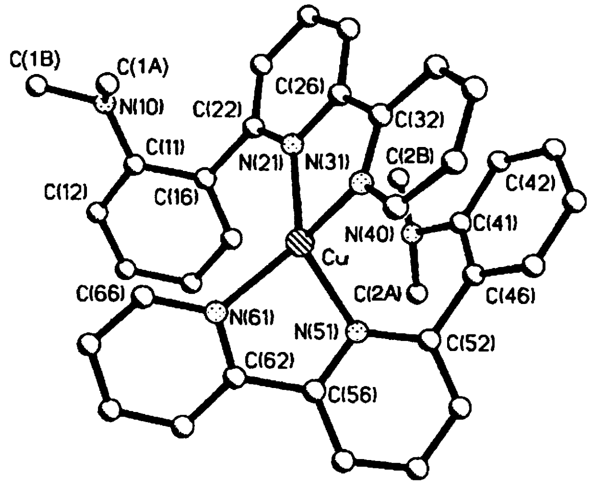

Fig. 1 Crystal structure of the cation of complex **1**

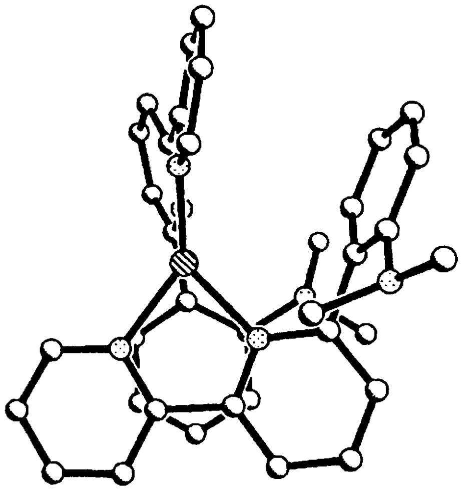

Fig. 2 Alternative view of **1** emphasising the aromatic stacking interactions

Table 1 Summary of crystal details, data collection and refinement for $[Cu(L^1)_2][PF_6]$ **1** and $[Cu(L^2)_2][PF_6]$ **2**

	1	**2**
Formula	$C_{36}H_{34}CuF_6N_6P$	$C_{40}H_{34}CuF_6N_6P$
M	759.2	807.2
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	9.223(4)	8.395(3)
b/Å	10.702(5)	27.506(11)
c/Å	17.710(7)	15.725(7)
α/°	88.59(3)	90
β/°	86.88(3)	90.89(3)
γ/°	84.53(3)	90
U/Å^3	1737.2(13)	3631(3)
Z	2	4
D_c/g cm^{-3}	1.451	1.477
μ(Mo-Kα)/mm^{-1}	0.743	0.716
$F(000)$	780	1656
Crystal dimensions/mm	0.8 × 0.4 × 0.3	0.7 × 0.3 × 0.3
Unique reflections measured	6085	4729
2θ Range/°	5.0 to 50.0	4.0 to 45.0
Index ranges	$-10 \leqslant h \leqslant 0$; $-12 \leqslant k \leqslant 12$; $-21 \leqslant l \leqslant 21$	$0 \leqslant h \leqslant 9$; $0 \leqslant k \leqslant 29$; $-16 \leqslant l \leqslant 16$
Final residuals		
wR_2[a]	0.102	0.123
R_1[b]	0.038	0.049
Weighting factors: a, b	0.0447, 1.0598	0.047, 3.6332
Largest difference peak, hole/e Å^{-3}	0.439, −0.276	0.314, −0.221

Details in common, collection method, Wyckoff ω-scan; refinement method, full-matrix least-squares on all F^2 data. [a] Structure was refined on F_o^2 using all data: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [b] The R_1 value is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$.

Table 2 Selected internuclear distances (Å) and angles (°) for complex **1**

Cu-N(61)	1.983(2)	Cu-N(31)	2.014(2)	Cu-N(21)	2.047(2)
Cu-N(51)	2.090(2)	N(21)-C(22)	1.347(3)	N(21)-C(26)	1.358(3)
N(31)-C(36)	1.339(4)	N(31)-C(32)	1.340(3)	N(51)-C(56)	1.349(3)
N(51)-C(52)	1.354(3)	N(61)-C(66)	1.338(3)	N(61)-C(62)	1.350(3)
N(61)-Cu-N(31)	136.87(10)	N(61)-Cu-N(21)	122.85(9)	N(31)-Cu-N(21)	81.27(9)
N(61)-Cu-N(51)	81.73(9)	N(31)-Cu-N(51)	111.76(9)	N(21)-Cu-N(51)	129.14(9)
C(22)-N(21)-C(26)	118.7(2)	C(22)-N(21)-Cu	129.1(2)	C(26)-N(21)-Cu	112.1(2)
C(36)-N(31)-C(32)	118.3(2)	C(36)-N(31)-Cu	127.5(2)	C(32)-N(31)-Cu	113.5(2)
C(56)-N(51)-C(52)	118.6(2)	C(56)-N(51)-Cu	110.4(2)	C(52)-N(51)-Cu	128.4(2)
C(66)-N(61)-C(62)	117.5(2)	C(66)-N(61)-Cu	126.7(2)	C(62)-N(61)-Cu	114.4(2)

Table 3 Atomic positional parameters (fractional coordinates × 10^4) for complex **1** with estimated standard deviations in parentheses

Atom	x	y	z
Cu	247(1)	105(1)	2820(1)
N(10)	−4412(3)	−2038(2)	2715(1)
C(1A)	−3641(4)	−2286(3)	3405(2)
C(1B)	−5345(4)	−3044(3)	2594(2)
C(11)	−3598(3)	−1602(2)	2085(2)
C(12)	−3443(4)	−2239(3)	1403(2)
C(13)	−2643(4)	−1803(3)	793(2)
C(14)	−1947(4)	−734(3)	838(2)
C(15)	−2085(3)	−75(3)	1509(2)
C(16)	−2911(3)	−480(2)	2126(2)
N(21)	−1896(2)	563(2)	3150(1)
C(22)	−3106(3)	316(2)	2809(2)
C(23)	−4478(3)	806(3)	3072(2)
C(24)	−4611(3)	1556(3)	3696(2)
C(25)	−3386(3)	1761(3)	4067(2)
C(26)	−2045(3)	1254(2)	3787(1)
N(31)	525(2)	737(2)	3859(1)
C(32)	−673(3)	1369(2)	4173(2)
C(33)	−619(4)	2041(3)	4829(2)
C(34)	679(4)	2049(3)	5170(2)
C(35)	1895(4)	1385(4)	4858(2)
C(36)	1780(3)	746(3)	4205(2)
N(40)	−1156(3)	3009(2)	1832(2)
C(2A)	−551(4)	3196(4)	1064(2)
C(2B)	−2738(4)	3296(3)	1881(2)
C(41)	−383(3)	3417(2)	2428(2)
C(42)	−1082(4)	4166(3)	3000(2)
C(43)	−330(5)	4618(3)	3566(2)
C(44)	1151(5)	4369(3)	3579(2)
C(45)	1866(4)	3597(3)	3036(2)
C(46)	1119(3)	3073(2)	2475(2)
N(51)	1545(2)	959(2)	1992(1)
C(52)	1975(3)	2133(3)	1978(2)
C(53)	3197(3)	2428(3)	1542(2)
C(54)	3980(4)	1529(3)	1112(2)
C(55)	3533(3)	337(3)	1110(2)
C(56)	2304(3)	83(3)	1554(2)
N(61)	919(2)	−1406(2)	2225(1)
C(62)	1759(3)	−1178(2)	1598(2)
C(63)	2074(3)	−2056(3)	1041(2)
C(64)	1533(4)	−3207(3)	1127(2)
C(65)	699(4)	−3453(3)	1766(2)
C(66)	408(3)	−2534(3)	2298(2)
P(1)	5000	5000	0
F(11)	3397(2)	4596(2)	−55(1)
F(12)	4393(2)	6435(2)	−92(1)
F(13)	4731(2)	5101(2)	895(1)
P(2)	−5000	5000	5000
F(22)	−3783(3)	4055(2)	5354(1)
F(21)	−4279(3)	4759(2)	4185(1)
F(23)	−5911(3)	3844(2)	4905(2)

being *ca.* 3.6 Å. The two stacking interactions are shown in Fig. 2; the non-equivalence of the ligands is clear. It is also apparent that the 23° dihedral twist between the two co-ordinated pyridyl rings of one of the ligands allows the inter-ligand stacking to be maximised.

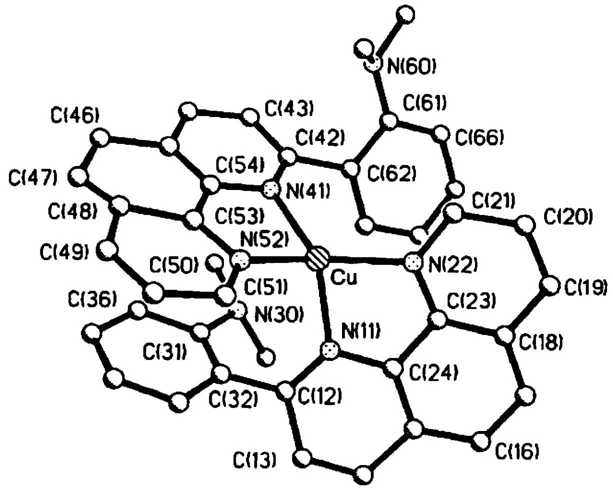

Fig. 3 Crystal structure of the cation of complex **2**

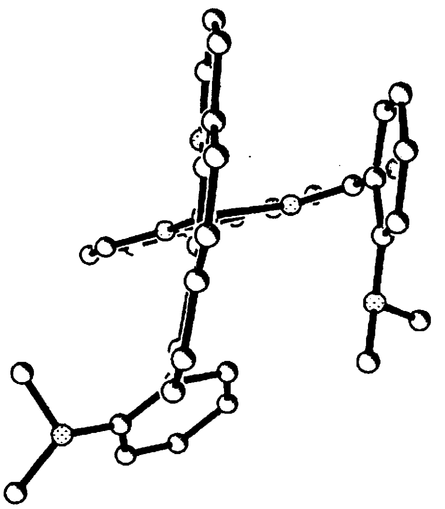

Fig. 4 Alternative view of **2** emphasising the aromatic stacking interactions

Complex **2** has a similar structure (Fig. 3; bond lengths and angles are given in Table 4, atomic coordinates in Table 5), with two phenanthroline fragments co-ordinated to the Cu^I centre and two pendant $C_6H_4NMe_2$ groups which are again twisted with respect to the phenanthroline fragments (torsion angles 68 and 52°). The range of Cu–N bond lengths [1.986(4)–2.074(4) Å] is similar to that observed for **1**, and the dihedral angle θ between the two CuN_2 planes is also similar at 76°. Again, the pendant aromatic group from each ligand lies stacked approximately parallel to the phenanthroline fragment of the other ligand. The two stacking interactions (Fig. 4) are different due to the inequivalence of the ligands in the solid

Table 4 Selected internuclear distances (Å) and angles (°) for complex **2**

Cu–N(22)	1.986(4)	Cu–N(52)	2.015(4)	Cu–N(41)	2.031(4)
Cu–N(11)	2.074(4)	N(11)–C(12)	1.341(6)	N(11)–C(24)	1.361(5)
C(21)–N(22)	1.333(6)	N(22)–C(23)	1.362(6)	N(41)–C(42)	1.331(5)
N(41)–C(54)	1.367(5)	C(51)–N(52)	1.324(6)	N(52)–C(53)	1.363(6)
N(22)–Cu–N(52)	136.3(2)	N(22)–Cu–N(41)	124.1(2)	N(52)–Cu–N(41)	83.1(2)
N(22)–Cu–N(11)	82.8(2)	N(52)–Cu–N(11)	109.2(2)	N(41)–Cu–N(11)	126.57(14)
C(12)–N(11)–C(24)	118.5(4)	C(12)–N(11)–Cu	130.7(3)	C(24)–N(11)–Cu	109.9(3)
C(21)–N(22)–C(23)	117.3(4)	C(21)–N(22)–Cu	130.0(4)	C(23)–N(22)–Cu	112.7(3)
C(42)–N(41)–C(54)	118.6(4)	C(42)–N(41)–Cu	131.0(3)	C(54)–N(41)–Cu	110.4(3)
C(51)–N(52)–C(53)	117.3(5)	C(51)–N(52)–Cu	131.2(4)	C(53)–N(52)–Cu	110.7(3)

state, the closer interaction having inter-ring separations in the range 3.4–3.6 Å, and the longer interaction having inter-ring separations in the range 3.3–4.7 Å.

Proton NMR spectroscopy shows that the inequivalence of the ligands is not maintained in solution and is therefore a consequence of solid-state packing. The aromatic region of the NMR spectrum of complex **2** is shown in Fig. 5, and clearly shows the presence of only 11 environments for the aromatic protons. These have not been assigned, but the low chemical shifts of some of the signals, due to ring-current effects, indicate that the aromatic stacking interaction is maintained in solution. This inhibits free rotation of the phenyl rings, resulting in the presence of two singlets at δ 2.15 and 2.23 for the NMe_2 group. The spectrum of complex **1** was less informative since a slight degree of aerial oxidation rendered the peaks very broad; the fact that this did not occur for **2** is consistent with the lower redox potential of **1** (see later). However we assume that complex **1** behaves in a similar manner to **2**, with the ligands becoming equivalent in solution and the stacking interaction being maintained.

The partial encapsulation of the Cu^I centre in these complexes provided by the inter-ligand stacking interactions is similar to that observed in copper(I) complexes of other *ortho*-substituted bipyridines and phenanthrolines[7–11] and results in considerable stabilisation of the Cu^I centre. This is reflected in the electrochemical data (see later), but is also apparent from the fact that **1** and **2** are moderately air-stable in solution, whereas $[Cu(bipy)_2]^+$ (bipy = 2,2′-bipyridine) undergoes an autoxidation reaction with O_2.[12]

Electrochemical and Spectroscopic Properties of Complexes of **1** *and* **2**.—The electrochemical properties of derivatives of $[Cu(bipy)_2]^+$ and $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline) are quite remarkably sensitive to the extent of encapsulation of the metal centre by substituents on the ligands *ortho* to the donor atoms.[10] Thus for $[Cu(phen)_2]^+$ the separation between the Cu^I–Cu^0 and Cu^{II}–Cu^I couples is 0.535 V, which is the 'redox-existence range' (r.e.r.) of the Cu^I state and is an indication of the thermodynamic stability of the Cu^I state of the complex. Addition of *ortho* methyl groups to the ligands in $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) results in an r.e.r. of 2.40 V for the Cu^I state, a huge *thermodynamic* stabilisation of the Cu^I state which arises because the partially encapsulated copper centre cannot rearrange so easily to the geometries required in other oxidation states. In addition, encapsulation of the metal results in *kinetic* stabilisation of the complex: for $[Cu(phen)_2]^+$, reduction to the (formally) Cu^0 state results in slow decomposition of the complex, whereas for the analogous catenate complex (in which the phenanthroline ligands are part of interlocked rings) the Cu^I–Cu^0 couple is reversible and the reduced Cu^0 complex shows no tendency to decompose.[10]

An electrochemical study of complex **1** shows the presence of Cu^{II}–Cu^I and Cu^I–Cu^0 couples separated by 2.45 V (Table 6). The Cu^{II}–Cu^I couple is reversible (cathodic and anodic peak currents equal, $\Delta E_p \approx 80$ mV and independent of scan rate). The reversibility of the Cu^I–Cu^0 couple for **1** is hard to judge: although a return wave is apparent, the process occurs in the rising background at the extreme of the solvent window and the cathodic and anodic peak currents cannot therefore be compared accurately. The r.e.r of complex **2** is 2.11 V, which is consistent with the observation that the r.e.r of the Cu^I state of $[Cu(phen)_2]^+$ is less than that of $[Cu(bipy)_2]^+$. The Cu^{II}–Cu^I couple of **2** is also reversible, but the Cu^I–Cu^0 couple appears not to be. The r.e.r. values of the Cu^I states of complexes **1** and **2** are comparable to those of copper(I) complexes of disubstituted phenanthrolines such as dmphen and 2,9-diphenyl-1,10-phenanthroline, and it is interesting that only one ligand substituent appears to be necessary to achieve this stabilising effect. Although copper(I) complexes of the monosubstituted phenanthrolines 2-(2-methylphenyl)-1,10-phenanthroline and 2-(2-ethoxyphenyl)-1,10-phenanthroline have been recently described,[11] only the Cu^I–Cu^0 couples were examined in detail so the r.e.r. values of the complexes are not known. Both **1** and **2** undergo a totally irreversible oxidation between + 0.6 and + 0.7 V *vs.* ferrocene–ferrocenium which we assign to the pendant $C_6H_4NMe_2$ fragments of the ligands since $[Cu(bipy)_2]^+$ and $[Cu(phen)_2]^+$ show no such oxidations.

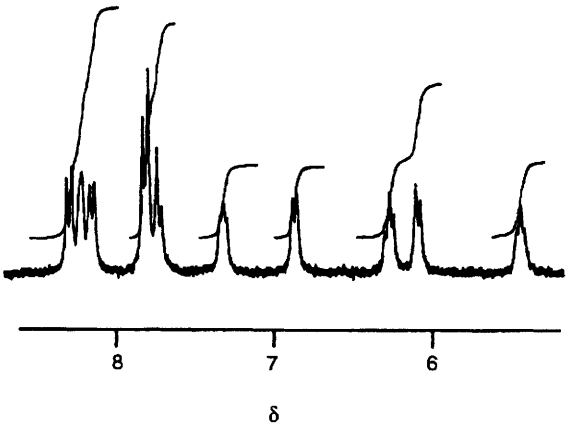

Fig. 5 Aromatic region of the ^1H NMR spectrum of complex **2** (MeCN, 270 MHz, 293 K)

The characteristic[11–15] metal-to-ligand charge-transfer (m.l.c.t.) bands in the electronic spectra of complexes **1** and **2** occur at 450 and 436 nm respectively (Table 6). There are at least three contributory factors to this which cannot easily be disentangled. First, electron-donating substituents on the ligands makes them better donors and causes a slight red-shift of the m.l.c.t. maximum compared to the parent complex.[14] Secondly, the steric bulk of the same substituents may cause lengthening of the Cu–N bonds and result in a compensatory blue-shift of the m.l.c.t. maximum, which is why λ_{max} for $[Cu(dpbipy)_2]^+$ (dpbipy = 6,6′-diisopropyl-2,2′-bipyridine) is virtually the same as for $[Cu(bipy)_2]^+$.[14] Thirdly, if the substituents are aromatic, inter-ligand stacking interactions may result in flattened structures ($\theta < 90°$) in solution,[15] which results in a blue-shift of the m.l.c.t. maximum.[11]

The λ_{max} value of 450 nm for complex **1** is slightly red-shifted compared to $[Cu(bipy)_2]^+$ (440 nm).[14] In contrast for **2** the position of λ_{max} (436 nm) is slightly blue-shifted compared to $[Cu(phen)_2]^+$ (441 nm in MeCN, measured in our laboratory). Both of these effects are slight. A better comparison for **2** is with the copper(I) complexes of the monosubstituted phenanthrolines 2-(2-methylphenyl)- and 2-(2-ethoxyphenyl)-1,10-phenanthroline [λ_{max}(m.l.c.t.) 452 and 451 nm respectively in CH_2Cl_2].[11] The blue-shift for **2** compared to these indicates that the distortion away from pseudo-tetrahedral symmetry in solution is more pronounced for **2** (lower value of θ), especially since the strongly electron-donating NMe_2 substituent would be expected to cause a red-shift of the m.l.c.t. maximum.[14]

Table 5 Atomic positional parameters (fractional coordinates × 10^4) for complex **2** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	1623(1)	1247(1)	1850(1)
N(11)	2006(4)	1991(1)	1842(2)
C(12)	1640(5)	2328(2)	1253(3)
C(13)	2298(6)	2795(2)	1293(4)
C(14)	3271(7)	2922(2)	1958(4)
C(15)	3658(6)	2580(2)	2587(4)
C(16)	4700(7)	2680(2)	3309(4)
C(17)	5056(7)	2330(3)	3870(4)
C(18)	4456(6)	1851(2)	3789(3)
C(19)	4811(7)	1474(3)	4349(4)
C(20)	4249(7)	1021(3)	4193(4)
C(21)	3320(6)	933(2)	3467(4)
N(22)	2938(4)	1281(2)	2909(2)
C(23)	3470(5)	1739(2)	3079(3)
C(24)	3017(5)	2116(2)	2491(3)
N(30)	−1791(5)	2114(2)	1403(3)
C(30A)	−1775(7)	2597(2)	1777(4)
C(30B)	−3348(6)	1885(2)	1492(4)
C(31)	−1032(6)	2060(2)	619(3)
C(32)	586(6)	2179(2)	530(3)
C(33)	1277(6)	2132(2)	−260(4)
C(34)	442(8)	1951(2)	−959(4)
C(35)	−1099(8)	1812(2)	−864(4)
C(36)	−1836(6)	1869(2)	−90(3)
N(41)	−515(4)	903(1)	1758(2)
C(42)	−1627(6)	823(2)	2336(3)
C(43)	−3069(6)	585(2)	2118(3)
C(44)	−3368(6)	453(2)	1306(3)
C(45)	−2218(7)	528(2)	680(3)
C(46)	−2398(8)	390(2)	−192(4)
C(47)	−1205(10)	453(2)	−745(4)
C(48)	290(8)	650(2)	−492(3)
C(49)	1592(10)	704(2)	−1033(4)
C(50)	2978(10)	883(2)	−724(4)
C(51)	3087(7)	1024(2)	127(4)
N(52)	1897(5)	984(2)	665(2)
C(53)	498(7)	798(2)	356(3)
C(54)	−787(6)	746(2)	943(3)
N(60)	−1828(5)	209(2)	3825(2)
C(60A)	−712(7)	−78(2)	3341(3)
C(60B)	−2434(7)	−59(2)	4547(3)
C(61)	−1484(5)	706(2)	3929(3)
C(62)	−1311(5)	1005(2)	3213(3)
C(63)	−919(6)	1491(2)	3326(3)
C(64)	−755(6)	1693(2)	4130(4)
C(65)	−972(7)	1402(2)	4820(3)
C(66)	−1332(6)	920(2)	4733(3)
P(1)	−6012(2)	−772(1)	2896(1)
F(1)	−5983(6)	−398(2)	3638(3)
F(2)	−5963(6)	−351(2)	2229(3)
F(3)	−4154(4)	−799(2)	2888(3)
F(4)	−7856(4)	−756(2)	2872(3)
F(5)	−6028(6)	−1191(2)	3548(3)
F(6)	−6036(5)	−1146(1)	2149(2)

The presence of an additional strong transition at 530 nm in the spectra of complexes **1** and **2**, which appears as a shoulder on the main m.l.c.t. peak (Fig. 6), gives further information regarding their solution structures. Although many solid-state structures of the type $[Cu(N\text{–}N)_2]^+$ show distortions from D_{2d} symmetry ($\theta < 90°$) as mentioned above, these may be imposed by crystal-packing forces and/or stacking interactions between molecules and therefore not persist in solution.[15] In such cases, of which $[Cu(dmphen)_2]^+$ is typical, the electronic spectrum of the solid spans a broader range of energies than that of the solution due to the lower symmetry which renders the d(π) orbitals non-degenerate: in particular a transition at around 500–550 nm in the solid, which is ascribed to a low-symmetry distortion,[16] becomes much weaker in solution where D_{2d} symmetry may be approached. However if the distortion in the solid state is due to aromatic π–π stacking interactions *within* the molecule, which commonly happens with 2,9-di(aryl)phenanthroline complexes,[8–10] then the distortion may persist in solution and manifest itself in a wider spread of m.l.c.t. energies and, in particular, a high intensity for the low-energy component of the m.l.c.t. band.[15] For $[Cu(phen)_2]^+$ in MeCN the low-energy shoulder has *ca.* 0.26 of the intensity of the main m.l.c.t. band; for **1** and **2** in MeCN the relative intensities are 0.43 and 0.33 respectively. The intensities of these shoulders in the spectra of complexes **1** and **2** therefore suggest that the deviations of θ from 90°, which arise from inter-ligand aromatic stacking interactions, are retained in solution despite the fact that the ligands are equivalent in solution. The same conclusion was reached earlier for **2** from the position of λ_{max} (m.l.c.t).

Complexes of the type $[Cu(N\text{–}N)_2]^+$ are often luminescent in solution due to emission from the m.l.c.t. excited state.[10,15,17–19] The photophysical properties, like the electrochemical properties, are strongly dependent on the extent of encapsulation of the Cu^I centre. Aryl substituents in the C^2 and C^9 positions of phenanthrolines appear to be particularly effective at promoting long emission lifetimes by shielding the metal centre from contact with potential quenching species such as counter ions or Lewis-basic solvents, which deactivate the excited state by forming a transient five-co-ordinate exciplex.[17–19] Thus, $[Cu(phen)_2]^+$ is not emissive in solution whereas $[Cu(dmphen)_2]^+$ is emissive, with τ = 250 ns.[10] Both **1** and **2** were found to be non-emissive in CH_2Cl_2 at room temperature at a range of concentrations. There are two possible reasons for this. First, if the metal centre is not sufficiently encapsulated, quenching may occur in the usual way *via* formation of a five-co-ordinate exciplex with solvent or counterion. Secondly, quenching could occur *via* an 'intramolecular exciplex' resulting from transient co-ordination

Table 6 Electrochemical and UV/VIS spectroscopic data for complexes **1** and **2**

	Redox potentials[a,b]		Electronic spectral data[b]
Complex	$E_{\frac{1}{2}}$/V		λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})
1	+0.64	−0.17 (80), −2.62	530 (sh), 450 (3.7), 330 (sh), 290 (33)
2	+0.68	−0.11 (80), −2.21	530 (sh), 436 (4.9), 350 (10), 274 (45)

[a] For chemically reversible processes (cathodic and anodic peak currents equal), the figure in parentheses is the peak–peak separation ΔE_p. For irreversible processes the peak potentials were taken from square-wave voltammograms. Potentials are given *versus* ferrocene–ferrocenium.
[b] Measurements made in MeCN.

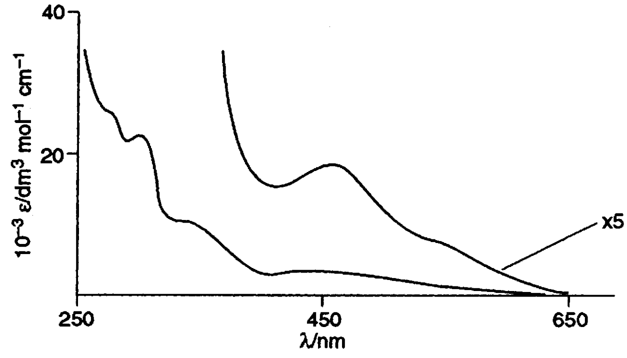

Fig. 6 The UV/VIS spectrum of complex **1** in MeCN

of one of the two pendant amine groups to the photo-generated Cu^{II} centre. This seems reasonable given the proximity of the NMe$_2$ groups to the metal (Cu ··· N 3.69 and 3.79 Å for **1** and **2** respectively) and the tendency of Cu^{II} to be five- or six-co-ordinate. Given that our electrochemical studies show that the presence of one aryl substituent per ligand in **1** and **2** has a similar stabilising effect to complexes of disubstituted ligands, and that only a slight degree of encapsulation seems to be necessary to allow emission as in [Cu(dmphen)$_2$]$^+$ (ref. 10), we incline towards the latter view.

EPR Spectra of Oxidised Forms of Complexes **1** *and* **2**.—Since the Cu^{II}–Cu^{I} couples of complexes **1** and **2** are at very modest potentials (slightly negative with respect to ferrocene–ferrocenium) it proved possible to oxidise them both to the Cu^{II} states (denoted **1**$^+$ and **2**$^+$) using the ferrocenium cation as oxidant. [Attempts to prepare copper(II) complexes directly by reaction of the ligands with copper(II) salts were unsuccessful, since the initially-formed green solids turned brown in solution during recrystallisation, presumably due to formation of **1** and **2**.] Treatment of brown solutions of **1** and **2** in MeCN with 1 equivalent of [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] instantly resulted in the formation of emerald green solutions which were stable in air for several days. The EPR spectrum of **1**$^+$ is shown in Fig. 7(*a*); the spectrum of **2**$^+$ is virtually superimposable. Generally, EPR spectra of copper(II) complexes have $g_{\parallel} > g_{\perp} > 2$, and the hyperfine splitting of the $g_{\parallel}$ signal [$A_{\parallel}$(Cu)] is much greater than that of $g_{\perp}$ (where it is usually unobservable). The spectra of **1** and **2** conform to this pattern; the parameters are summarised in Table 7. The values of $A_{\perp}$(Cu) were calculated from the known values of $A_{\parallel}$(Cu) (from the 77 K spectra) and the values of A_{iso} (from room-temperature solution spectra, 61 G for **1**$^+$ and 63 G for **2**$^+$) using the relationship $A_{iso} = (A_{\parallel} + 2A_{\perp})/3$. A possible small temperature dependence of A_{iso} renders approximate the values of $A_{\perp}$(Cu) derived from them. Superhyperfine coupling to nitrogen is apparent on the $g_{\perp}$ signal; it becomes much more apparent on differentiation of the signal where nine lines are apparent [Fig. 7(*b*)], indicating that all four heterocyclic N atoms remain co-ordinated (coupling to four equivalent N atoms should give a nine-line spectrum with the relative intensities 1:4:10:16:19:16:10:4:1, which is approximately what is observed). It is quite possible that the coordination number may increase in solution to five or six by association of solvent molecules or a pendant NMe$_2$ group, or even by weak association of PF$_6^-$ counterions. Attachment of one or two NMe$_2$ groups would not necessarily change the superhyperfine nitrogen coupling, since (*i*) the NMe$_2$ group has no π-accepting character and the unpaired electron would not therefore be delocalised onto it, and (*ii*) assuming a basically tetragonal structure for the copper(II) complex with the unpaired electron in the $d_{x^2-y^2}$ orbital, the NMe$_2$ group would lie on the z axis and therefore be orthogonal to the magnetic orbital.

The EPR spectra of copper(II) complexes provide a useful indication of complex geometry: the value of $A_{\parallel}$(Cu) tends to decrease with increasing tetrahedral character, and the value of $A_{\perp}$(Cu) similarly changes in an antiparallel fashion.[20] Thus a planar copper(II) complex with four pyrazole ligands has $A_{\parallel}$(Cu) = 618 MHz whereas a tetrahedral complex with the same donor set has $A_{\parallel}$(Cu) = 285 MHz,[21] and the gradual distortion from planar towards tetrahedral in a series of copper(II) 'tropocoronand' complexes is accompanied by a decrease in the value of $A_{\parallel}$(Cu) from 653 to 426 MHz.[22] Other studies on related pairs of tetrahedral and planar complexes show the same behaviour.[23] For **1**$^+$ and **2**$^+$ the best comparisons are with [Cu(bipy)$_2$]$^{2+}$ (ref. 24) as an example of a non-encapsulated complex, and [CuL'$_2$]$^{2+}$ [L' = 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline] and its related catenate complex [Cu(cat-30)]$^{2+}$ (cat-30 = a caternated ligand comprising two interlocked 30-membered macrocyclic rings) as examples of encapsulated complexes.[10] The rather high value of $A_{\parallel}$(Cu) (170G, equivalent to 550 MHz at the field setting used)

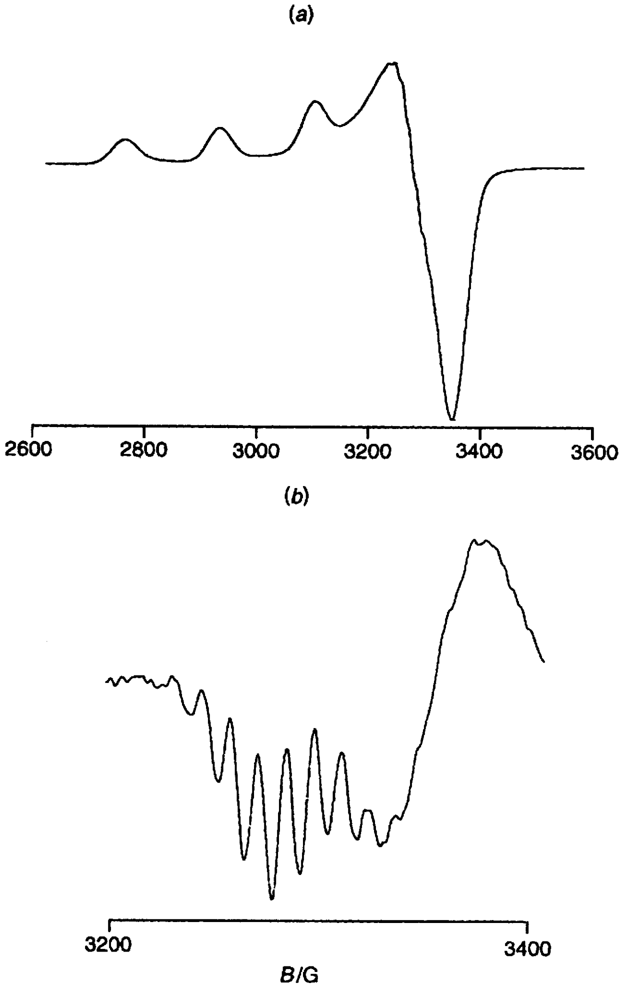

Fig. 7 (*a*) The EPR spectrum of **1**$^+$ at 77 K in a MeCN–tetrahydrofuran glass. (*b*) Derivative of the $g_{\perp}$ component, emphasising the nine-line superhyperfine nitrogen coupling

Table 7 EPR spectral parameters for **1**$^+$ and **2**$^+$

Complex	$g_{\parallel}$[a]	$g_{\perp}$	$A_{\parallel}$(Cu)/G	$A_{\perp}$(Cu)[b]/G	$A_{\perp}$(N)/G
1$^+$	2.310	2.128	170	7	13
2$^+$	2.312	2.128	169	10	13

G = 10^{-4} T. [a] Spectra recorded at 77 K in frozen MeCN–tetrahydrofuran (1 : 1, v/v) glass. [b] Calculated values (see text).

for 1^+ and 2^+ is slightly higher than that of $[Cu(bipy)_2]^{2+}$ (527 MHz) which, in the solid state at least, has $\theta = 44.6°$ and is therefore midway between tetrahedral and planar geometries.[24] In contrast, for $[CuL'_2]^{2+}$ and $[Cu(cat\text{-}30)]^{2+}$, the values of $A_{\|}(Cu)$ from frozen solution spectra are 390 and 370 MHz respectively, which was taken as evidence that the encapsulated metal ions retain a geometry close to tetrahedral on oxidation to the Cu^{II} state.[10] Oxidation of **1** and **2** therefore results in a change of geometry somewhat larger than that which occurs on oxidation of $[Cu(bipy)_2]^+$, and we may reasonably suggest a θ value of less than 44° for 1^+ and 2^+ in solution, in contrast to 75° for **1** and 76° for **2** in the solid state. The 'partial encapsulation' of the copper(I) centres by the monosubstituted phenanthroline ligands L^1 and L^2, whilst being sufficient to give a wide r.e.r. for the Cu^I states, is apparently not sufficient to prevent considerable distortion away from tetrahedral geometry on oxidation: in this respect L^1 and L^2 behave in a manner intermediate between simple bidentate ligands like bipy and phen, and strongly encapsulating disubstituted ligands such as 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline.

Conclusion

In the copper(I) complexes of L^1 and L^2 only the diimine fragments of the ligands co-ordinate, to give four-co-ordinate complexes with highly distorted tetrahedral structures. This is the third different binding mode observed for these ligands, the others being N_3 terdentate and N_2C-cyclometallating terdentate. The metal centres are partially encapsulated due to intramolecular stacking interactions involving the pendant aromatic substituents. There are two types of distortion evident: a distortion of the $Cu(NN)_2$ centres away from pseudo-tetrahedral towards square-planar geometry (*i.e.* $\theta < 90°$), and the inequivalence of the two ligands. The first of these is retained in solution and is therefore caused by the inter-ligand aromatic stacking interactions; the second is not retained in solution and is therefore a consequence of crystal-packing forces. The electrochemical properties of the complexes are similar to those of copper(I) complexes with disubstituted bipyridines and phenanthrolines. The EPR spectra of the copper(II) complexes, prepared by chemical oxidation, indicate that in the Cu^{II} state the complexes are flexible enough to allow a substantial structural change towards square-planar geometry. The 'partially encapsulated' structure is therefore rigid enough to retain in solution some of the distortions evident in the solid-state structure of the copper(I) complexes, but flexible enough to allow a considerable change of geometry on oxidation to the Cu^{II} state.

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