Synthesis of the Potentially Pentadentate Ligand 6,6″-Bis(2-hydroxyphenyl)-2,2′:6′,2″-terpyridine (H_2L) and the Crystal Structure and Magnetic Properties of $[\{Cu(HL)\}_2][PF_6]_2{\cdot}5MeCN$†

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The new potentially pentadentate (ONNNO donor) ligand 6,6″-bis(2-hydroxyphenyl)-2,2′:6′,2″-terpyridine (H_2L) reacted with Cu^{II} to form the complex $[\{Cu(HL)\}_2][PF_6]_2$. X-Ray structural analysis of $[\{Cu(HL)\}_2][PF_6]_2{\cdot}5MeCN$ revealed that the complex exists as centrosymmetric dimers. The monomeric unit is four-co-ordinate $Cu(HL)^+$, in which the copper(II) ion is co-ordinated by one phenolate oxygen and three pyridyl nitrogen atoms of HL, with the remaining phenol group protonated and not co-ordinated but involved in hydrogen-bonding interactions with $[PF_6]^-$ ions or lattice MeCN molecules. The geometry is best approximated as square planar within the constraints imposed by the ligand. Two of these units are stacked such that the copper(II) centre of one monomeric unit is co-ordinated axially by the phenolate ligand of the other, forming a $Cu_2(\mu\text{-}O)_2$ core with (approximately) elongated square-pyramidal copper(II) centres. This results in aromatic stacking between the two ligands. Low-temperature magnetic susceptibility measurements indicate a weak antiferromagnetic coupling between the metals. The EPR spectrum (CH_2Cl_2–dimethylformamide glass at 77 K) is a typical triplet with a well resolved double-quantum transition and a septet hyperfine coupling pattern, showing that the dimer remains intact in the solvent mixture used. However in the presence of pyridine the dimeric units break up *via* axial ligation of pyridine, resulting in an EPR spectrum characteristic of mononuclear copper(II) species.

It is now well established by various groups that long oligopyridyl compounds (⩾4 pyridyl rings) can form polynuclear transition-metal complexes which have double-stranded helical structures.[1,2] It has also become apparent recently from our own studies that small oligopyridyl-based compounds which contain a terminal phenolate donor in place of a pyridyl can form polynuclear structures due to the propensity of phenolate to bridge two metal centres; various magnetically coupled bi-[3,4] and tetra-nuclear[5] complexes have been prepared. The presence of phenolate ligands in the co-ordination sphere of a complex can also allow for polynucleation to occur *via* strong hydrogen bonding between monomeric units.[6]

We therefore decided to try to combine these two types of behaviour by preparing the potentially pentadentate ONNNO-donor 6,6″-bis(2-hydroxyphenyl)-2,2′:6′,2″-terpyridine (H_2L) and studying its co-ordination chemistry. The compound is long enough to support helical molecular architectures in the same manner as that of 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) if required, and the terminal phenolate groups may also allow bridging behaviour. A common feature of the mixed pyridine–phenol has been the unpredictability of the structures of their complexes, *cf.* the formation of high-nuclearity complexes with the simple 2-hydroxypyridine and its derivatives,[7] and we were interested to see how H_2L might behave given its potential for displaying various different kinds of interesting co-ordination behaviour. This paper describes the synthesis and characterisation of H_2L and the preparation, crystal structure, EPR and magnetic properties of the binuclear copper(II) complex $[\{Cu(HL)\}_2][PF_6]_2$.

Experimental

The instrumentation used for routine spectroscopic investigations was as follows: ^1H NMR, JEOL GX270 or GX400 spectrometers; fast-atom bombardment (FAB) and electron-impact (EI) mass spectrometry, VG-Autospec instrument; EPR at 77 K, Bruker ESP-300E spectrometer; electronic spectroscopy, Perkin-Elmer Lambda 2 spectrometer. Magnetic data were recorded with a Faraday balance accordng to a published method.[8] 2,6-Diacetylpyridine, 2-methoxyacetophenone and dimethylamine hydrochloride were obtained from Aldrich and used as received. The bis-Mannich base hydrochloride **1** was prepared according to the published method.[9]

Preparations.—1-[2-(2-*Methoxyphenyl*)-2-*oxoethyl*]*pyridinium iodide* **2**. To a warm solution of I_2 (12.69 g, 50 mmol) in freshly distilled pyridine (50 cm^3) was added 2-methoxyacetophenone (7.50 g, 50 mmol) dropwise with constant stirring. The mixture was heated to reflux for 1.5 h and then allowed to cool. After evaporation of most of the pyridine *in vacuo* the remaining slurry was partitioned between water and CH_2Cl_2. The organic layer was separated, and the aqueous phase extracted with several additional portions of CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* until precipitation just started; the solution was then cooled in an ice–salt bath, upon which a brown crystalline mass precipitated. This was filtered off, washed with a little ice-cold CH_2Cl_2, and dried in air. A second crop of crystals was obtained by further concentration/cooling of the filtrate. Overall yield: 10.5 g (59%). ^1H NMR [270 MHz, $(CD_3)_2SO$]: δ 4.05 (3 H, s, OCH_3), 6.24 (2 H,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

s, CH_2), 7.16 (1 H, td, J = 7.6, 0.9, phenyl H^4 or H^5), 7.37 (1 H, d, J = 7.9, phenyl H^3 or H^6), 7.76 (1 H, m, phenyl H^5 or H^4), 7.89 (1 H, dd, J = 7.9, 1.8, phenyl H^6 or H^3), 8.25 (2 H, m, pyridyl H^3, H^5), 8.72 (1 H, m, pyridyl H^4) and 9.00 (2 H, dd, J = 6.8, 1.3 Hz, pyridyl H^2, H^6). FAB mass spectrum: m/z = 228 (mass of cation). (Found: C, 47.0; H, 3.9; N, 3.7. $C_{14}H_{14}INO_2$ requires C, 47.3; H, 3.9; N, 3.9%).

6,6″-Bis(2-*methoxyphenyl*)-2,2′:6′,2″-*terpyridine* **3**. A mixture of the Mannich base pyridine-2,6-bis(*N*,*N*-dimethyl-3-oxopropanamine) hydrochloride **1** (1.20 g, 3.4 mmol), **2** (2.49 g, 7 mmol), and ammonium acetate (1.5 g, excess) in methanol (50 cm^3) was heated to reflux for 8 h. After cooling, water was added dropwise to the solution until a yellow solid precipitated. After filtration, washing with water and drying *in vacuo*, the crude material was purified by column chromatography on alumina with CH_2Cl_2. The desired product was the first to elute from the column and is intensely luminescent under long-wave UV light (366 nm irradiation with a hand-held UV lamp). Compound **3** was then recrystallised by slow evaporation from a CH_2Cl_2–EtOH mixture to give long white needles. Yield: 0.35 g (23%). EI mass spectrum: m/z = 445 (M^+). ^1H NMR (270 MHz, $CDCl_3$): δ 3.90 (6 H, s, 2 OCH_3), 7.04 (2 H, d, J = 8.4, 2 H^6 of phenyl), 7.14 (2 H, td, J = 7.5, 1.1, 2 H^4 of phenyl), 7.41 (2 H, td, J = 7.8, 1.7, 2 H^5 of phenyl), 7.8–8.0 (5 H, m, pyridyl $H^{4'}$, $H^{4,4''}$ and $H^{3,3''}$ or $H^{5,5''}$), 8.58 (2 H, dd, J = 7.5, 1.3, pyridyl $H^{5,5''}$ or $H^{3,3''}$) and 8.60 (2 H, d, J = 7.9 Hz, pyridyl $H^{3',5'}$). Despite prolonged drying *in vacuo* the elemental analyses were consistent with the presence of varying amounts of CH_2Cl_2 (0.5–1 molecules per molecule of **3**) in the crystal lattice; consequently reliable and reproducible analytical data could not be obtained. The ^1H NMR spectrum, however, was clean.

6,6″-Bis(2-*hydroxyphenyl*)-2,2′:6′,2″-*terpyridine* (H_2L). The compound H_2L was prepared from **3** by demethylation with molten pyridine hydrochloride at 200 °C for 2 h under N_2 according to a published method.[10] After cooling, addition of water to the mixture and neutralisation, crude H_2L precipitated as a grey solid in 80% yield. The crude solid was redissolved in a small amount of methanol at reflux and filtered whilst hot to remove insoluble matter. Trituration of the filtrate with water resulted in reprecipitation of H_2L as a cream solid. EI mass spectrum: m/z = 417 (M^+). ^1H NMR (270 MHz, $CDCl_3$): δ 6.96 (2 H, td, J = 7.5, 1.2, phenyl H^4), 7.09 (2 H, dd, J = 8.3, 1.1, phenyl H^6), 7.36 (2 H, td, J = 7.7, 1.6, phenyl H^5), 7.87 (2 H, dd, J = 8.0, 1.5, phenyl H^3), 7.9–8.1 (5 H, m, pyridyl $H^{4'}$, H^4, $H^{4''}$ and H^3, $H^{3''}$ or H^5, $H^{5''}$), 8.25 (2 H, d, J = 8.0, pyridyl $H^{3'}$, $H^{5'}$), 8.49 (2 H, dd, J = 7.4, 1.3 Hz, pyridyl H^5, $H^{5''}$ or H^3, $H^{3''}$) and 14.65 (2 H, br s, phenolic OH) (Found: C, 74.7; H, 5.0; N, 9.8. $C_{27}H_{19}N_3O_2{\cdot}H_2O$ requires C, 74.5; H, 4.8; N, 9.7%).

$[\{Cu(HL)\}_2][PF_6]_2$. A mixture of $Cu(O_2CMe)_2{\cdot}H_2O$ (50 mg, 0.25 mmol) and H_2L (104 mg, 0.25 mmol) in methanol was heated to reflux for 10 min to afford a bottle-green solution. After addition of NH_4PF_6 and concentration *in vacuo* a dark green solid precipitated which was filtered off and dried. Recrystallisation from MeCN–Et_2O by vapour diffusion afforded large green blocks suitable for X-ray studies. FAB mass spectrum: m/z = 479 [Cu(HL)] and 958 [$Cu_2(HL)_2$] (based on ^{63}Cu) (Found: C, 52.1; H, 3.2; N, 8.3. $C_{27}H_{18}CuF_6N_3O_2{\cdot}$MeCN: C, 52.3; H, 3.2; N, 8.4%).

Crystal Structure Determination of $[\{Cu(HL)\}_2][PF_6]_2{\cdot}5MeCN$.—Crystals were grown as green blocks from MeCN–Et_2O by vapour diffusion. They lost solvent very rapidly in the air, so those selected were sealed in glass capillary tubes with some of the mother-liquor present as a precaution against solvent loss. Data were collected using a Siemens R3m/V four-circle diffractometer [293(2) K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 73 Å]. They were corrected for Lorentz and polarisation effects, and for absorption effects using an empirical method based on azimuthal scan data.[11] Systematic monitoring of check reflections showed no significant loss of intensity. Details of the crystal data, intensity collection and refinement are summarised in Table 1.

Table 1 Details of crystal data, intensity data collection, and structure refinement for $[\{Cu(HL)\}_2][PF_6]_2{\cdot}5MeCN$

Formula	$C_{64}H_{51}Cu_2F_{12}N_{11}O_4P_2$
M	1455.18
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.205(2)
b/Å	16.338(5)
c/Å	21.039(5)
α/°	68.12(2)
β/°	86.29(2)
γ/°	80.59(2)
U/Å^3	3211.3(14)
Z	2
D_c/g cm^{-3}	1.505
μ(Mo-Kα)/mm^{-1}	0.804
F(000)	1480
Crystal dimensions (mm)	0.4 × 0.6 × 0.55
Unique reflections measured	5973 (R_{int} = 0.0420)
Collection method	Wyckoff ω scan
2θ range/°	5–40
hkl ranges	0–9, −15 to 15, −20 to 20
Refinement method	Full-matrix least squares on all F^2 data
Data, restraints, parameters	5973, 6, 863
Goodness of fit on F^2	1.051
Final residuals	$wR_2 = 0.175^a$ ($R_1 = 0.063$)^b
Weighting factors	0.0918, 8.32^a
Largest difference peak, hole/e Å^{-3}	0.708, −0.457

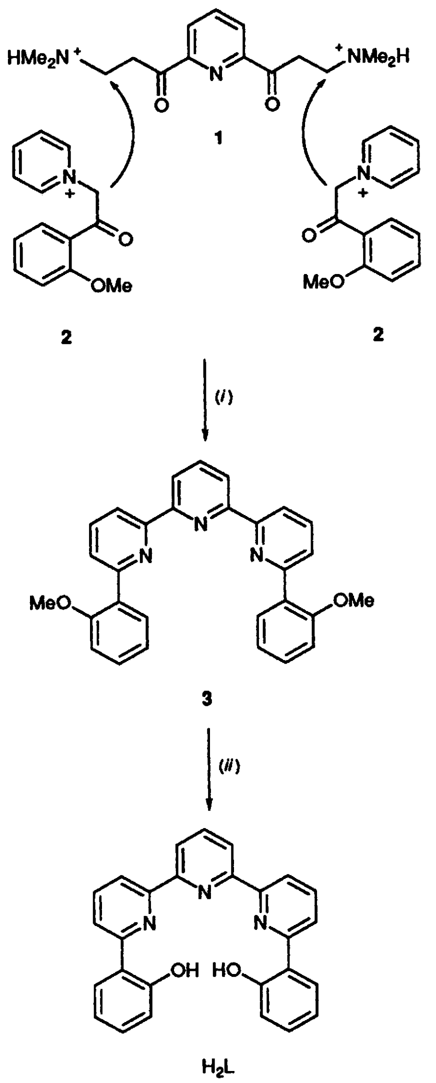
[a] The structure was refined on F_o^2 using all data: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [b] The value in parentheses is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$.

The structure of $[\{Cu(HL)\}_2][PF_6]_2{\cdot}5MeCN$ was 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 programs.[11] The final least-squares refinement on F^2 was then carried out on a Silicon Graphics Indigo R4000 computer using SHELX 93.[11] Scattering factors with corrections for anomalous dispersion were taken from ref. 12. Selected bond lengths and angles are in Table 2, and atomic coordinates in Table 3. The unit cell contains two independent but similar dimeric $[\{Cu(HL)\}_2]^{2+}$ units, four hexafluorophosphate ions and ten molecules of MeCN solvent of crystallisation. The two Cu_2 dimers lie astride inversion centres and have crystallographically imposed inversion symmetry.

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

Results and Discussion

The new ligand H_2L was prepared according to the method outlined in Scheme 1. It is a standard Kröhnke synthesis,[9] similar to that used for preparation of quinquepyridine, in which the second and fourth of the sequence of five aromatic rings are generated by closure of 1,5-dicarbonyl groups (prepared *in situ* by the Michael reaction of the enolate equivalent **2** with the enone equivalent **1**) with ammonium acetate. The resulting protected ligand **3** was demethylated with pyridinium chloride to liberate the terminal phenol groups.[10] The structure of H_2L was confirmed by ^1H NMR spectrometry, mass spectrometry and elemental analysis; in the ^1H NMR spectrum the broad singlet at δ 14.65 is characteristic of the



Scheme 1 (*i*) Ammonium acetate, MeOH, reflux; (*ii*) pyridine hydrochloride, 200 °C

phenolic OH protons which are hydrogen-bonded to the adjacent pyridyl N atoms.[3]

Reaction of H_2L with $Cu(O_2CMe)_2 \cdot H_2O$ in methanol afforded a clear dark green solution. We thought it possible that a neutral complex would occur if the metal : ligand ratio were 1 : 1, since the two negative charges per ligand (deprotonated phenolates) would balance the +2 charge on each metal. However a cationic complex was formed which precipitated on addition of hexafluorophosphate. The FAB mass spectrum of this material showed a strong peak at $m/z = 479$, with an isotopic pattern characteristic of one Cu atom, and a very weak one at $m/z = 958$ with an isotopic pattern characteristic of two Cu atoms. The first of these corresponds to Cu(HL), a mononuclear fragment in which the ligand is not fully deprotonated; the second corresponds to the dimer $\{Cu(HL)\}_2$. The fact that such a strong peak for the mononuclear species was observed suggested that the ligand is not directly bridging two metals, in contrast to complexes of qpy where the ligand typically donates three binding sites to one metal ion and two to a second.[1] The weak peak at $m/z = 958$ could therefore arise from association of mononuclear complex units in the gas phase. The elemental analysis of the dried crystals confirmed the stoichiometry $[Cu(HL)][PF_6]$ with one associated MeCN per metal.

Two views of the crystal structure of the complex are shown in Fig. 1. They confirm that a binuclear complex $[\{Cu(HL)\}_2][PF_6]_2$ forms in the solid state. The dimeric structure comprises two $Cu(HL)^+$ units in which the ligand HL is tetradentate, *via* the three pyridyl rings and one deprotonated phenolate, with the remaining phenol protonated and not co-ordinated. Two monomers are stacked such that the co-ordinated phenolate residue of each $Cu(HL)^+$ unit also co-ordinates axially to the other copper(II) centre, resulting in a $Cu_2(\mu\text{-}O)_2$ core. This is a common structural motif in planar copper(II) complexes which contain ligands capable of bridging.[4,13,14] There are two crystallographically independent but similar dimeric units in the unit cell, of which only one is shown in Fig. 1. The co-ordination geometry about each Cu^{II} is best described as elongated square pyramidal, with the four donor atoms of one ligand crudely in a plane and a long axial interaction to the neighbouring phenolate, and is consistent with the stereochemical requirements of the Jahn–Teller effect. The copper atoms are displaced slightly out of the mean planes defined by the coordinating O,N,N,N atoms of each ligand (by 0.052 and 0.019 Å in the independent dimers), which is usual in square-pyramidal complexes. However this is not a fully satisfactory description of the geometry since the co-ordinating O,N,N,N atoms are not coplanar: it is evident from Fig. 1 that the CuN_3 group is nearly coplanar with the co-ordinated

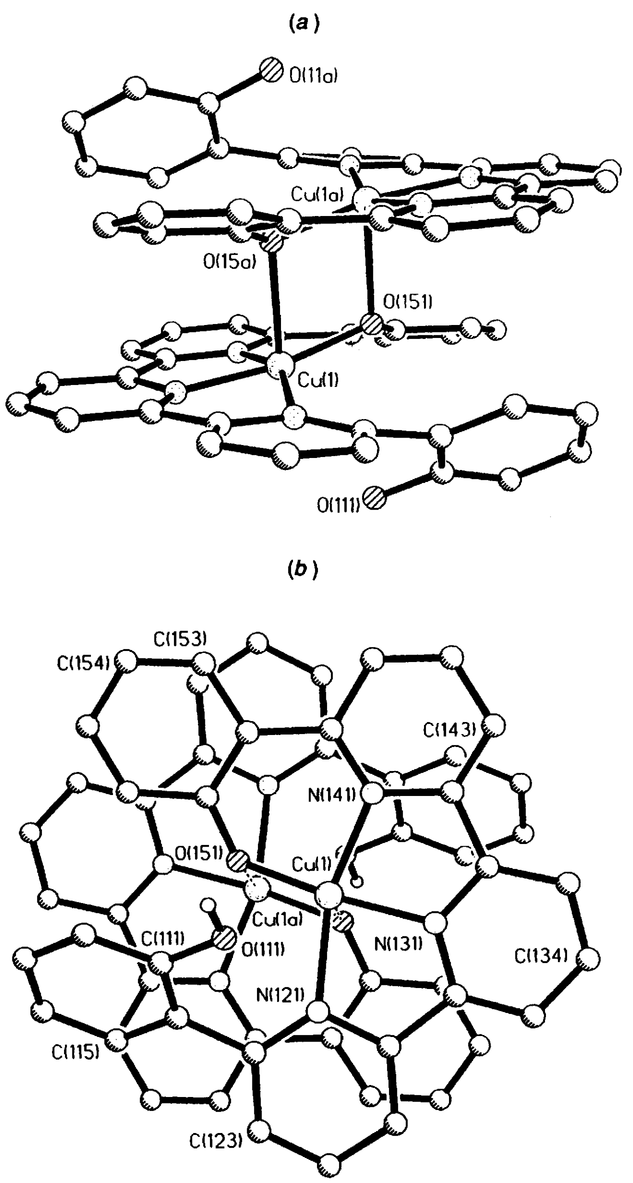


Fig. 1 Two views of the crystal structure of the cation of $[\{Cu(HL)\}_2][PF_6]_2 \cdot 5MeCN$

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Cu(HL)\}_2][PF_6]_2\cdot5MeCN$

Cu(1)–O(151)	1.870(5)	Cu(1)–N(131)	1.932(6)	Cu(1)–N(141)	2.001(6)	Cu(1)–N(121)	2.095(6)
Cu(1) • • • Cu(1a)	3.345	Cu(1) • • • O(15a)	2.453	Cu(2)–O(251)	1.882(5)	Cu(2)–N(231)	1.940(7)
Cu(2)–N(241)	2.002(6)	Cu(2)–N(221)	2.113(6)	Cu(2) • • • Cu(2a)	3.324	Cu(2) • • • O(25a)	2.389

O(151)–Cu(1)–N(131)	169.4(2)	O(151)–Cu(1)–N(141)	93.7(2)	N(131)–Cu(1)–N(141)	81.5(3)
O(151)–Cu(1)–N(121)	107.4(2)	N(131)–Cu(1)–N(121)	79.0(3)	N(141)–Cu(1)–N(121)	157.0(3)
O(151)–Cu(1)–O(15a)	79.4(2)	N(131)–Cu(1)–O(15a)	92.9(2)	N(141)–Cu(1)–O(15a)	107.4(2)
N(121)–Cu(1)–O(15a)	85.9(2)	C(122)–N(121)–C(126)	120.0(6)	C(122)–N(121)–Cu(1)	128.2(5)
C(126)–N(121)–Cu(1)	110.8(5)	C(132)–N(131)–C(136)	123.3(7)	C(132)–N(131)–Cu(1)	119.1(5)
C(136)–N(131)–Cu(1)	116.5(5)	C(146)–N(141)–C(142)	121.0(7)	C(146)–N(141)–Cu(1)	125.8(5)
C(142)–N(141)–Cu(1)	113.2(5)	C(151)–O(151)–Cu(1)	121.7(5)	C(151)–O(151)–Cu(1a)	121.6(4)
Cu(1)–O(151)–Cu(1a)	100.6(2)	O(151)–C(151)–C(156)	116.0(8)	O(151)–C(151)–C(152)	125.5(7)
C(156)–C(151)–C(152)	118.4(8)	O(251)–Cu(2)–N(231)	169.4(3)	O(251)–Cu(2)–N(241)	93.2(3)
N(231)–Cu(2)–N(241)	81.2(3)	O(251)–Cu(2)–N(221)	109.1(2)	N(231)–Cu(2)–N(221)	78.5(3)
N(241)–Cu(2)–N(221)	154.5(3)	O(251)–Cu(2)–O(25a)	78.4(2)	N(231)–Cu(2)–O(25a)	94.9(2)
N(241)–Cu(2)–O(25a)	110.2(2)	N(221)–Cu(2)–O(25a)	86.9(2)	C(222)–N(221)–C(226)	119.1(7)
C(222)–N(221)–Cu(2)	129.3(5)	C(226)–N(221)–Cu(2)	110.9(5)	C(232)–N(231)–C(236)	123.5(8)
C(232)–N(231)–Cu(2)	119.3(6)	C(236)–N(231)–Cu(2)	116.4(6)	C(246)–N(241)–C(242)	121.3(7)
C(246)–N(241)–Cu(2)	125.9(6)	C(242)–N(241)–Cu(2)	112.8(6)	C(251)–O(251)–Cu(2)	123.0(5)
C(251)–O(251)–Cu(2a)	121.8(4)	Cu(2)–O(251)–Cu(2a)	101.5(2)	O(251)–C(251)–C(256)	117.5(7)
O(251)–C(251)–C(252)	125.4(7)	C(256)–C(251)–C(252)	117.1(7)		

Table 3 Atomic coordinates (× 10^4) for $[\{Cu(HL)\}_2][PF_6]_2\cdot5MeCN$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	1 578(1)	9 651(1)	9 843(1)	C(232)	1 407(9)	6 200(7)	15 183(5)
O(111)	2 403(6)	10 275(4)	8 460(3)	C(233)	360(9)	6 358(8)	15 600(5)
C(111)	1 376(8)	10 931(6)	8 160(4)	C(234)	−179(10)	5 648(9)	16 043(5)
C(112)	726(10)	10 948(7)	7 599(5)	C(235)	253(10)	4 784(8)	16 067(5)
C(113)	−323(12)	11 599(9)	7 306(5)	C(236)	1 279(9)	4 661(7)	15 643(5)
C(114)	−713(10)	12 257(8)	7 565(5)	N(241)	2 939(7)	3 879(4)	15 145(3)
C(115)	−43(9)	12 259(6)	8 123(5)	C(242)	1 886(9)	3 820(6)	15 585(4)
C(116)	1 014(8)	11 590(5)	8 432(4)	C(243)	1 455(9)	3 011(8)	15 934(5)
N(121)	2 217(6)	10 900(4)	9 513(3)	C(244)	2 111(12)	2 266(7)	15 842(5)
C(122)	1 750(7)	11 643(5)	8 995(4)	C(245)	3 162(11)	2 335(6)	15 414(5)
C(123)	2 019(9)	12 475(6)	8 963(5)	C(246)	3 577(9)	3 161(6)	15 035(4)
C(124)	2 829(9)	12 511(6)	9 446(5)	O(251)	5 129(5)	4 703(3)	14 470(2)
C(125)	3 380(8)	11 733(6)	9 955(5)	C(251)	5 365(8)	4 005(5)	14 281(4)
C(126)	3 060(7)	10 934(5)	9 980(4)	C(252)	4 674(8)	3 260(5)	14 525(4)
N(131)	3 065(6)	9 394(5)	10 446(3)	C(253)	5 061(11)	2 567(6)	14 269(5)
C(132)	3 568(7)	10 067(6)	10 498(4)	C(254)	6 050(11)	2 598(7)	13 803(6)
C(133)	4 480(8)	9 908(6)	11 003(4)	C(255)	6 728(9)	3 319(6)	13 568(5)
C(134)	4 806(8)	9 048(7)	11 449(5)	C(256)	6 377(8)	4 001(5)	13 798(4)
C(135)	4 278(8)	8 343(6)	11 407(4)	C(1)	3 113(18)	2 965(10)	12 582(10)
C(136)	3 367(8)	8 546(6)	10 878(4)	C(2)	3 039(12)	3 787(9)	12 736(7)
N(141)	1 752(6)	8 319(4)	10 218(3)	N(1)	2 964(10)	4 375(7)	12 886(6)
C(142)	2 675(8)	7 917(6)	10 730(4)	C(3)	3 179(17)	7 259(11)	8 463(9)
C(143)	2 909(9)	7 013(6)	11 063(5)	C(4)	3 773(16)	7 588(13)	8 900(9)
C(144)	2 127(11)	6 514(6)	10 891(6)	N(2)	4 237(21)	7 850(18)	9 221(10)
C(145)	1 208(9)	6 910(6)	10 388(5)	C(5)	9 339(20)	1 542(12)	13 084(10)
C(146)	1 033(8)	7 835(5)	10 026(4)	C(6)	9 733(17)	619(17)	13 422(11)
O(151)	−34(5)	9 805(3)	9 408(3)	N(3)	10 016(22)	−138(14)	13 767(13)
C(151)	−324(7)	9 205(6)	9 165(4)	C(7)	2 545(18)	56(11)	14 949(9)
C(152)	120(8)	8 275(6)	9 445(4)	C(8)	1 781(22)	953(15)	14 632(11)
C(153)	−358(10)	7 742(7)	9 138(5)	N(4)	1 090(25)	1 609(14)	14 400(14)
C(154)	−1 207(11)	8 088(9)	8 608(6)	C(9)	4 990(54)	14 954(35)	9 094(24)
C(155)	−1 651(10)	8 990(8)	8 331(5)	C(10)	3 731(56)	14 557(20)	9 717(29)
C(156)	−1 209(8)	9 538(6)	8 609(4)	N(5)	3 010(46)	14 453(30)	10 281(24)
Cu(2)	3 445(1)	5 105(1)	14 756(1)	P(1)	563(3)	5 452(2)	8 291(2)
O(211)	3 105(6)	5 770(4)	13 295(3)	F(11)	185(14)	6 281(9)	7 673(8)
C(211)	4 279(9)	6 091(5)	13 095(4)	F(12)	−905(9)	5 469(7)	8 493(6)
C(212)	5 134(9)	5 827(5)	12 646(4)	F(13)	978(11)	4 563(5)	8 864(6)
C(213)	6 315(10)	6 161(6)	12 462(4)	F(14)	2 067(10)	5 434(8)	8 123(7)
C(214)	6 654(9)	6 770(7)	12 698(5)	F(15)	405(13)	4 890(10)	7 872(8)
C(215)	5 796(9)	7 041(5)	13 134(4)	F(16)	753(11)	5 966(8)	8 736(8)
C(216)	4 591(8)	6 717(5)	13 348(4)	P(2)	4 575(4)	9 702(2)	6 951(2)
N(221)	3 056(6)	6 511(4)	14 303(3)	F(21)	3 736(28)	10 132(12)	6 397(9)
C(222)	3 691(8)	7 067(6)	13 791(4)	F(22)	5 614(25)	10 009(16)	6 509(14)
C(223)	3 491(9)	7 978(6)	13 670(5)	F(23)	5 465(19)	9 354(18)	7 461(13)
C(224)	2 619(10)	8 316(6)	14 061(6)	F(24)	3 429(14)	9 434(7)	7 473(8)
C(225)	1 900(10)	7 750(7)	14 565(5)	F(25)	4 689(14)	8 895(7)	6 814(9)
C(226)	2 147(8)	6 851(6)	14 673(4)	F(26)	4 229(14)	10 589(7)	7 075(6)
N(231)	1 815(6)	5 366(5)	15 218(3)				

Table 4 Magnetic susceptibility data for $[\{Cu(HL)\}_2][PF_6]_2$

T/K	$10^3\chi^a$/cm^3 mol^{-1}	$\mu_B{}^b$
84.7	4.52	1.75
99.0	4.03	1.79
118.0	3.56	1.83
137.7	3.13	1.85
157.2	2.87	1.90
176.4	2.54	1.90
196.2	2.33	1.91
215.4	2.19	1.94
234.8	2.07	1.97
264.2	1.83	1.97
292.3	1.66	1.97

[a] Accuracy: ±4%. [b] Magnetic moment per copper(II) ion, *i.e.* per half of formula weight.

phenolate displaced out of this plane towards the other copper atom, to which it provides the axial interaction. The phenolate oxygens are displaced by 0.595 and 0.551 Å respectively from the CuN_3 mean planes in the independent dimers.

The ligands are not planar but have a shallow helical twist, partly because the two phenol rings are oriented 'into' and 'out of' the dimer unit due to their separate (copper co-ordination, hydrogen-bonding) interactions, and partly no doubt to avoid steric interactions between the terminal phenol rings. A similar feature was observed in $[Ag(qpy)]^+$.[15] The torsion angles between successive pairs of aromatic rings in the dimer depicted are 39 (pendant phenol to co-ordinated pyridyl), 4 and then 6 (pyridyl–pyridyl), and finally 16° (pyridyl to co-ordinated phenolate), all in the same sense. In the independent dimer the corresponding ligand torsion angles are 42, 3, 4 and 19°. Formation of the dimer permits stacking interactions between overlapping sections of the two ligands; this is emphasised in Fig. 1(*b*).

It appears in this case that the stereochemical requirements of Cu^{II} outweigh the natural tendency of the ligand to use all of its binding sites to form bonds; there is no obvious steric reason why a double-stranded helix, as found for the binuclear copper complexes of qpy, could not form. This is in interesting contrast to $[Pd_2(qpy)_2]^{4+}$ in which a metal ion with a strong preference for square-planar geometry is attached to a pentadentate ligand;[16] the resulting double-helical structure imposes distorted five-co-ordinate geometries on the palladium(II) ions but ensures that all co-ordination sites are used. In $[\{Cu(HL)\}_2][PF_6]_2$ however the pendant phenol groups are stabilised by being involved in hydrogen-bonding interactions. In one dimer both pendant phenols form O–H $\cdots$ F hydrogen bonds to hexafluorophosphate ions (H $\cdots$ F 2.177 Å); in the other dimer both pendant phenols form O–H $\cdots$ N hydrogen bonds to acetonitrile molecules in the lattice (H $\cdots$ N 1.936 Å). (The hydroxyl hydrogen atoms were not located directly, but were included in optimum calculated positions on the basis of a rotating group refinement.[11]) Two other lattice MeCN molecules form a mutually hydrogen-bonded 'head-to-tail' pair. The hydrogen bonding of acetonitrile in the crystal may explain why full desolvation *in vacuo* was not achieved, since the analytical data indicated one MeCN per copper(II) centre remaining in the dried material.

The presence of oxygen bridges between two copper(II) centres is well known to lead to antiferromagnetic exchange between the metal centres,[17] and accordingly the magnetic properties of $[\{Cu(HL)\}_2][PF_6]_2$ were determined (Table 3). The data are consistent with a weak antiferromagnetic coupling: the magnetic moment decreases from 1.97 μ_B per Cu^{II} at room temperature to 1.75 μ_B per Cu^{II} at 85 K. A plot of χ^{-1} against temperature is linear and gives an antiferromagnetic Weiss constant of 38 K. It is quite possible that the solid sample contains some monomeric material as well as dimeric: although it is possible to calculate the magnetic coupling constant J with a modified version of the Bleaney–Bowers equation,[18] which takes into account the presence of a mononuclear impurity, we prefer not to do this considering the relatively high error associated with the data. We note simply that the decrease of μ_B with temperature for $[\{Cu(HL)\}_2][PF_6]_2$ is comparable to that observed for some other phenolate-bridged copper(II) dimers which were estimated to have $J = 52 \pm 8$ cm^{-1}.[4]

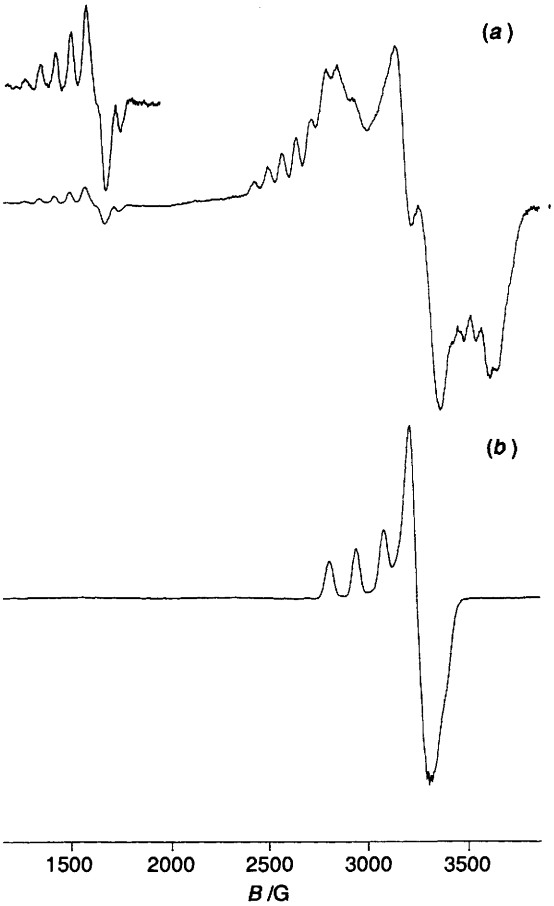


Fig. 2 The EPR spectra of $[\{Cu(HL)\}_2][PF_6]_2$ as frozen glasses at 77 K: (*a*) in CH_2Cl_2–dmf (4:1, v/v); (*b*) after thawing, addition of a drop of pyridine and refreezing

The solution behaviour of the dimer was established by EPR spectroscopy. The spectrum at 77 K in a CH_2Cl_2–dimethylformamide (dmf) (4:1) glass is shown in Fig. 2(*a*) and is a well resolved triplet the main characteristics of which are similar to those of other spectra of copper(II) dimers that we have examined recently.[4] The main part of the signal is expected to have six features ($-1 \longrightarrow 0$ and $0 \longrightarrow +1$ transitions, each with x, y and z components). Since the metal–metal separation is larger than in the complexes described in ref. 4 (3.3–3.4 as opposed to 3.0–3.1 Å), the zero-field spitting parameter $2D$ is smaller [$D = (g_{eff})^2(\mu_B)^2/r^3$, where r is the metal–metal distance]. The separation between the components of the $-1 \longrightarrow 0$ and $0 \longrightarrow +1$ transitions is correspondingly less and it is not possible to disentangle the six signals with certainty, but two positive-going signals (one with well resolved hyperfine splitting of 72 G between peaks) at approximately 2640 and 2770 G ($g = 2.55$ and 2.43 respectively) and two inflexions at 3180 and 3313 G ($g = 2.12$ and 2.03 respectively) may be identified. The two negative-going features are not separately identifiable but occur in the region of the spectrum between 3300 and 3700 G. In addition there is a 'forbidden' double-quantum transition ($-1 \longrightarrow +1$) at 1620 G ($g = 4.15$) with well resolved hyperfine splitting (76 G between peaks). Coupling to two equivalent copper(II) centres ($I = \frac{3}{2}$) should give a 1:2:3:4:3:2:1 septet hyperfine pattern: all seven lines are apparent on the double-quantum transition and the first five are apparent on the first positive-going feature of the main part of the spectrum. Owing to the difficulty in accurately measuring the positions of the six overlapping components of the main signal, and the likelihood of significant amounts of monomer (see below), simulation has not been attempted. However the spectrum conclusively shows that in CH_2Cl_2–dmf (4:1) at 77 K the $Cu(HL)^+$ units are still largely associated into phenolate-bridged dimers, as observed in the crystal structure.

After thawing out of the glass, addition of one drop of pyridine, and refreezing, the spectrum shown in Fig. 2(*b*) was obtained. This is a typical spectrum for a mononuclear copper(II) complex with $g_{\parallel} = 2.24$, $g_{\perp} = 2.07$ and $A_{\parallel}(Cu) = 137$ G. Copper hyperfine splitting on the 'perpendicular' component is not observable which is common for Cu^{II}; however superhyperfine coupling to nitrogen is apparent near the minimum [$A(N) = 13$ G]. There is no trace of any double-quantum transition in the half-field region. The presence of pyridine has therefore completely split the dimer into monomeric units by co-ordination at the axial copper(II) sites. Addition of weaker axial ligands results in partial splitting of the dimer: the EPR spectrum recorded in a MeCN–tetrahydrofuran (thf) glass gave a spectrum similar to that of Fig. 2(*b*) but with some components due to the dimer still present such as a weak trace of the double-quantum transition at half-field, indicating that dissociation was not complete. The complex therefore exists in solution as a solvent-dependent mixture of monomer and dimer.[19] It was not possible to monitor the equilibrium by electronic spectroscopy since the associated and dissociated species gave essentially identical d–d spectra ($\lambda_{max} = 560$ nm). The observed hyperfine splitting for the dimer (72 G) is approximately half that for the monomer (137 G), which occurs in triplet species when the modulus of J is much greater than the hyperfine interaction A.[20] Since a hyperfine interaction of 100 G is equivalent to approximately 0.01 cm^{-1} this condition is very easily satisfied even when the antiferromagnetic coupling is weak.

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