Copper(II) complexes of new potentially hexadentate N_3S_3- or N_6-donor podand ligands based on the tris(pyrazolyl)borate or tris(pyrazolyl)methane core

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The mononuclear copper(II) complexes of the following potentially hexadentate podand ligands have been prepared and crystallographically characterised: tris[3-{2-(methylsulfanyl)phenyl}pyrazol-1-yl]hydroborate $[L^1]^-$, phenyltris[3-(2-pyridyl)pyrazol-1-yl]methane (L^2), and tris[3-{(6-methyl)-pyrid-2-yl}pyrazol-1-yl]hydroborate $[L^3]^-$. Of these, $[L^1]^-$ [a potentially N_3S_3 donor with three pyrazolyl and three thioether groups, based on a tris(pyrazolyl)borate core] and L^2 [a potentially N_6 donor with three pyrazolyl and three pyridyl groups, based on a tris(pyrazolyl)methane core] have been prepared for the first time. In $[Cu(L^1)][PF_6]$ the Cu(II) centre is in a five-coordinate N_3S_2 coordination environment which is approximately square pyramidal; the pendant thioether group has a weak, long-range interaction with the sixth coordination site of Cu(II). $[Cu(L^1)][PF_6]$ undergoes a reversible Cu(I)–Cu(II) redox conversion. In $[Cu(L^2)(MeOH)][PF_6]_2$ the ligand is four-coordinate *via* two bidentate pyridyl/pyrazolyl arms, with the third arm pendant; an axial methanol ligand completes the square-pyramidal coordination. In $[Cu(L^3)(H_2O)][PF_6]$, which is five coordinate and approximately trigonal bipyramidal, $[L^3]^-$ acts as an N_4 donor *via* all three pyrazolyl groups but only one pyridyl group; the two pendant pyridyl groups are involved in O–H···N hydrogen-bonding interactions with the coordinated water molecule. This 'second-sphere' stabilisation of a coordinated ligand is strongly reminiscent of the cooperative interactions by which substrates are bound to the active sites of metalloproteins. The EPR spectra of this complex are solvent-dependent, showing a change from a d_{z^2} ground state in non-donor solvents to a $d_{x^2-y^2}$ ground state in donor solvents.

Tripodal ligands (podands) in which three polydentate coordinating arms are attached to a central linking group are popular ligands for conferring high stability on metal complexes and imposing upon them relatively rigid and well defined donor sets. The vast majority of these are hexadentate and have all-nitrogen, all-oxygen or mixed N,O-donor sets.[1] We have recently started to develop new tripodal ligands of this type based on the well known tris(pyrazolyl)borate core.[2] Our first example of this was the ligand Tp^{Py}, in which attachment of a 2-pyridyl group to the C^3 position of the pyrazolyl rings makes each arm a bidentate chelate.[3,4] This completely changes the character of the ligand compared to the parent Tp ligand and its simple substituted derivatives, and resulted in (*inter alia*) (i) an extensive coordination chemistry with lanthanide ions,[3] and (ii) multinuclear complexes with first-row transition metals displaying unusual multinuclear cage-like structures.[4]

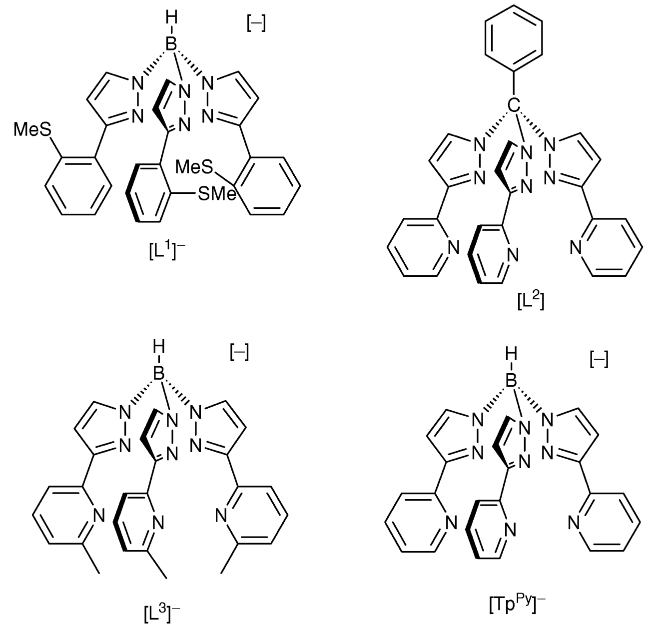
We describe here the preparation of two new potentially hexadentate podand ligands. The first is tris[3-{2-(methylsulfanyl)phenyl}pyrazol-1-yl]hydroborate $[L^1]^-$, a potentially N_3S_3-donor hexadentate podand in which $-C_6H_4SMe$ substituents are attached at the pyrazolyl C^3 positions, such that each arm is now potentially an N,S-bidentate chelate. There are a very few examples of tripodal ligands with N_3S_3 donor sets, the two principal classes being the 'sarcophaganes' of Sargeson, Hambley and coworkers,[5] and the triazacyclononane derivatives of Wieghardt and coworkers which contain aromatic thiols pendant from the N_3-donor macrocyclic ring.[6] The second new podand is phenyltris[3-(2-pyridyl)pyrazol-1-yl]methane (L^2), an analogue of our parent tris(pyrazolyl)borate Tp^{Py} in which the anionic BH head-group is replaced by a CPh group. Although L^2 is structurally similar to $[Tp^{Py}]$ it therefore differs in being neutral rather than anionic, which is likely to make a significant difference to its coordination behaviour. Tris(pyrazolyl)methanes have received less attention than their tris(pyrazolyl)borate analogues, although recently a systematic comparison of the structures of several main-group complexes with tris(pyrazolyl)methanes with those of their tris(pyrazolyl)borate analogues has been undertaken by Reger and coworkers.[7] The syntheses for both new ligands, together with the crystal structures of their complexes with copper(II), are described in this paper.

Also included is the structure of the copper(II) complex of the related podand ligand tris[3-{(6-methyl)-pyrid-2-yl}-pyrazol-1-yl]hydroborate $[L^3]^-$. The synthesis of this ligand, a derivative of Tp^{Py} in which sterically hindering methyl groups are attached to the C^6 positions of the pyridyl rings, was reported recently together with the structures and luminescence properties of some lanthanide complexes.[8] However no complexes with first-row transition metal ions have been reported until now. The ligand structures are shown in Scheme 1.

Experimental

General details

Instrumentation used for routine spectroscopic and electrochemical studies has been described in previous papers.[3,4,8] 3-(2-Pyridyl)pyrazole (Hpypz),[3] 2-(methylsulfanyl)acetophenone (**I**)[9] and KL^3 (ref. 8) were prepared according to the published methods.



Scheme 1 Ligands used in this study.

Preparations

1-[(2-Methylsulfanyl)phenyl]-3-dimethylamino-2-propen-1-one (II). A solution of 2-(methylsulfanyl)acetophenone (3.00 g, 0.018 mol) in dimethylformamide–dimethylacetal (5 cm^3, a large excess) was heated to reflux for 8 h under N_2. After this time the excess solvent was removed *in vacuo* to leave a red oil. Purification by column chromatography using CH_2Cl_2–thf (93 : 7, v/v) afforded **II** as a yellow oil (2.90 g, 73%). EIMS: *m/z* 206 (M^+ – Me). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (1 H, d, $J = 12$, vinylic CH), 7.45 (1 H, d, $J = 7.5$, phenyl), 7.30 (2 H, m, 2 × phenyl), 7.16 (1 H, td, $J = 7.2$, 1.5, phenyl), 5.48 (1 H, d, $J = 12$ Hz, vinylic CH), 3.11 (3 H, s, NCH_3), 2.90 (3 H, s, NCH_3), 2.44 (3 H, s, SCH_3). (Found: C, 63.2; H, 7.3; N, 6.2. $C_{12}H_{15}NOS \cdot 0.5H_2O$ requires C, 62.6; H, 7.0; N, 6.1%).

3-[2-(methylsulfanyl)phenyl]pyrazole (III). A mixture of **II** (2.90 g, 0.013 mmol) and hydrazine hydrate (4 cm^3, excess) in EtOH (30 cm^3) was heated to reflux for 30 minutes, after which it was cooled and water (100 cm^3) added. A white solid started to precipitate; the mixture was refrigerated overnight to allow precipitation to complete. The solid was filtered off, washed with water, and dried *in vacuo*. Recrystallisation from $CHCl_3$–hexane afforded **III** as an off-white crystalline solid (1.70 g, 68%). EIMS: *m/z* = 190 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.00 (1 H, d, $J = 3.0$, pyrazolyl), 7.66 (1 H, dd, $J = 7.5$, 1.5, phenyl), 7.44 (1 H, t, $J = 7.8$, phenyl), 7.30 (2 H, m, 2 × phenyl), 6.96 (1 H, d, $J = 3.0$, pyrazolyl), 2.46 (3 H, s, SCH_3) (Found: C, 63.0; H, 5.5; N, 14.7. $C_{10}H_{10}N_2S$ requires: C, 63.2; H, 5.3; N, 14.7%).

Potassium tris[3-{2-(methylsulfanyl)phenyl}pyrazol-1-yl]-hydroborate (KL^1). A mixture of **III** (1.45 g, 7.6 mmol) and KBH_4 (0.118 g, 2.2 mmol) was ground together to ensure intimate mixing and was then heated gradually to 200 °C. The mixture melted at *ca.* 90 °C, and started to evolve H_2 at *ca.* 110 °C. After 2 h at 200 °C the mixture was cooled to leave a glassy solid which was dissolved in warm toluene (100 cm^3) with the aid of an ultrasound cleaning bath. After addition of pentane (100 cm^3) to the toluene solution a white precipitate of KL^1 formed which was filtered off and dried *in vacuo* (0.77 g, 57%) (Found: C, 58.5; H, 4.8; N, 13.6. $C_{30}H_{28}BKN_6S_3$ requires: C, 58.3; H, 4.5; N, 13.6%). IR (KBr disc): ν_{B-H} 2409 cm^{-1}. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.78 (3 H, d, $J = 2.2$, pyrazolyl), 7.59 (3 H, d, $J = 7.3$, phenyl H^6), 7.23 (6 H, m, 2 × phenyl), 7.10 (3 H, m, phenyl), 6.46 (3 H, d, $J = 2.2$ Hz, pyrazolyl), 2.43 (9 H, s, SCH_3).

Phenyltris[3-(2-pyridyl)pyrazol-1-yl]methane (L^2). A mixture of 3-(2-pyridyl)pyrazole (1.00 g, 6.9 mmol) and NaH (0.248 g, 10 mmol) in toluene (60 cm^3) was heated at reflux under N_2, with vigorous stirring, for 2 hours. After cooling to room temperature, α,α,α-trichlorotoluene (0.449 g, 2.3 mmol) and NBu_4I (0.085 g, 0.23 mmol) were added to the reaction mixture which was then heated at reflux under N_2 for 12 h. After cooling, the mixture was filtered, placed in a separating funnel and shaken with water. The organic phase was collected, dried with $MgSO_4$ and evaporated to dryness *in vacuo*. The crude product was purified by column chromatography on alumina, initially using neat CH_2Cl_2 and then using CH_2Cl_2 containing 1–2% MeOH (v/v) as the eluent. The fourth fraction to elute was the desired product L^2, and repeated chromatography was usually necessary to get it clean. Yield: 0.097 g, 8%. EIMS: *m/z* 521 (M^+). (Found: C, 66.8; H, 4.5; N, 22.7. $C_{31}H_{23}N_9 \cdot 2H_2O$ requires C, 66.8; H, 4.8; N, 22.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (3 H, d, $J = 4.2$, pyridyl H^6), 7.92 (3 H, d, $J = 7.9$, pyridyl H^3), 7.66 (3 H, td, $J = 7.7$, 1.8, pyridyl H^4), 7.62 (3 H, d, $J = 2.7$, pyrazolyl H^4 or H^5), 7.50 (1 H, td, $J = 4.6$, 1.5, phenyl H^4), 7.43 (2 H, m, phenyl H^3/H^5), 7.35 (2 H, dd, $J = 7.2$, 1.6, phenyl H^2/H^6), 7.21 (3 H, ddd, $J = 7.3$, 4.9, 1.1, pyridyl H^5), 7.07 (3 H, d, $J = 2.7$ Hz, pyrazolyl H^5 or H^4).

$[Cu(L^1)][PF_6]$. A mixture of KL^1 (0.062 g, 0.1 mmol) and $Cu(O_2Me)_2 \cdot H_2O$ (0.020 g, 0.1 mmol) dissolved in 20 cm^3 MeOH was stirred at room temperature to give a clear green-brown solution. Addition of excess aqueous KPF_6 precipitated a brown solid which was filtered off and washed with water, and dried *in vacuo*. Recrystallisation by diffusion of Et_2O vapour into a concentrated MeCN solution of the complex afforded X-ray quality crystals.

$[Cu(L^2)(MeOH)][PF_6]_2$. A mixture of L^2 (0.050g, 0.096 mmol) and $Cu(O_2Me)_2 \cdot H_2O$ (0.019 g, 0.095 mmol) dissolved in 20 cm^3 MeOH was stirred at room temperature to give a clear green solution. Addition of excess aqueous KPF_6 precipitated a green solid which was filtered off and washed with water, and dried *in vacuo*. Recrystallisation by diffusion of Et_2O vapour into a concentrated MeCN solution of the complex afforded X-ray quality crystals.

$[Cu(L^3)(H_2O)][PF_6]$. A mixture of $Cu(O_2Me)_2 \cdot H_2O$ (7.6 mg, 0.038 mmol) and KL^3 (0.020 g, 0.038 mmol) in MeOH (50 cm^3) was stirred at room temperature for 1 h. Addition of aqueous KPF_6 precipitated a pale green solid, which was extracted from the aqueous suspension with CH_2Cl_2. Concentration of the organic layer followed by diffusion of pentane into the green solution resulted in a crop of X-ray quality crystals.

Characterisation data for the complexes are summarised in Table 1.

X-Ray crystallography

Suitable crystals were quickly transferred from the mother liquor to a stream of cold N_2 on a Siemens SMART diffractometer fitted with a CCD-type area detector. In all cases a full sphere of data was collected at –100 °C using graphite-monochromatised Mo-Kα radiation. A detailed experimental description of the methods used for data collection and inte-

Table 1 Characterisation and spectroscopic data for the new complexes

	Mass spectrum		Elemental analysis[a] (%)			UV–VIS spectra[b]	EPR spectra[c]		
Complex	m/z	Assignment	C	H	N	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$(Cu)/G
$[Cu(L^1)][PF_6]$	642[d]	$\{Cu(L^1)\}^+$	45.0 (44.7)	3.4 (3.7)	10.3 (10.4)	290 (sh), 370 (3.1), 630 (sh)[e]	2.19	2.02	156
$[Cu(L^2)(MeOH)][PF_6]_2$	584[d]	$\{Cu\{L^2)\}^+$	42.1 (42.4)	2.8 (3.0)	13.7 (13.9)	241 (44), 279 (36), 660 (0.12)[e]	2.25	2.06	169
$[Cu(L^3)(H_2O)][PF_6]$	549[f]	$\{Cu(L^3)\}^+$	44.8 (45.5)	4.3 (4.7)	14.4 (14.5)	242 (25), 286 (19), 785 (0.12)[e]	2.33	2.06	153[g]

[a] Required values in parentheses. [b] Recorded in MeCN. [c] Recorded as frozen CH_2Cl_2–thf glasses at 77 K. All spectra are consistent with a $d_{(x^2-y^2)}$ ground state. [d] FAB mass spectrum. [e] Cu(II)-centred d–d transition. [f] ES mass spectrum. [g] This EPR spectrum is strongly solvent dependent; see main text.

gration using the SMART system has been published.[3] Table 2 contains a summary of the crystal parameters, data collection and refinement. The absorption corrections were applied using SADABS.[10] In all cases the structures were solved by conventional direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.03 package on a Silicon Graphics Indy computer.[11] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atom.

In $[Cu(L^1)][PF_6]\cdot H_2O$ the asymmetric unit contains one complex cation and one complete water molecule, as well as three hexafluorophosphate ions whose P atoms lie on sites of threefold symmetry such that one-third of each of the three anions lies within the asymmetric unit. In $[Cu(L^2)(MeOH)][PF_6]_2\cdot H_2O\cdot 2MeOH$ the F atoms of one of the hexafluorophosphate anions were disordered over two

Table 2 Crystallographic data for the three new complexes

Compound	$[Cu(L^1)][PF_6]\cdot H_2O$	$[Cu(L^2)(MeOH)][PF_6]_2\cdot H_2O\cdot 2MeOH$	$[Cu(L^3)(H_2O)][PF_6]\cdot CH_2Cl_2\cdot C_5H_{12}$
Formula	$C_{30}H_{30}BCuF_6N_6OPS_3$	$C_{34}H_{37}CuF_{12}N_9O_4P_2$	$C_{33}H_{41}BCl_2CuF_6N_9OP$
M	806.1	989.2	870.0
System, space group	Cubic, $Pa\bar{3}$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a/Å	27.283(3)	19.585(3)	10.020(2)
b/Å	27.283(3)	9.9751(9)	13.254(2)
c/Å	27.283(3)	20.884(2)	15.142(3)
α/°	90	90	105.878(13)
β/°	90	92.845(11)	106.30(2)
γ/°	90	90	92.291(14)
U/Å^3	20308(4)	4075.0(8)	1841.5(6)
Z	24	4	2
D_c/g cm^{-3}	1.582	1.612	1.569
μ/mm^{-1}	0.947	0.720	0.855
Crystal size/mm	0.40 × 0.36 × 0.14	0.50 × 0.40 × 0.12	0.26 × 0.20 × 0.04
Reflections collected: total, independent, R_{int}	81102, 4431, 0.1297	25058, 9265, 0.0429	15701, 6449, 0.0583
Data, restraints, parameters	4427, 15, 472	9265, 0, 617	6426, 74, 516
Final R_1, wR_2[b, c]	0.0601, 0.1279	0.0577, 0.1692	0.0627, 0.1811
Weighting factors[c]	0.0369, 86.3345	0.1061, 0	0.087, 1.84
Largest residuals/e Å^{-3}	+1.689, −0.443	+1.079, −0.813	+0.639, −0.899

[a] Details in common: Mo–Kα radiation (0.71073 Å); temperature for data collection, 173(2) K; 2θ limit for data collected, 55°. [b] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\, w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 3 Selected bond lengths (Å) and angles (°) for the new structures

$[Cu(L^1)][PF_6]\cdot H_2O$		$[Cu(L^2)(MeOH)][PF_6]_2\cdot H_2O\cdot 2MeOH$		$[Cu(L^3)(H_2O)][PF_6]\cdot CH_2Cl_2\cdot C_5H_{12}$	
Cu(1)–N(12)	1.968(5)	Cu(1)–N(21)	1.944(3)	Cu(1)–N(52)	1.898(4)
Cu(1)–N(32)	2.048(5)	Cu(1)–N(41)	1.950(3)	Cu(1)–O(1)	1.901(4)
Cu(1)–N(52)	2.141(5)	Cu(1)–N(31)	2.051(3)	Cu(1)–N(32)	2.171(4)
Cu(1)–S(27)	2.313(2)	Cu(1)–O(3)	2.156(3)	Cu(1)–N(12)	2.212(4)
Cu(1)–S(67)	2.372(2)	Cu(1)–N(51)	2.059(3)	Cu(1)–N(62)	2.212(4)
N(12)–Cu(1)–N(32)	88.1(2)	N(21)–Cu(1)–N(41)	84.34(11)	N(52)–Cu(1)–O(1)	177.2(2)
N(12)–Cu(1)–N(52)	90.4(2)	N(21)–Cu(1)–N(31)	79.98(11)	N(52)–Cu(1)–N(32)	88.4(2)
N(32)–Cu(1)–N(52)	89.3(2)	N(41)–Cu(1)–N(31)	160.34(11)	O(1)–Cu(1)–N(32)	94.4(2)
N(12)–Cu(1)–S(27)	89.9(2)	N(21)–Cu(1)–N(51)	159.98(11)	N(52)–Cu(1)–N(12)	87.0(2)
N(32)–Cu(1)–S(27)	158.48(14)	N(41)–Cu(1)–N(51)	79.80(11)	O(1)–Cu(1)–N(12)	93.6(2)
N(52)–Cu(1)–S(27)	112.13(13)	N(31)–Cu(1)–N(51)	112.47(11)	N(32)–Cu(1)–N(12)	86.1(2)
N(12)–Cu(1)–S(67)	167.7(2)	N(21)–Cu(1)–O(3)	103.29(11)	N(52)–Cu(1)–N(62)	76.9(2)
N(32)–Cu(1)–S(67)	93.06(14)	N(41)–Cu(1)–O(3)	105.89(12)	O(1)–Cu(1)–N(62)	100.8(2)
N(52)–Cu(1)–S(67)	77.39(13)	N(31)–Cu(1)–O(3)	89.30(11)	N(32)–Cu(1)–N(62)	135.2(2)
S(27)–Cu(1)–S(67)	93.36(6)	N(51)–Cu(1)–O(3)	92.81(11)	N(12)–Cu(1)–N(62)	133.9(2)

sites whose site occupancies refined to 0.6/0.4; the position of the P atom was common to both components of the disorder. In $[Cu(L^3)(H_2O)][PF_6] \cdot CH_2Cl_2 \cdot C_5H_{12}$ the Cl atoms of the CH_2Cl_2 were disordered over two sites with fractional occupancies of 0.3 and 0.7; restraints were applied to the geometric and thermal parameters of this solvent molecule to keep the refinement stable. In addition there was a collection of five closely-spaced electron-density peaks which clearly corresponds to a disordered alkane; these refined successfully as carbon atoms with unit site occupancy (corresponding to a disordered molecule of pentane).

Selected bond lengths and angles for all three structures are collected in Table 3.

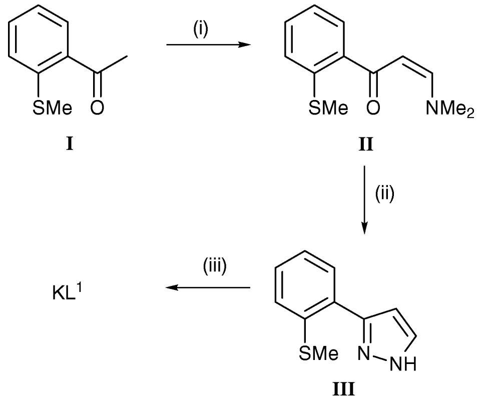
CCDC reference number 440/096. See http://www.rsc.org/suppdata/nj/1999/417/ for crystallographic files in .cif format.

Results and discussion

Synthesis of KL^1 and the crystal structure of $[Cu(L^1)][PF_6] \cdot H_2O$

The new ligand $[L^1]^-$ was prepared (as its potassium salt) according to Scheme 2. The key intermediate in the synthesis is 2-(methylsulfanyl)acetophenone **I**, which was prepared according to the literature method[9] from commercially available 2-sulfanylbenzoic acid by methylation of the thiol with MeI, followed by conversion of the carboxylic acid function to an acetyl group with two equivalents of methyl lithium in thf. Conversion of the acetyl group to a pyrazole in two steps is facile, following the route we have used before:[3,8] (i) reaction with neat dmf–dimethylacetal at reflux for 8 h to give the dimethylamino-substituted enone **II**, followed by (ii) ring-closure to the pyrazole **III** by reaction with an excess of hydrazine in EtOH at reflux for 30 minutes. Finally, the tris(pyrazolyl)borate $[L^1]^-$ was prepared in the usual manner by melting together a mixture of KBH_4 and **III** (1 : 3.5 molar ratio) at 200 °C for 3 h under N_2, followed by recrystallisation of the resultant glassy solid from toluene–pentane (1 : 1).

Reaction of KL^1 with copper(II) acetate hydrate in MeOH afforded a green solution from which a precipitate was isolated after treatment with methanolic KPF_6. Recrystallisation from MeCN–diethyl ether afforded X-ray quality crystals of a material whose mass spectrum and elemental analysis suggested the formulation $[Cu(L^1)][PF_6] \cdot H_2O$, and this was subsequently confirmed crystallographically. The structure of the complex cation is shown in Fig. 1. The metal ion is in a five-coordinate N_3S_2 coordination environment which may be approximately described as square pyramidal, with N(52) being the axial ligand and N(12), S(27), S(67) and N(32) comprising the basal plane [mean separation of these four atoms from the best mean plane through them, 0.31 Å; separation of the metal atom from the mean basal plane, 0.09 Å]. According to the method of Addison *et al.* for classifying five-coordinate geometries,[12] the parameter τ for this complex is 0.15, where 0 denotes a perfect square-based pyramid and 1 denotes a perfect trigonal bipyramid. The remaining donor atom S(47) is too far from the metal to be considered as forming a normal coordinate bond [Cu(1)···S(47), 3.053(2) Å] but its weak interaction with the second axial coordination site is consistent with the stereoelectronic requirements of the Jahn–Teller effect. The bidentate arms are not individually coplanar because of substantial dihedral twists between the pyrazolyl and phenyl rings [19.8° between rings 1 and 2; 42.6° between rings 3 and 4; 31.3° between rings 5 and 6, where ring 1 contains N(11) to C(15), ring 2 contains C(21) to C(26), *etc.*].



Scheme 2 Preparation KL^1: (i) dimethylformamide–dimethylacetal; (ii) hydrazine hydrate, EtOH, reflux; (iii) KBH_4, melt.

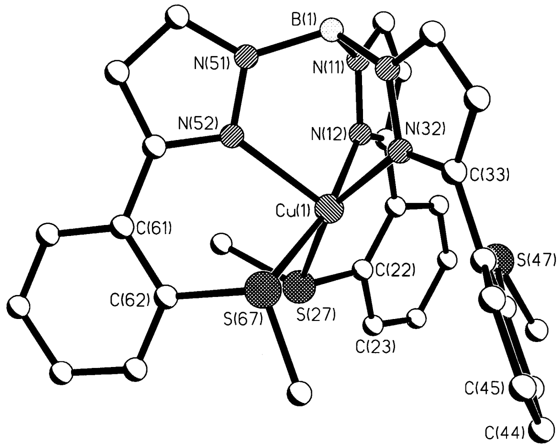


Fig. 1 Crystal structure of the complex cation of $[Cu(L^1)][PF_6] \cdot H_2O$.

Copper(II) complexes with mixed N/S donor sets based on heterocyclic N donors and thioether S donors have been of interest as structural and spectroscopic models for various type I copper proteins which have similar coordination spheres.[13,14] Of particular interest is the Cu(I)–Cu(II) redox potential, which is related to both the geometry of the coordination sphere and the nature of the donor atoms. For $[Cu(L^1)][PF_6]$ in MeCN, cyclic voltammetry showed a symmetric, reversible redox process at $E_{1/2} = -0.42$ V *vs.* ferrocene–ferrocenium (peak–peak separation, 90 mV) which we assign to the Cu(I)–Cu(II) couple. This translates to *ca.* 0.0 V *vs.* NHE, and may be compared to the redox potential range of type 1 copper proteins which runs from +0.18 V (stellacyanin) to +0.68 V (rusticyanin).[14] In $[Cu(L^1)][PF_6]$ therefore the Cu(II) state is stabilised compared to related biological systems, which we ascribe to the higher coordination number; stabilisation of Cu(I) in type 1 copper proteins is ascribable in part to the fact that the metal centres are basically four-coordinate and pseudo-tetrahedral.

Synthesis of L^2 and the crystal structure of $[Cu(L^2)(MeOH)][PF_6]_2 \cdot H_2O \cdot 2MeOH$

The standard synthesis of tris(pyrazolyl)methanes involves reaction of the appropriate pyrazole (three equivalents) with $CHCl_3$ under phase transfer conditions using aqueous NaOH as base.[15] The reaction requires substitution of all three chlorine atoms of $CHCl_3$ by the pyrazole anion, and competing side-reactions occur due to the formation of the reactive $:CCl_2$ diradical by loss of HCl from $CHCl_3$ in the strongly basic conditions. Nonetheless reasonable yields of simple tris(pyrazolyl)methanes may be obtained. However all attempts to prepare the tris(pyrazolyl)methane from 3-(2-pyridyl)pyrazole (Hpypz) under these conditions failed, giving crude reaction mixtures containing small amounts of large numbers of products. To reduce the likelihood of carbene-based side-reactions we therefore replaced $CHCl_3$ by $PhCCl_3$

in the synthesis. By this method we managed to obtain modest amounts of L^2, although there were still numerous by-products of which the most abundant was (on the basis of its mass spectrum) Ph(pypz)C=C(pypz)Ph, showing that carbene-based side reactions were not entirely eliminated. The new ligand L^2 was satisfactorily characterised on the basis of its mass and NMR spectra, and elemental analysis.

Reaction of L^2 with copper(II) acetate followed by precipitation of the complex as its hexafluorophosphate salt afforded a material whose FAB mass spectrum indicated formation of a 1 : 1 Cu : L^2 complex. The crystal structure of $[Cu(L^2)(MeOH)][PF_6]_2 \cdot H_2O \cdot 2MeOH$ is shown in Fig. 2 (see also Table 3) and shows that L^2 is coordinated as a tetradentate ligand *via* two bidentate arms, resulting in a square-pyramidal Cu(II) centre whose fifth (axial) ligand is a molecule of methanol. The four atoms N(31), N(22), N(42) and N(51) form a near-perfect plane (the mean deviation from the mean plane through them is 0.028 Å), and the metal atom is displaced 0.291 Å out of this mean basal plane towards the axial methanol ligand. The third pyrazolyl-pyridine arm is pendant with the pyrazolyl and pyridyl rings being *trans*-coplanar to maximise the separation between the lone pairs on N(61) and N(71). The axial methanol ligand is involved in an O–H···O hydrogen-bonding interaction with one of the lattice MeOH molecules [O(3)···O(7), 2.670(5) Å], which in turn is hydrogen-bonded to the other lattice MeOH molecule [O(7)···O(5), 2.537(5) Å]. In addition the pendant pyridyl residue is involved in an N···H–O hydrogen-bonding interaction with the lattice water molecule [N(71)···O(8), 2.767(5) Å]. The neutral tris(pyrazolyl)methane L^2 therefore coordinates to Cu(II) in essentially the same way as the isostructural but negatively charged tris(pyrazolyl)borate analogue $[Tp^{Py}]^-$,[16] which forms a square-pyramidal complex $[Cu(Tp^{Py})(H_2O)][PF_6]$, although in this latter case the pendant arm is involved in hydrogen-bonding interactions with the axial water ligand. This is consistent with the recent observations of Reger and coworkers that simple tris(pyrazolyl)borates and tris(pyrazolyl)methanes can display essentially identical structures in their metal complexes.[7]

Synthesis, crystal structure and EPR spectra of $[Cu(L^3)(H_2O)][PF_6] \cdot CH_2Cl_2 \cdot C_5H_{12}$

We showed recently that the luminescence properties of Eu(III) and Tb(III) complexes of $[L^3]^-$ were considerably different from those of the parent (unsubstituted) ligand $[Tp^{Py}]^-$ because of the changes in coordination geometry caused by the sterically hindering methyl substituents.[8] We were therefore interested to examine first-row transition-metal complexes with $[L^3]^-$ to see how they compared with $[Tp^{Py}]^-$, and the crystal structure of $[Cu(L^3)(H_2O)][PF_6]$ is shown in Fig. 3 (see also Table 3). The metal centre is five coordinate from the three pyrazolyl donors, one pyridyl donor and one water molecule. The parameter τ is 0.70,[12] indicating that the structure lies nearer the trigonal bipyramidal limit than the square pyramidal limit; the two axial ligands in this description are N(52) and O(1), with N(12), N(32) and N(62) forming the equatorial plane. The two pendant pyridyl donors are involved in N···H–O hydrogen-bonding interactions with the protons of the coordinated water molecule [O(1)···N(22) 2.642(7) Å, O(1)···N(42) 2.685(7) Å]. The water molecule is therefore a conventional first-sphere ligand, and the pendant groups which coordinate in turn to the water are 'second-sphere ligands' in that they constitute the second coordination sphere of the metal ion. This is very similar behaviour to that of the lanthanide complexes of $[L^3]^-$;[8] the steric interference between the pyridyl methyl substituents which would result if the ligand were hexadentate, with the methyl groups all directed towards one another, is relieved by two of the pyridyl ligands twisting away from the metal and binding instead to the water ligand. Consequently these pyridyl/pyrazolyl arms are not planar, with dihedral twist angles of 33.5° between rings 3 and 4, and 22.4° between rings 5 and 6 [where ring 3 contains N(31)–C(35), *etc.*]. This also results in the associated Cu–N(pyrazolyl) distances being stretched as the pyridyl groups move away from the metal atom: the distances Cu(1)–N(32) and Cu(1)–N(12) [2.171(4) and 2.212(4) Å, respectively] are considerably longer than Cu(1)–N(52) [1.898(4) Å].

This 'second-sphere' stabilisation of a coordinated ligand is strongly reminiscent of the cooperative interactions by which substrates are bound to the active sites of metalloproteins.[14] It is relatively rare in simple coordination complexes because it requires a ligand of sufficient complexity and flexibility to bond the metal with some of its donors whilst simultaneously interacting with a coordinated substrate with the others, but has recently become the focus of interest in the areas of host-guest, supramolecular and biomimetic chemistry.[17] The structure of $[Cu(L^3)(H_2O)][PF_6]$ is in interesting contrast to that of $[Cu(Tp^{Py})(H_2O)][PF_6]$,[16] which is recalled in Fig. 4. In this latter structure two bidentate arms of Tp^{Py} and a water ligand also form a five-coordinate structure, but in contrast to $[Cu(L^3)(H_2O)][PF_6]$ it is square-pyramidal. Adoption of such a structure with L^3 would result in an unfavourable steric interaction between the methyl substituents of the two coordinated pyridyl ligands.

We recorded EPR spectra of all of the complexes described in this paper as part of their routine characterisation (Table 1),

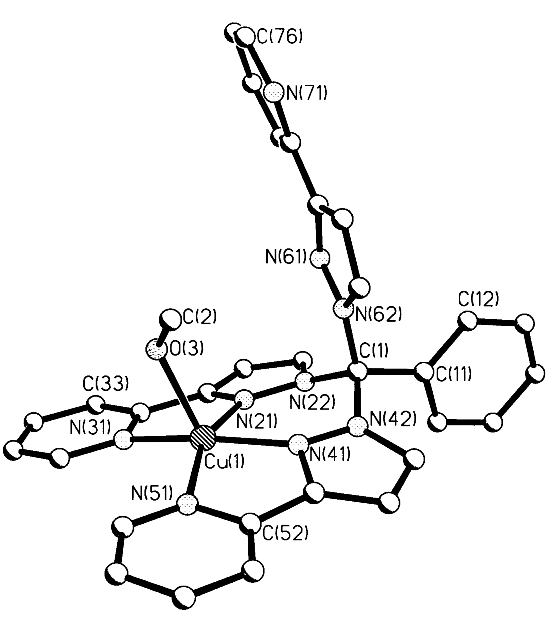


Fig. 2 Crystal structure of the complex cation of $[Cu(L^2)(MeOH)][PF_6]_2 \cdot H_2O \cdot 2MeOH$.

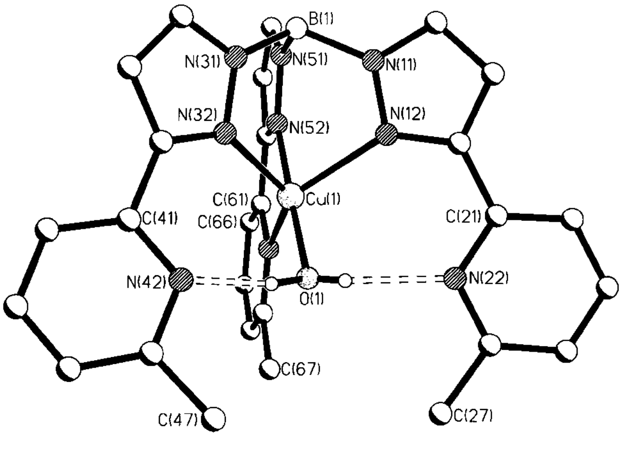


Fig. 3 Crystal structure of the complex cation of $[Cu(L^3)(H_2O)][PF_6] \cdot CH_2Cl_2 \cdot C_5H_{12}$.

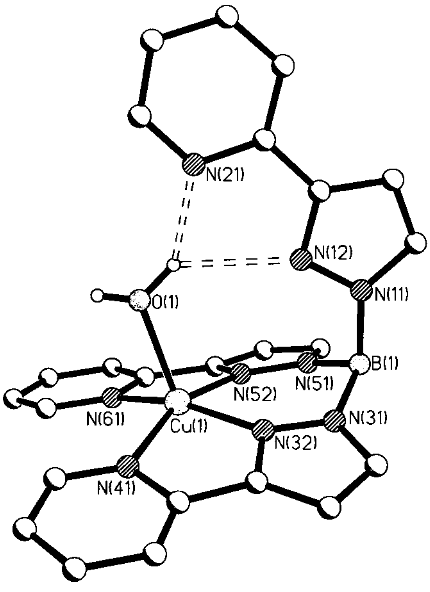


Fig. 4 Crystal structure of the complex cation of $[Cu(Tp^{Py})(H_2O)][PF_6]$ (from ref. 16).

and noticed two unusual features in the spectrum of $[Cu(L^3)(H_2O)][PF_6]$ recorded as a CH_2Cl_2–thf glass at 77 K [Fig. 5(b)]. Firstly, the spectrum indicates a $d_{x^2-y^2}$ ground state, which is very common for tetragonally-elongated four-, five- or six-coordinate Cu(II) complexes but is not consistent with the basically trigonal bipyramidal crystal structure, for which a d_{z^2} ground state would be expected.[18,19] This suggests that the structure observed in the solid state changes on dissolution in this particular solvent combination, either due to solvation or to rearrangement (*e.g.* coordination of one of the pendant pyridyl residues). Secondly, the spectrum appears to be of rather poor quality with evidence for what we assumed to be impurities but which appeared consistently even after recrystallisation, suggesting the presence of a mixture of species in solution. Both of these observations prompted us to investigate the solvent-dependence of the EPR spectrum of this complex.

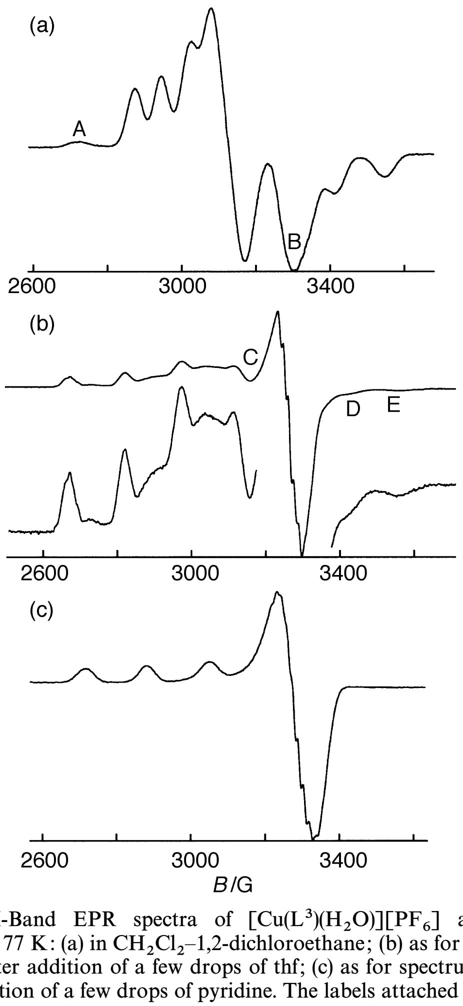


Fig. 5 X-Band EPR spectra of $[Cu(L^3)(H_2O)][PF_6]$ as frozen glasses at 77 K: (a) in CH_2Cl_2–1,2-dichloroethane; (b) as for spectrum (a) but after addition of a few drops of thf; (c) as for spectrum (a) but after addition of a few drops of pyridine. The labels attached to particular features of the spectra are explained in the text.

In a non-donor solvent mixture (1 : 1 dichloromethane–dichloroethane) the spectrum of Fig. 5(a) was obtained at 77 K, and it is suggestive of a d_{z^2} ground state arising from an approximately trigonal bipyramidal structure.[18,19] There are three g-values rather than two however, consistent with significant distortion from ideal trigonal bipyramidal geometry, and the parameters are $g_1 = 2.26$ ($A_1 \approx 70$ G), $g_2 = 2.16$, and $g_3 = 2.02$ ($A_3 \approx 130$ G). The peaks marked **A** and **B**, which are not reproduced by simulation with the above parameters, are consistent with a small proportion of a species with a $d_{x^2-y^2}$ ground state and in fact correspond closely to features in the spectrum of Fig. 5(c) (see later). Thus it appears that the crystal structure is largely retained in this non-donor solvent, with only a small proportion of the complex being converted to some other geometry which has a $d_{x^2-y^2}$ ground state (presumably, either by solvation or by attachment of one of the pendant pyridyl groups). We emphasise that the presence of the second set of peaks (**A** and **B**) make simulation difficult and render the paremeters for the main part of the spectrum somewhat unreliable, although the basic pattern of the spectrum is clear.

On thawing the sample, addition of a few drops of thf, and re-freezing to 77 K, the spectrum changes substantially [Fig. 5(b)]. This shows that most of the sample is converted to a solvated species (presumably a thf adduct) with a basically tetragonal geometry giving a $d_{x^2-y^2}$ ground state. The parameters are $g_{\parallel} = 2.33$ ($A_{\parallel} = 153$ G); $g_{\perp} = 2.06$. The relatively high value of $g_{\parallel}$ and the relatively low value of $A_{\parallel}$ [*cf.* the spectrum of Fig. 5(c)] are both indicative of a tetrahedral distortion of the four equatorial ligands.[20] We can also see how the additional features in this spectrum, which we initially ascribed to impurities, arise from a small proportion of the unchanged non-solvated species [Fig. 5(a)]. In particular the inflexion labelled **C** and the two weak features to the high-field side of the main signal (**D** and **E**) correspond almost exactly to features in the spectrum of Fig. 5(a).

On addition of a drop of pyridine to the dichloromethane–dichloroethane solution of the complex, the spectrum of Fig. 5(c) is obtained. This is a clean spectrum and consistent with complete conversion of the complex to a tetragonal structure (presumably a pyridine adduct) with a $d_{x^2-y^2}$ ground state; the parameters are $g_{\parallel} = 2.27$ ($A_{\parallel} = 170$ G); $g_{\perp} = 2.06$. The fact that addition of pyridine results in a single solvated species, whereas addition of thf results in a mixture due to only partial solvation, is in accord with the fact that pyridine is a much better ligand for Cu(II) than is thf.

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