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Coordination chemistry of mixed pyridine-phenol ligands; mononuclear palladium(II) and dinuclear copper(II) complexes of derivatives of bidentate *N,O*-chelating ligands based on 2-(2-hydroxyphenyl)pyridine

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Abstract—The new ligands 2-(2-hydroxyphenyl)-4-'butyl-pyridine (HL^1), 2-(2-hydroxyphenyl)-6-methyl-pyridine (HL^2) and 2-(2-hydroxyphenyl)-6-[(2-phenyl)ethyl]pyridine (HL^3) were prepared. They are all substituted derivatives of the simple *N,O*-bidentate chelating ligand 2-(2-hydroxyphenyl)pyridine. HL^1 is solubilised derivative bearing a 'Bu substituent in a position which will not sterically interfere with metal-ion coordination; HL^2 and HL^3 contain substituents at C^6 of the pyridyl ring, adjacent to the N atom, which will therefore sterically hinder metal-ion coordination. The complexes $[PdL_2]$ (L = L^1, L^2 and L^3) were prepared and structurally characterised to determine the effects (if any) of the substituents on the structures of the metal complexes. All are four-coordinate complexes with square planar coordination geometry about the Pd(II) ion, but the sterically hindered ligands L^2 and L^3 have to adopt a different conformation from L^1 to allow planar coordination, resulting in "bowl-like" structures. $[Cu_2(L^1)_4]$ was also prepared and found to be a phenolate-bridged dinuclear complex in the solid state, both by X-ray crystallography and EPR measurements. In solution, however, it dissociates to give $[Cu(L^1)_2]$ monomeric units. Cu(II) complexes of L^2 and L^3 could not be isolated. © 1997 Elsevier Science Ltd

Keywords: copper; palladium; crystal structures.

As part of our continuing study on the synthesis and coordination chemistry of mixed-donor polydentate ligands [1–5], we describe here some derivatives of the simple bidentate ligand 2-(2-hydroxyphenyl)pyridine HL, an *N,O*-donor chelate. Remarkably little coordination chemistry of this simple ligand was described until recently, despite its appeal as a hydrolytically stable structural and electronic analogue of salicylaldimines, because it was difficult to prepare; prior to our work the sole structurally characterised complexes were $[PdL_2]$ and $[CoL_3]$ [6]. We recently developed [4] a simple, high-yield synthesis of HL and subsequently described the crystal structures, electrochemical and spectroscopic properties of a series of ruthenium (II and III) and chromium(III) complexes [4,5].

In this paper we describe the preparation of three new substituted derivatives of HL. Ligand HL^1, containing a tertiary-butyl substituent at the C^4 position of the pyridyl ring, is a soluble analogue of HL which was prepared to facilitate characterisation of those complexes of HL which were only poorly soluble. Ligands HL^2 and HL^3 contain substituents at the C^6 position of the pyridyl ring, which are intended to provide steric hindrance to square-planar or octahedral coordination. Ligands which can impose an irregular geometry on metal ions may provide the basis for selective extraction of metal ions other than Cu(II) from a mixture [7] and we were therefore interested to see the extent to which addition of bulky substituents at the C^6 positions of these ligands would result in distortions away from regular coordination geometries.

The preparations and crystal structures of the three

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mononuclear Pd(II) complexes $[Pd(L^1)_2]$, $[Pd(L^2)_2]$ and $[Pd(L^3)_2]$, and the dinuclear Cu(II) complex $[Cu_2(L^1)_4]$, are described in this paper.

EXPERIMENTAL

Preparation of 2-(2-methoxyphenyl)-4-^{t}butyl-pyridine (MeL^1)

A solution containing 2-lithioanisole was prepared by adding lithium pieces (388 mg, 56 mmol) to 2-bromoanisole (6.89 g, 37 mmol) in dry ether (50 cm^3) under N_2, and stirring the mixture at room temperature for 2 h. This solution was added to a solution of 4-tert-butylpyridine (4.99 g, 37 mmol) in dry toluene (40 cm^3), and the resultant mixture was stirred at 50°C under N_2 for 48 h. The solvents were removed under reduced pressure, and the residue was dissolved in acetone (50 cm^3). A saturated solution of $KMnO_4$ in acetone (3×100 cm^3) was added to oxidise the dihydropyridine, and the MnO_2 was removed by filtration through Celite. Evaporation of the acetone afforded a brown oil which was purified by column chromatography on alumina, using CH_2Cl_2 as the eluent to give a yellow oil. Yield: 1.27 g (14%). EIMS: $m/z = 241$ (M^+), 196 (M^+—^{t}Bu), 136 (M^+—C_7H_8O). Anal. Found C, 79.1; H, 8.0; N, 6.0%. Required for $C_{16}H_{19}NO$: C, 79.3; H, 7.5; N, 6.2%. See Table 1 for ^{1}H NMR data.

Preparation of 2-(2-hydroxyphenyl)-4-^{t}butyl-pyridine (HL^1)

This was prepared by demethylation of the precursor MeL^1 (1.20 g, 5 mmol) using molten pyridinium chloride at 190°C for 1.75 h according to the published method [8]. The mixture was allowed to cool, water (50 cm^3) was added and the dark red solution was neutralised using aqueous KOH. The resulting precipitate was extracted into CH_2Cl_2 and purified further on silica using CH_2Cl_2 as the eluent to give a yellow solid. Yield: 0.50 g (45%). EIMS: $m/z = 227$ (M^+). Anal. Found C, 78.8; H, 7.1; N 5.9. Required for $C_{15}H_{17}NO$: C, 79.6; H, 7.1; N, 6.2. See Table 1 for ^{1}H NMR data.

Preparation of 2-bromo-6-methylpyridine

This preparation is based on a published method [9]. To a three necked flask fitted with a mechanical stirrer, a low temperature thermometer, and containing 45% HBr (60 cm^3), 2-amino-6-picoline (17.5 g, 0.16 mol) was carefully added. The mixture was cooled to −40°C and bromine (24 cm^3, 0.47 mol) was added dropwise with vigorous stirring. A solution of sodium nitrite (27.5 g, 0.40 mol) in water (60 cm^3) was then added dropwise to the orange perbromide, whilst maintaining the temperature below −10°C. A solution of sodium hydroxide (60 g, 1.5 mol) in water (60 cm^3) was added slowly, maintaining the temperature

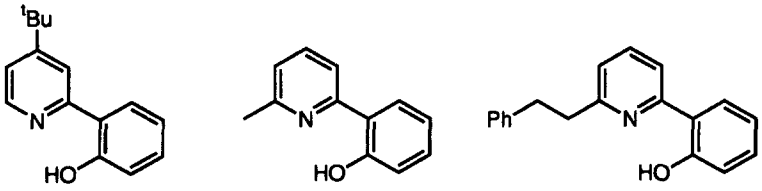

Table 1. ^{1}H NMR spectral data for the new ligands and their methylated precursors ($CDCl_3$, 300 MHz, 293 K)[a]

	Pyridyl protons	Phenyl protons	Other protons
MeL^1	8.60 (dd), 7.79 (d), 7.72 (dd)	7.37 (ddd), 7.21 (dd), 7.07 (td), 7.01 (dd)	3.86 (3H, OMe)
HL^1	8.42 (dd), 7.91 (d), 7.84 (dd)	7.30 (td), 7.26 (dd), 7.02 (dd), 6.92 (td)	*b*
MeL^2	7.73 (dd), 7.56 (2H, m)	7.37 (ddd), 7.21 (dd), 7.07 (td), 7.01 (dd)	3.80 (3H, OMe); 2.60 (3H, Me)
HL^2	7.79 (dd), 7.71 (2H, m)	7.29 (td), 7.08 (t), 7.02 (dd), 6.89 (td)	14.79 (1H, OH)
MeL^3	7.76 (dd), 7.63 (2H, m)	7.38 (td), 7.18–7.30 (5H, m), 7.09 (td), 7.02 (2H, m)	3.86 (3H, OMe); 3.1–3.2 (4H, CH_2CH_2)
HL^3	7.80 (dd), 7.74 (2H, m)	7.25–7.35 (3H, m), 7.15–7.22 (3H, m), 7.06 (dd), 7.02 (dd), 6.92 (td)	3.1–3.2 (4H, CH_2CH_2)[b]

[a] All signals correspond to one proton unless stated otherwise.
[b] Hydroxyl proton not visible.

below 0°C. After warming up to room temperature, the mixture was extracted with ether (2×100 cm^3) and the product purified using column chromatography on silica with CH_2Cl_2 as the eluent. Yield 18.5 g (67%). EIMS: $m/z = 171$ (M^+) (based on ^{79}Br). Anal. Found C, 42.0; H, 3.7; N, 7.7%. Required for C_6H_6NBr: C, 42.1; H, 3.5; N, 8.2%.

Preparation of 2-(2-methoxyphenyl)-6-methylpyridine (MeL^2)

To an ice-cold mixture of $Ni(dppe)Cl_2$ (0.53 g, 1 mmol) and 2-bromo-6-methylpyridine (5.68 g, 33 mmol) in dry THF (50 cm^3) under N_2, a solution of the Grignard reagent prepared from 2-bromoanisole (9.26 g, 50 mmol) and magnesium turnings (1.2 g, 50 mmol) in THF (50 cm^3) was added. The mixture was allowed to warm up slowly to room temperature, and then stirred under N_2 for 24 h. The reaction was quenched with water (50 cm^3), and the solvents were removed under reduced pressure. The remaining oil was purified by column chromatography on alumina with CH_2Cl_2/MeOH (98:2) as the eluent to give a straw-coloured oil. Yield: 4.22 g (71%). EIMS: $m/z = 199$ (M^+), 169 (M^+—OMe). Anal. Found C, 78.0; H, 6.4; N, 7.1%. Required for $C_{13}H_{13}NO$: C, 78.4; H, 6.6; N, 7.0%. See Table 1 for ^{1}H NMR data.

Preparation of 2-(2-hydroxyphenyl)-6-methylpyridine (HL^2)

This was prepared by demethylation of the precursor MeL^2 (0.82 g, 4 mmol) using molten pyridinium chloride at 190°C for 1.75 h according to the published method [8]. After allowing the mixture to cool to room temperature, water (50 cm^3) was added and the resultant dark red solution was neutralised using aqueous KOH. The resulting precipitate was extracted into CH_2Cl_2, and purified on silica using CH_2Cl_2 as the eluent to give HL^2 as a yellow solid. Yield: 0.52 g (70%). EIMS: $m/z = 185$ (M^+). Anal. Found C, 77.7; H, 5.8; N 7.4%. Required for $C_{12}H_{11}O$: C, 77.8; H, 6.0; N, 7.6%. See Table 1 for ^{1}H NMR data.

Preparation of 2-bromo-6-[(2-phenyl)ethyl]-pyridine

This preparation is based on a published method for alkylation of the methyl group of 2-bromo-6-methylpyridine [10]. A solution containing lithium diisopropylamide (LDA; 40 mmol) was prepared by mixing diisopropylamine (4.05 g, 40 mmol) and *n*-butyllithium (26.6 cm^3 of a 1.5 M solution in hexanes, 40 mmol) at −78°C under N_2 and then allowing the mixture to warm up to 0°C. The solution was cooled back to −78°C, and a solution of 2-bromo-6-methylpyridine (6.23 g, 36 mmol) in dry THF (20 cm^3, precooled to −10°C) was added and the mixture stirred at −78°C for 0.5 h. Benzyl bromide (6.84 g, 40 mmol) was added, and the mixture was allowed to warm up to room temperature and stirred for 24 h. Removal of the THF afforded a dark brown residue which was dissolved in ether and washed with aqueous NaOH. The organic layer was purified by column chromatography on flash silica using CH_2Cl_2/hexane (2:1, v/v) as the eluent, to give a pale yellow oil which slowly crystallised on standing. Yield: 6.17 g (66%). EIMS: $m/z = 261$ (M^+), 185 (M^+—C_6H_5), 171 (M^+—C_7H_8) (all based on ^{79}Br). Anal. Found C, 58.7; H, 4.7; N, 5.6%. Required for $C_{13}H_{12}NBr$: C, 59.8; H, 4.6; N, 5.4%.

Preparation of 2-(2-methoxyphenyl)-6-[(2-phenyl) ethyl]pyridine (MeL^3)

To an ice cold mixture of $Ni(dppe)Cl_2$ (0.53 g, 1 mmol) and 2-bromo-6-[(2-phenyl)ethyl]pyridine (5.0 g, 19 mmol) in dry THF (50 cm^3), a solution of the Grignard reagent prepared from 2-bromoanisole (4.30 g, 23 mmol) and magnesium turnings (0.55 g, 23 mmol) in THF (50 cm^3) was added. The mixture was allowed to warm up slowly to room temperature, and was then stirred under N_2 for 24 h. The reaction was quenched with water (50 ml), and the solvents were removed under reduced pressure. The remaining oil was purified using column chromatography on alumina with CH_2Cl_2/MeOH (98:2) as the eluent to give a straw-coloured oil. Yield: 1.27 g (23%). EIMS: $m/z = 289$ (M^+), 258 (M^+—OMe), 212 (M^+—C_6H_5). Anal. Found C, 82.6; H, 6.7; N, 4.7%. Required for $C_{20}H_{19}NO$: C, 82.8; H, 6.9; N, 4.8%. See Table 1 for ^{1}H NMR data.

Preparation of 2-(2-hydroxyphenyl)-6-[(2-phenyl) ethyl]pyridine (HL^3)

This was prepared by demethylation of the precursor MeL^3 (1.00 g, 3.5 mmol) using molten pyridinium chloride at 190°C for 1.75 h according to the published method [8]. The mixture was allowed to cool, water (50 cm^3) was added and the dark red solution was neutralised using aqueous KOH. The resulting precipitate was extracted into CH_2Cl_2 and purified further on silica using CH_2Cl_2 as the eluent to give a yellow crystalline solid. Yield: 0.56 g (59%). EIMS: $m/z = 274$ (M^+). Anal. Found, 82.6; H, 6.7; N, 4.7%. Required for $C_{19}H_{17}NO$: C, 82.8; H, 6.9; N, 4.8%. See Table 1 for ^{1}H NMR data.

Preparation of complexes with Pd(II) and Cu(II)

The complexes $[Pd(L^1)_2]$, $[Pd(L^2)_2]$ and $[Pd(L^3)_2]$, and $[Cu_2(L^1)_4]$ were all prepared by reaction of the appropriate metal acetate (1 equivalent) with the appropriate ligand (2 equivalents) in MeOH at reflux for 30 min. The typical reaction scale was 0.5 mmol

of metal and 1 mmol of ligand in 20 cm^3 of solvent. After evaporation of the solvent *in vacuo*, the residue was recrystallised from CH_2Cl_2/hexane by layering the hexane onto a concentrated solution of the crude complex in CH_2Cl_2 and slowly allowing the layers to mix. This afforded a crop of X-ray quality crystals in every case. The crude yields were near-quantitative; the yields of crystalline material were much lower (10–40%) but not optimised. FAB mass spectral data (3-nitrobenzylalcohol matrix) were as follows: $[Pd(L^1)_2]$, $m/z = 558$ (M^+); $[Pd(L^2)_2]$, $m/z = 474$ (M^+); $[Pd(L^3)_2]$, $m/z = 655$ (M^+) and 381 $\{Pd(L^3)\}$; $[Cu_2(L^1)_4]$, $m/z = 804$ $\{Cu_2(L^1)_3\}$, 579 $\{Cu_2(L^1)_2\}$, 516 $\{Cu(L^1)_2\}$ and 289 $\{Cu(L^1)\}$. Satisfactory elemental analytical data were obtained for each complex.

X-ray crystallography

Suitable crystals were coated with paraffin oil, mounted on a brass pin, and quickly transferred to the diffractometer under a stream of cold N_2. Data were collected using a Siemens SMART three-circle diffractometer with a CCD area detector (173 K, graphite-monochromatised Mo—K_α X-radiation, $\lambda = 0.71073$ Å); a full description of the general experimental method has been given elsewhere [11]. Data were collected for Lorentz/polarisation effects, and for absorption effects by an empirical method based on multiple measurements of equivalent data. Details of the crystal parameters, data collection and refinement are in Table 2, and bond lengths and angles are in Tables 3 and 4. The structures were solved by conventional direct or heavy-atom methods, and refined by the full-matrix least-squares method on all F^2 data, using the SHELX suite of programs [12] on a Silicon Graphics Indy computer. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters.

RESULTS AND DISCUSSION

Ligand syntheses

Preparation of the 2-(2-hydroxyphenyl)pyridine core of HL^2 follows the previously-published method used for HL; viz. Ni(dppe)Cl_2-catalysed coupling of the Grignard reagent 2-$MeOC_6H_4$–MgBr with a substituted 2-bromopyridine [4] (in this case 2-bromo-6-methyl-pyridine which is readily prepared from the commercially available 2-amino-6-methyl-pyridine) to give the protected MeL^2, followed by deme-

Table 2. Crystallographic data for the four new complexes

Complex	$[Pd(L^1)_2]$	$[Pd(L^2)_2]$	$[Pd(L^3)_2]$	$[Cu_2(L^1)_4]$
Formula	$C_{30}H_{32}N_2O_2Pd$	$C_{24}H_{20}N_2O_2Pd$	$C_{38}H_{32}N_2O_2Pd$	$C_{60}H_{64}Cu_2N_4O_4$
M	558.98	474.82	655.06	1032.24
System, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a/Å	12.127(2)	9.657(3)	8.875(2)	9.762(2)
b/Å	11.932(2)	10.398(4)	12.093(2)	15.523(3)
c/Å	8.9543(12)	10.598(4)	27.719(5)	17.038(4)
α/°	90	77.16(3)	90	90
β/°	93.514(13)	84.58(3)	99.10(2)	95.02(2)
γ/°	90	65.33(3)	90	90
U/Å^3	1293.2(3)	942.9(5)	2937.3(9)	2571.9(9)
Z	2	2	4	2
D_c/g cm^{-3}	1.435	1.672	1.481	1.333
μ/mm^{-1}	0.747	1.008	0.670	0.879
$F(000)$	576	480	1344	1084
T/K	173	173	173	173
Crystal size/mm^3	0.1 × 0.4 × 0.5	0.6 × 0.3 × 0.25	0.5 × 0.15 × 0.15	0.4 × 0.4 × 0.5
2θ	3–55	5–50	3–50	5–50
Reflections collected (total, independent, R_{int})	8026, 2936, 0.0193	4450, 3190, 0.0233	14,624, 5161, 0.556	12,037, 4499, 0.0278
Data, restraints, parameters	2936, 0, 170	3189, 0, 264	5161, 0, 388	4496, 0, 353
Weighting factors (a, b)[a]	0.0339, 0	0.0308, 1.7641	0.0621, 0	0.0279, 2.5201
Final R_1, wR_2[a,b]	0.0200, 0.0565	0.0261, 0.0700	0.0574, 0.1322	0.0317, 0.0806
Largest peak, hole/e Å^{-3}	+0.574, −0.516	+1.061, −0.760	+1.640, −1.233	+0.312, −0.348

[a] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[b] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with refinements based on F_o with a threshold of $F \geqslant 4\sigma(F)$.

Table 3. Selected bond lengths (Å) and angles (°) for the three Pd(II) complexes

$[Pd(L^1)_2]^a$		$[Pd(L^2)_2]$		$[Pd(L^3)_2]$	
Pd(1)—O(20)	1.9662(12)	Pd—O(21)	2.017(2)	Pd(1)—O(10)	2.000(3)
Pd(1)—N(11)	2.0236(14)	Pd—O(41)	2.007(2)	Pd(1)—O(40)	2.011(3)
		Pd—N(11)	2.036(2)	Pd(1)—N(21)	2.034(4)
		Pd—N(31)	2.034(2)	Pd(1)—N(51)	2.047(4)
O(20)—Pd(1)—O(20A)	180	O(41)—Pd—O(21)	176.01(7)	O(10)—Pd(1)—O(40)	179.79(12)
N(11)—Pd—N(11A)	180	N(31)—Pd—N(11)	177.66(8)	N(21)—Pd(1)—N(51)	171.7(2)
O(20)—Pd(1)—N(11A)	91.01(5)	O(41)—Pd—N(31)	86.31(9)	O(10)—Pd(1)—N(21)	86.70(14)
O(20)—Pd(1)—N(11)	88.99(5)	O(21)—Pd—N(31)	93.84(9)	O(40)—Pd(1)—N(21)	93.51(13)
		O(41)—Pd—N(11)	94.34(9)	O(10)—Pd(1)—N(51)	94.41(14)
		O(21)—Pd—N(11)	85.35(9)	O(40)—Pd(1)—N(51)	85.38(14)

[a] Complex is centrosymmetric.

Table 4. Selected bond lengths (Å) and angles (°) for $[Cu_2(L^1)_4]$

Cu(1)—O(10)	1.889(2)	Cu(1)—N(51)	2.050(2)
Cu(1)—O(40)	1.9147(14)	Cu(1)—O(40A)	2.193(2)
Cu(1)—N(21)	2.028(2)		
O(10)—Cu(1)—O(40)	168.75(6)	O(10)—Cu(1)—N(21)	90.01(7)
O(40)—Cu(1)—N(21)	94.52(7)	O(10)—Cu(1)—N(51)	94.44(7)
O(40)—Cu(1)—N(51)	87.85(7)	N(21)—Cu(1)—N(51)	144.42(7)
O(10)—Cu(1)—O(40A)	91.60(6)	O(40)—Cu(1)—O(40A)	77.19(6)
N(21)—Cu(1)—O(40A)	109.53(7)	N(51)—Cu(1)—O(40A)	105.61(6)

thylation of the methoxy group with molten pyridinium chloride. HL^3 was likewise prepared from the cross-coupling of 2-bromo-6-[(2-phenyl)ethyl] pyridine (readily prepared by alkylation of deprotonated 2-bromo-6-methyl-pyridine with benzyl bromide) and 2-$MeOC_6H_4$–MgBr, followed by demethylation of the methoxy group. Ligand HL^1 in contrast was prepared by this route, as the required 2-bromo-4-*tert*-butyl-pyridine is not easily available. Instead, it was prepared by the direct reaction of the lithium reagent 2-$MeOC_6H_4Li$ with 4-*tert*-butyl-pyridine to give MeL^1, followed by demethylation. This is a low-yield reaction but allows preparation of reasonable quantities of HL^1 if done on a large scale, and would doubtless also be effective as route preparing the parent ligand HL. The identities of all three new ligands were confirmed by mass spectrometry and ^1H NMR spectroscopy, as well as the crystal structures of their complexes.

Syntheses and structures of $[Pd(L^1)_2]$, $[Pd(L^2)_2]$ *and* $[Pd(L^3)_2]$

We were interested in the Pd(II) complexes of these ligands to see if the various ligand substituents were capable of imposing a distorted coordination geometry on a metal ion that has a very pronounced stereoelectronic preference for regular square-planar geometry. Reaction of each ligand with 0.5 equivalents of palladium(II) acetate afforded neutral, CH_2Cl_2-soluble complexes for which analytical data in each case indicated a 1 : 2 metal : ligand ratio. All three of these were crystallographically characterised and the structures are in Figs 1, 2 and 3.

$[Pd(L^1)_2]$ (Fig. 1) is mononuclear and centrosymmetric, and the coordination geometry is a near-perfect square plane with a *trans* N_2O_2 donor set and unremarkable bond lengths. The ligands each have an angle of 35° between the pyridyl and phenolate rings, and the ligands are disposed such that the phenyl rings are directed towards opposite faces of the PdN_2O_2 plane for steric reasons. This structure is similar to that of $[PdL_2]$ [6]. This arrangement of ligands could not tolerate the addition of bulky substituents to the pyridyl C^6 position, as these substituents would be directed towards the phenyl ring of the alternate ligand, one on each side of the PdN_2O_2 plane.

The structure of $[Pd(L^2)_2]$ (Fig. 2) shows how the ligand conformation has changed to alleviate unfavourable steric effects involving the methyl groups, whilst still allowing the metal centre to retain a regular square-planar geometry. The ligands are

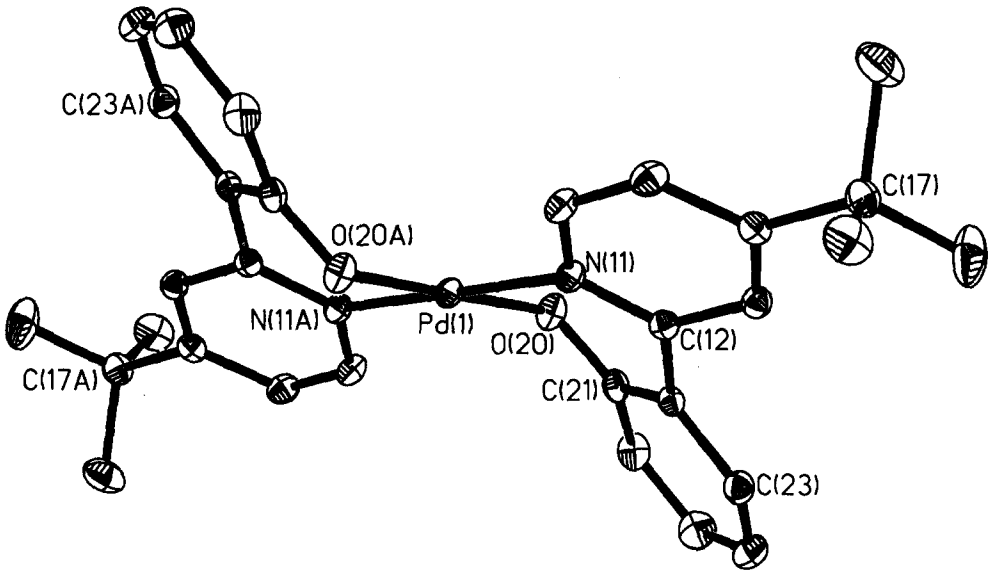

Fig. 1. Crystal structure of $[Pd(L^1)_2]$ (thermal ellipsoids at 40% probability level).

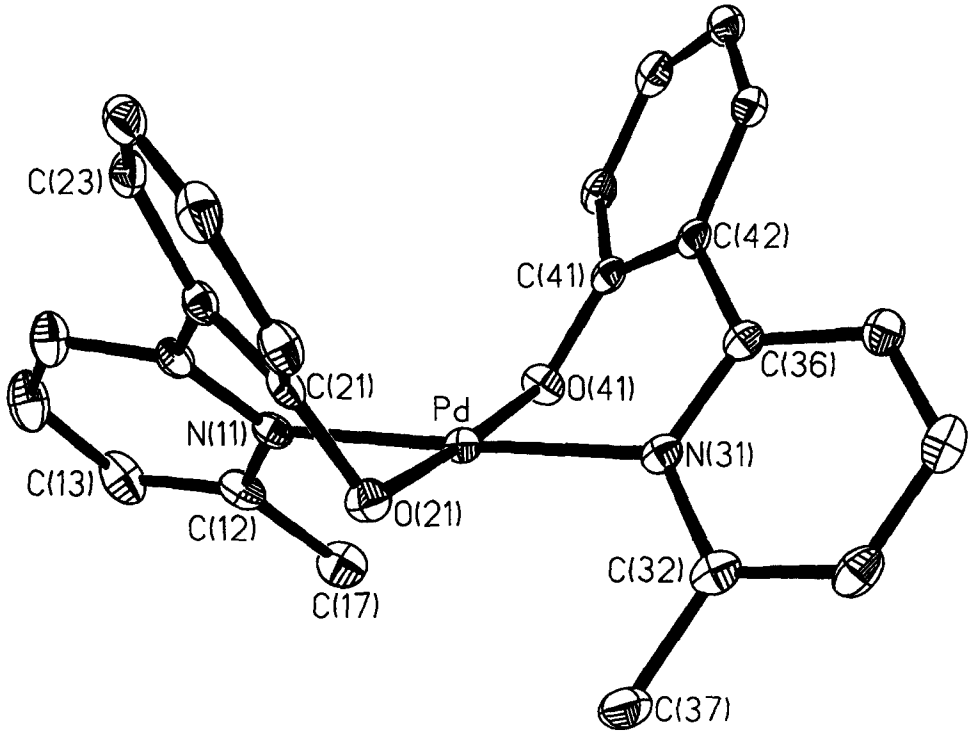

Fig. 2. Crystal structure of $[Pd(L^2)_2]$ (thermal ellipsoids at 40% probability level).

now disposed such that both phenyl rings are directed towards the same face of the *trans*-PdN_2O_2 plane, with both methyl groups directed to the opposite face. The dihedral angles between the mean planes of the aromatic rings within each ligand are 39.6° between rings 1 and 2, and 33.5° between rings 3 and 4, where the ring number is given by the first digit of the crystallographic atom numbering scheme [e.g., ring N(21) to C(26) is ring 2]. All of the metal-ligand bond distances are fractionally longer in $[Pd(L^2)_2]$ than in $[Pd(L^1)_2]$, by about 0.01 Å, which is about five standard deviations and therefore just significant.

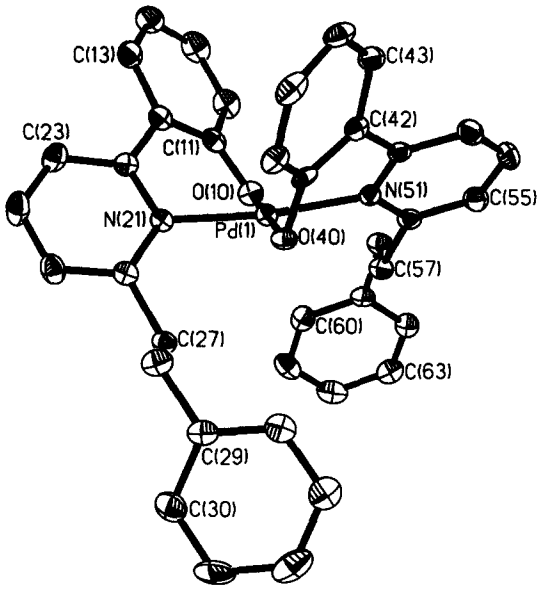

Fig. 3. Crystal structure of $[Pd(L^3)_2]$ (thermal ellipsoids at 40% probability level).

In $[Pd(L^3)_2]$ (Fig. 3) the same type of behaviour is observed. The two CH_2CH_2Ph substituents pendant from the C^6 position of the pyridyl rings are directed to one face of the *trans*-PdN_2O_2 plane, and the two phenyl rings lie on the other side. The disposition of the pyridine/phenol fragments of each ligand are very similar to that observed in $[Pd(L^2)_2]$, which allows relief of all unfavourable steric effects whilst maintaining the planar geometry about the metal centre. The dihedral angles between the mean planes of the aromatic rings within each ligand are 34.8° between rings 1 and 2, and 37.0° between rings 3 and 4. The Pd—O and Pd—N bond lengths are not significantly different from those of $[Pd(L^2)_2]$.

An interesting feature of the latter two structures is that the non-planar conformation of the ligands results in the formation of cavities enclosed by ligand fragments on either face of the metal coordination plane. In both $[Pd(L^2)_2]$ and $[Pd(L^3)_2]$ the two phenyl groups form the base of a bowl-like cavity on one face of the complex. Addition of more substituents to the C^4 positions of the phenyl rings, which should be synthetically straightforward, could extend the bowl and form a "calixarene-like" cavity which could protect/enclose guest species such as solvent molecules or axial ligands. On the other face of the complex, the CH_2CH_2Ph substituents of $[Pd(L^3)_2]$ perform the same function, forming a protective cavity around the space directly "under" the metal centre to which an axial ligand would coordinate. By attachment of suitable "upwardly-directed" substituents at the phenyl C^4 positions, and/or "downwardly-directed" substituents to the pyridyl C^6 position, complexes may be formed which can bind a guest molecule within the protective cavity adjacent to a (coordinatively unsaturated) metal centre, with interesting implications for catalysis. Investigations along these lines are in progress. We note, however, that our original aim of preventing the adoption of a regular square planar geometry about the metal centre was unsuccessful because of the flexibility of the ligands.

Syntheses and structure of $[Cu_2(L^1)_4]$

The Cu(II) complex $[CuL_2]$ was described earlier by Ganis *et al.* but not characterised except by elemental analysis [6]. In view of the tendency of phenolate-containing ligands to form phenolate-bridged dimeric complexes with Cu(II) [3], we were interested to re-investigate $[CuL_2]$. However crystallographic (and spectroscopic) characterisation of $[CuL_2]$ was prevented by its poor solubility, so we instead prepared the Cu(II) complex of the more soluble ligand HL^1. A material analysing as $Cu(L^1)_2$ was easily prepared, and gave X-ray quality crystals from CH_2Cl_2/hexane.

The crystal structure (Figs 4 and 5) shows this complex to be in fact the phenolate-bridged dimer $[Cu_2(L^1)_4]$. The complex is centrosymmetric. Each Cu(II) ion is in an irregular 5-coordinate N_2O_3 geometry, arising from two bidentate ligands $[L^1]^-$ and an additional (bridging) phenolate from a ligand associated with the other metal. The geometry is approximately square-pyramidal, with the basal plane containing N(21), O(10), O(40) and N(51) within each $Cu(L^1)_2$ monomeric unit. The metal atom is situated 0.219 Å out of the mean plane of these four donor atoms, displaced towards to the two oxygen donors. The axial site is used for the bridging interaction to O(40A) associated with the other metal centre. The

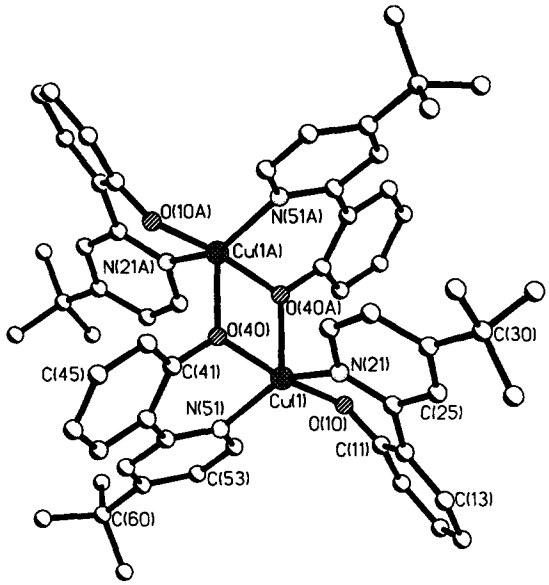

Fig. 4. Crystal structure of $[Cu_2(L^1)_4]$.

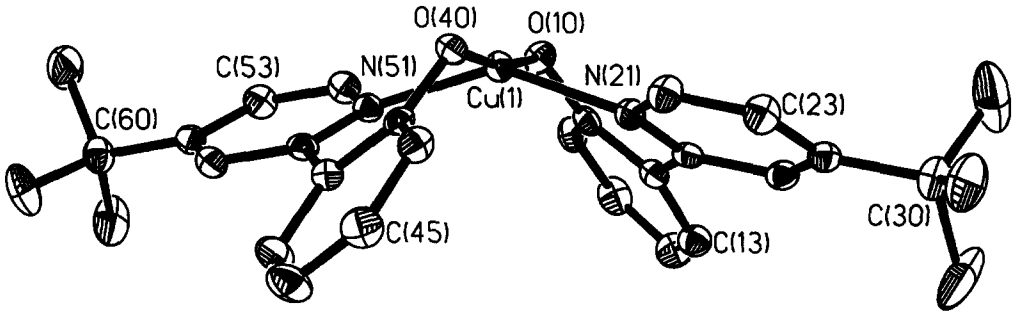

Fig. 5. Crystal structure of the monomer unit of $[Cu_2(L^1)_4]$ (thermal ellipsoids at 40% probability level).

axial metal–ligand bond distance at 2.193(2) Å is significantly longer than the four equatorial ones due to the expected Jahn–Teller distortion. As usual, there is a substantial twist between the mean planes of the pyridyl and phenolate rings within each ligand because of the steric constraints of the six-membered chelate rings: the dihedral angles are 28.8° between rings 1 and 2, and 29.5° between rings 4 and 5. The Cu···Cu separation is 3.215 Å.

EPR spectroscopic studies on this complex gave some interesting information on its solution structure (Fig. 6). A room-temperature spectrum of the powdered microcrystalline material is poorly resolved [Fig. 6(a)], but has the appropriate number of features for a triplet species [2] including a half-field transition at 1580 G ($g = 4.44$), which confirms the presence of the dimer that was apparent from the crystal structure. Figures 6(b) and 6(c) show the spectra of $[Cu_2(L^1)_4]$ dissolved in CH_2Cl_2/thf (2:1, v/v) at room temperature and at 77 K respectively. These spectra in contrast are entirely characteristic of isolated, mononuclear Cu(II) centres with a basically planar structure and the unpaired electron in the $d(x^2-y^2)$ orbital. The axial bridging interactions of $[Cu_2(L^1)_4]$ therefore break in solution to give mononuclear $[Cu(L^1)_2]$ fragments. The spectral parameters are as follows: room temperature; $g_{iso} = 2.114$, $A_{iso} = 70$ G: 77 K; $g_{\parallel} = 2.257$, $g_{\perp} = 2.046$, $A_{\parallel} = 171$ G. Also apparent in the room temperature spectrum is superhyperfine coupling to the N atoms, which can be seen clearly on the highest-field component of the signal and is also just apparent on the adjacent component. Differentiation of the signal [Fig. 6(d)] shows this superhyperfine coupling much more clearly, and a 1:2:3:2:1 quintet is apparent with $A_N = 13$ G, consistent with coupling to two equivalent nitrogen atoms, which is what we would expect in the $[Cu(L^1)_2]$ monomer assuming a high-symmetry (probably planar) structure.

The 77 K frozen glass spectrum showed no evidence for the half-field signal that would be expected if the dimeric structure were retained in solution [2,3]. It is

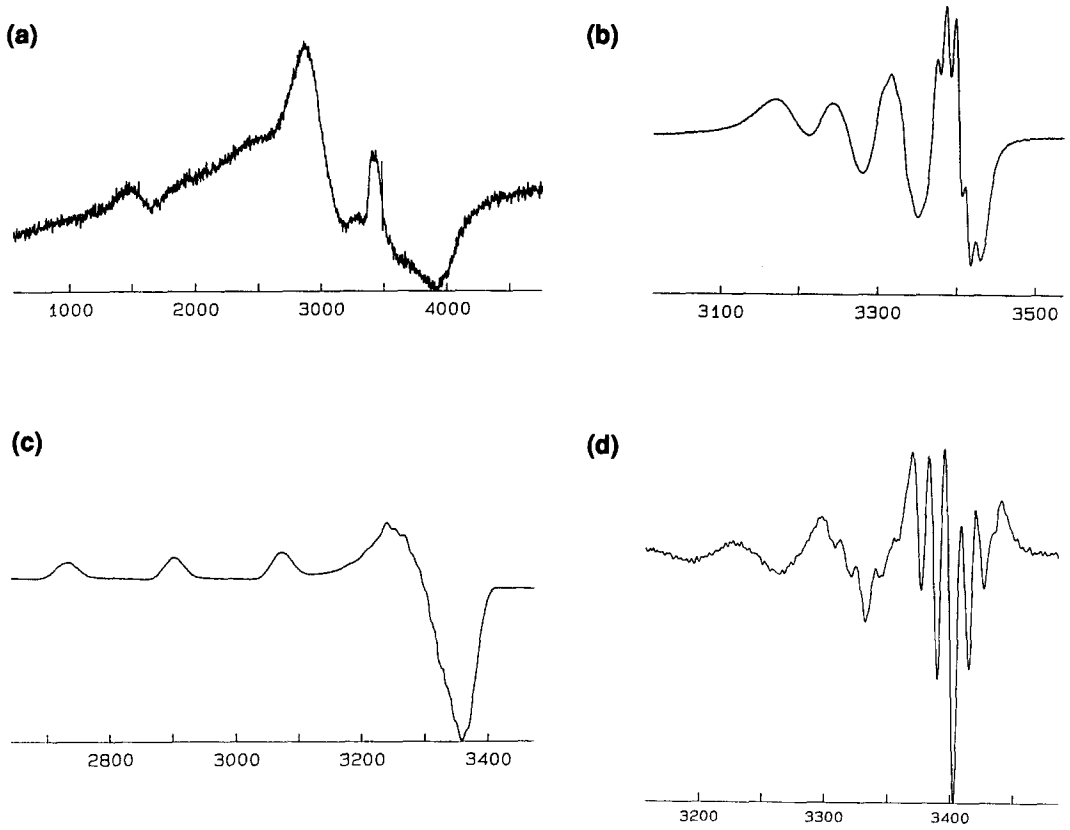

Fig. 6. X-band EPR spectra of $[Cu_2(L^1)_4]$: (a) microcrystalline powdered solid at room temperature; (b) CH_2Cl_2/thf solution at room temperature; (c) CH_2Cl_2/thf frozen glass at 77 K; (d) derivative of (b) emphasising the superhyperfine nitrogen coupling (1 : 2 : 3 : 2 : 1 quintet). Units on the x-axes are Gauss in every case.

perhaps surprising that the dimer is cleaved so easily. In a related dimeric Cu(II) complex with much weaker phenolate bridges [Cu—O(axial) $\approx$ 2.4 Å] the dimeric structure was largely retained in CH_2Cl_2/dmf solution, and addition of pyridine was required to break up the dimer. In this case, however, there was crystallographic evidence for aromatic π-stacking between the aromatic ligands of two near-planar monomeric units, and it may be that this aided association in solution. In $[Cu_2(L^1)_4]$ by contrast there is no evidence for strong inter-component π-stacking interactions, and the dimer dissociates more readily despite the stronger Cu—O(axial) bonds.

Attempts to prepare Cu(II) complexes with the more sterically hindering ligands HL^2 and HL^3 were unsuccessful. Although reaction of the ligand with $Cu(OAc)_2 \cdot 2H_2O$ in methanol immediately afforded a dark green solution similar in colour to solutions of $[Cu_2(L^1)_4]$, these decomposed on concentration and recrystallisation. It appears that the addition of bulky substituents at the pyridyl C^6 position is sufficient to destabilise the planar Cu(II) complexes even though planar Pd(II) complexes could be prepared with the same ligands.

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