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FULL PAPER

Synthesis of the terpyridyl pendant-arm azamacrocycle 4′-(*p*-1,4,7-triazacyclonon-1-ylmethylphenyl)-2,2′:6′,2″-terpyridine (L) and complexes of L with copper(II) and nickel(II). Crystal structure of $[Cu(HL)(H_2O)_2][PF_6]_3$

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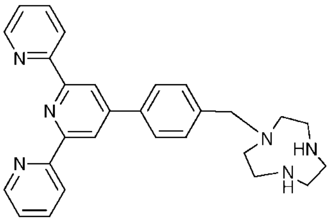
The azamacrocyclic ligand 4′-(*p*-1,4,7-triazacyclonon-1-ylmethylphenyl)-2,2′:6′,2″-terpyridine (L) has been prepared, and some of the complexes it forms with hydrated copper(II) and nickel(II) have been isolated as the $[PF_6]^-$ salts. X-Ray crystallography has been used to determine the solid state structure of the distorted trigonal bipyramidal complex $[Cu(HL)(H_2O)_2][PF_6]_3$, in which the copper(II) is co-ordinated to the terpyridyl group and the azamacrocycle is monoprotonated and non-co-ordinating. A bis(2,2′:6′,2″-terpyridine)nickel(II) complex, $[Ni(H_2L)_2][PF_6]_6$ has also been isolated, in which each azamacrocycle is diprotonated.

Recent attention has focused on the production of suitably designed supramolecular multicomponent systems to obtain photoinduced migration of electronic energy and/or charge separation by covalently linked photosensitizers.[1,2] Although ruthenium(II) complexes of bipyridine-type ligands, such as $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine), are well documented photosensitisers, their chirality causes problems from the geometric viewpoint for the construction of well defined supramolecular systems. In contrast, the complexes of the $[Ru(terpy)_2]^{2+}$ family (terpy = 2,2′:6′,2″-terpyridine) offer several synthetic and structural advantages, while exhibiting less favourable photophysical properties. However, suitable substituents in the 4′ position of terpy can yield ruthenium(II) complexes which display room temperature luminescence.[3] Attention has now been directed towards the derivatization of terpyridyl ligands, the formation of homo- and hetero-leptic $[Ru(terpy)_2]^{2+}$-type complexes, and the formation of back-to-back mixed metal polynuclear complexes.[3–7]

To date the attachment of terpyridyl derivatives to novel subunits displaying contrasting metal complex co-ordination geometries has received little attention. For example, the modes of co-ordination of macrocycles with transition metals are diverse, and often vary with changing metal cation for the same macrocyclic ligand. It is our intention to combine derivatized terpyridyl ligands with polyaza macrocycles of increasing ring size, systematically to develop polynuclear complexes of mixed geometry. The systematic increase of repeating subunits has the potential to produce oligomeric species, and may give rise to the self assembly of new inorganic materials.[7]

In this paper we report the synthesis of a new azamacrocyclic ligand, 4′-(*p*-1,4,7-triazacyclonon-1-ylmethylphenyl)-2,2′:6′,2″-terpyridine (L), that has both a meridionally co-ordinating subunit (terpy), and a facially co-ordinating triazamacrocycle (1,4,7-triazacyclononane). This new ligand has been synthesized using an approach developed by Weisman *et al.*,[8] where the terpyridylbenzyl pendant arm is introduced into the macrocyclic structure by reaction with the tricyclic orthoamide of 1,4,7-triazacyclononane.[8] Copper(II) and nickel(II) complexes of L of formulae $[Cu(HL)(H_2O)_2][PF_6]_3$ and $[Ni(H_2L)_2][PF_6]_6{\cdot}H_2O$ have been isolated, and characterized by elemental analyses, liquid secondary ion mass spectrometry (LSIMS) and electrospray mass spectrometry. The complexes were further investigated by UV/VIS spectroscopy and cyclic voltammetry, and the crystal and molecular structure of $[Cu(HL)(H_2O)_2][PF_6]_3$ determined by X-ray crystallography.



L

Experimental

Materials

Reagent grade commercial compounds were used as starting materials, and their purity was checked by ^1H and ^{13}C NMR.

Spectra, analyses and other procedures

The 250 MHz ^1H NMR and proton-decoupled 62.9 MHz ^{13}C NMR spectra were obtained with a Bruker AC250 spectrometer, UV/VIS and electron-impact mass spectra with Shimadzu 365 and Kratos MS80 spectrometers respectively and LSIMS spectra obtained with a Kratos Concept II HH four-sector tandem mass spectrometer (Kratos Analytical Ltd, Manchester, UK). Elemental analyses were made with a Leeman Laboratories CE 440 elemental analyser. Cyclic voltammetry was performed under argon at 20 °C with an Oxford Electrodes potentiostat and triangular wave generator (Oxford, UK) and an Advance Bryons X-Y chart recorder. The working electrode was a platinum electrode, with a platinum wire counter electrode and a saturated calomel reference electrode. The supporting electrolyte was $NaClO_4$ (0.1 mol dm^{-3}).

Preparations

The synthetic route to L is outlined in Scheme 1.

4′-(*p*-Tolyl)-2,2′:6′,2″-terpyridine (ttpy). The procedure was modified from those described by Collin and Constable.[6,9] A mixture of acetamide (183 g, 3.1 mol), ammonium acetate (118 g, 1.5 mol), *p*-tolualdehyde (12.4 g, 103 mmol) and

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2-acetylpyridine (25 g, 206 mmol) was refluxed for 2 h. The mixture was then cooled to 120 °C, and a solution of sodium hydroxide (90 g) in water (200 cm^3) added. After standing for 2 h at 120 °C, the solution was cooled to room temperature and left to stand overnight. A dark brown solidified "glass" was broken up and separated from the quickly solidifying solution, washed with water and dissolved in glacial acetic acid (60 cm^3). The hydrogen bromide salt was precipitated by adding 48% HBr (60 cm^3), and the resulting solid filtered from the solution and dissolved in water (200 cm^3). The aqueous solution was made alkaline to pH 10 with KOH, and the resulting suspension extracted into CH_2Cl_2 (3 × 200 cm^3). After drying the combined extracts with anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue recrystallized from ethanol (400 cm^3) to give white needles (8.4 g). The product was dissolved in EtOH–CH_2Cl_2 (1 : 1, 380 cm^3), and a solution of ammonium iron(II) sulfate hexahydrate (4.5 g) in water (76 cm^3) added to give a deep purple solution. The dichloromethane was removed under reduced pressure and then a solution of KPF_6 (4.27 g) in water (38 cm^3) added. The purple precipitate was collected by suction filtration and extracted with toluene (3 × 100 cm^3). The combined toluene extracts were dried with anhydrous $MgSO_4$, filtered, then taken to dryness under reduced pressure to isolate the minor by-product, 6′-*p*-tolyl-2,2′ : 4′,2″-terpyridine (2 g, 6% yield). δ_H (250 MHz, solvent $CDCl_3$) 8.89 (1 H, d), 8.79 (1 H, d), 8.74–8.69 (2 H, m), 8.51 (1 H, d), 8.18 (2 H, d), 8.03 (1 H, d), 7.84 (2 H, q), 7.34 (4 H, m) and 2.36 (3 H, s); δ_C (62.9 MHz, solvent $CDCl_3$) 157.2, 156.2 (2C), 155.1, 149.9, 148.9, 148.1, 139.0, 136.9, 136.8, 136.4, 129.3 (2C), 126.9 (2C), 123.7, 123.6, 121.4, 121.2, 117.6, 116.4 and 21.3. The remaining purple precipitate was dissolved in acetonitrile (100 cm^3) and an equal volume of water added. The pH of the aqueous layer was increased to pH > 12 with KOH. Hydrogen peroxide (30%) was then added dropwise (**CARE**: this reaction is accompanied by copious effervescence) until the purple acetonitrile layer had disappeared to form one layer containing a heavy orange precipitate and a flocculent pale lavendar precipitate that cannot be removed or decolourized by further addition of hydrogen peroxide. The solution was filtered and the pale lavendar precipitate scraped from the top of the remaining residue and discarded. The remainder was boiled with decolourizing charcoal and chloroform (50 cm^3). The solution was filtered, and then taken to dryness under reduced pressure to give a bright white powder (6 g, 18% yield). δ_H (250 MHz, solvent $CDCl_3$) 8.73 (2 H, s), 8.70 (2 H, m), 8.62 (2 H, d), 7.82 (4 H, m), 7.30 (4 H, m) and 2.40 (3 H, s); δ_C (62.9 MHz, solvent $CDCl_3$) 156.2 (2C), 155.7 (2C), 150.0, 149.0 (2C), 139.0, 136.7 (2C), 135.3, 129.6 (2C), 127.0 (2C), 123.6 (2C), 121.2 (2C), 118.5 (2C) and 21.2.

4′-(*p*-Bromomethylphenyl)-2,2′ : 6′,2″-terpyridine. This was prepared from 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine using the procedure described by Collin *et al.*[9] (yield: 37%). δ_H (250 MHz, solvent $CDCl_3$) 8.72 (4 H, m), 8.65 (2 H, d), 7.86 (4 H, m), 7.52 (2 H, d), 7.34 (2 H, m) and 4.55 (2 H, s); δ_C (62.9 MHz, solvent $CDCl_3$) 156.0 (2C), 155.9 (2C), 149.3, 149.0 (2C), 138.5 (2C), 136.8 (2C), 129.5 (2C), 127.7 (2C), 123.8 (2C), 121.3 (2C), 118.7 (2C) and 32.9.

4′-(*p*-1,4,7-Triazacyclonon-1-ylmethylphenyl)-2,2′ : 6′,2″-terpyridine (L). A solution of "capped" 1,4,7-triazacyclononane (0.15 g, 1.07 mmol; prepared as described[8]) and 4′-(*p*-bromomethylphenyl)-2,2′ : 6′,2″-terpyridine (0.433 g, 0.886 mmol) in tetrahydrofuran (30 cm^3) was stirred at room temperature for 24 h. The resulting white precipitate of the bromide salt was filtered off and washed with diethyl ether (yield: 480 mg, 0.886 mmol, 83%). δ_H (250 MHz, solvent D_2O) 7.66 (2 H, d), 7.15 (4 H, m), 6.89–6.71 (8 H, m), 5.45 (1 H, s), 4.16 (2 H, s), 3.50 (4 H, m), 3.18 (2 H, m), 2.97 (4 H, m) and 1.64 (2 H, m). A solution of the bromide salt (0.47 g, 8.68 mmol) in water (10 cm^3) was refluxed for 3.5 h, then cooled to 0 °C and made basic (pH 10) by dropwise addition of NaOH (8 mol dm^{-3}). The solution was immediately extracted with $CHCl_3$ (5 × 20 cm^3). The combined organic extracts were dried with anhydrous $MgSO_4$, filtered and taken to dryness under reduced pressure to yield the ligand precursor as a viscous pale yellow oil (0.40 g, 96% yield). δ_H (250 MHz, solvent $CDCl_3$) 8.64 (4 H, m), 8.58 (2 H, d), 8.02 (1 H, d), 7.78 (4 H, m), 7.35 (2 H, d), 7.25 (2 H, m), 3.64 (2 H, s), 3.38–3.27 (3 H, m), 3.11 (1 H, m), 2.99 (3 H, m), 2.89 (1 H, m), 2.81 (1 H, m), 2.67 (1 H, m), 2.57 (2 H, s) and 2.47 (1 H, m); δ_C (62.9 MHz, solvent $CDCl_3$) 163.7, 163.6, 156.0, 155.8, 155.7, 149.7, 149.6, 149.0, 140.6, 140.4, 137.2, 137.0, 136.7 (2C), 129.5, 129.4, 127.2, 127.1, 123.7, 121.2, 118.6, 61.8 (2C), 57.4, 55.6, 53.2, 52.4, 52.2, 50.2, 49.2, 48.0, 47.9, 47.1 and 46.7. A solution of the ligand precursor (0.40 g, 0.835 mmol) and KOH (1 g, 18 mmol) in ethanol (15 cm^3) and water (5 cm^3) were refluxed for 48 h, cooled and taken to dryness under reduced pressure. The residue was dissolved in the minimum volume of water and extracted with $CHCl_3$ (5 × 20 cm^3). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and evaporated to yield a yellow oil (0.31 g, 6.89 mmol, 82% yield). δ_H (250 MHz, solvent $CDCl_3$) 8.69 (2 H, s), 8.67 (2 H, m), 8.60 (2 H, d), 7.80 (4 H, m), 7.42 (2 H, d), 7.28 (2 H, m), 3.71 (2 H, s), 2.74 (4 H, s), 2.61 (8 H, s) and 2.23 (2 H, br s); δ_C (62.9 MHz, solvent $CDCl_3$) 156.1 (2C), 155.8 (2C), 149.9, 149.0 (2C), 140.9, 137.0, 136.7 (2C), 129.4 (2C), 127.1 (2C), 123.6 (2C), 121.2 (2C), 118.6 (2C), 61.3, 53.2 (2C), 47.1 (2C) and 46.7 (2C). Electron-impact mass spectrum: found, *m*/*z* 451; calc. for M^+, 451.

$[Cu(HL)(H_2O)_2][PF_6]_3$. A solution of $Cu(NO_3)_2\cdot3H_2O$ (48 mg) in ethanol (4 cm^3) was added to a cooled, filtered solution of ligand L (0.18 g) in ethanol (4 cm^3). The reaction mixture was refluxed for 1 h, and upon cooling to room temperature afforded a blue-green insoluble precipitate (0.13 g). The precipitate was suspended in ethanol–water (1 : 1, 5 cm^3) and three drops of concentrated HPF_6 were slowly added. The reaction mixture was gently heated until the solution turned turquoise and a pale lavender precipitate formed. The precipitate was filtered from the solution, rinsed with water (20 cm^3) followed by ethanol (20 cm^3) and diethyl ether (3 × 20 cm^3), then air dried (yield: 60 mg). The remaining turquoise filtrate was heated to reflux then allowed to cool to room temperature overnight. In this way, turquoise rectangular crystals of $[Cu(HL)(H_2O)_2][PF_6]_3$ suitable for X-ray analysis were produced. The crystals were collected by filtration, washed with ethanol (20 cm^3) then diethyl ether (3 × 20 cm^3), and allowed to air dry (yield: 0.10 g, 51%). LSIMS: found, *m*/*z* 694; calc. for M^+, 694. Found: C, 34.0; H, 3.5; N, 8.3. $C_{28}H_{35}CuF_{18}N_6O_2P_3$ requires C, 34.1; H, 3.6; N, 8.5%.

$[Ni(H_2L)_2][PF_6]_6\cdot H_2O$. A solution of $Ni(NO_3)_2\cdot 6H_2O$ (30 mg) in ethanol (2 cm^3) was added to a cooled, filtered solution of ligand L (90 mg) in ethanol (2 cm^3). The reaction mixture was refluxed for 1 h, and upon cooling to room temperature afforded a pale yellow powder. The precipitate was suspended in ethanol–water (1 : 1, 2 cm^3) and three drops of concentrated HPF_6 were slowly added. The reaction mixture was gently refluxed until the precipitate dissolved, then allowed to cool very slowly to room temperature to afford a golden microcrystalline powder. The powder was collected by filtration, washed with ethanol (10 cm^3) then diethyl ether (3 × 10 cm^3), and allowed to air dry (yield: 0.15 g, 80%). Electrospray MS: found, *m*/*z* 1105; calc. for $[Ni(L)_2(PF_6)]^+$, 1105. Found: C, 36.6; H, 3.9; N, 8.8. $C_{56}H_{66}F_{36}N_{12}NiOP_6$ requires C, 36.3; H, 3.6; N, 9.1%.

Crystal structure analysis of $[Cu(HL)(H_2O)_2][PF_6]_3$

Crystals of $[Cu(HL)(H_2O)_2][PF_6]_3\cdot4H_2O$ suitable for single crystal X-ray diffraction studies were obtained as turquoise rectangular plates by slow recrystallization from ethanol–water

(1 : 1). Data were collected using a Delft Instruments FAST TV area-detector diffractometer. No absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data using SHELXL 97.[10] A difference electron density plot failed to locate the H atoms associated with the water molecules, and hence they were not included in the final refinement.

Crystal data. $C_{28}H_{43}CuF_{18}N_6O_6P_3$, $M = 1058.13$, triclinic, $a = 8.654(2)$, $b = 11.277(2)$, $c = 21.593$ Å, $\alpha = 74.93(3)$, $\beta = 79.94(3)$, $\gamma = 86.42(3)°$, $U = 2003.2(7)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.799$ mm^{-1}, 9155 reflections measured, 5832 unique ($R_{int} = 0.097$). The final values of $R1$ [$I > 2\sigma(I)$] and $wR2$ were 0.057 and 0.116 respectively. Selected bond lengths and angles are given in Table 1.

CCDC reference number 186/1788.

See http://www.rsc.org/suppdata/dt/a9/a907717k/ for crystallographic files in .cif format.

Results and discussion

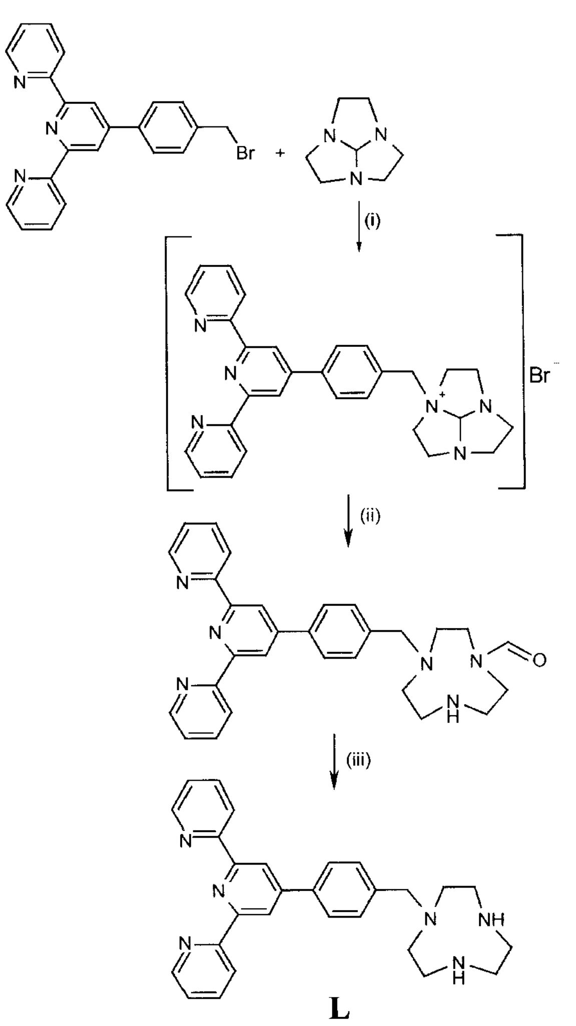
Ligand synthesis

The ligand, L, was prepared (Scheme 1) by reaction of 4′-(*p*-bromomethylphenyl)-2,2′ : 6′,2″-terpyridine with the tricyclic orthoamide of 1,4,7-triazacyclononane (9N3). This general approach allows controlled stepwise addition of pendant arms to the macrocycle. Aqueous hydrolysis affords the formyl derivative that is then subjected to base hydrolysis to give the desired ligand. This strategy produces the ligand in fairly good yield. The ligand is characterized by its ^{1}H, ^{13}C NMR and mass spectra, and by the analytical data for its metal complexes.

On repeating the synthesis of 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine (ttpy) described by Collin *et al.*[6] we frequently found that during attempts to extract the minor by-product, 6′-(*p*-tolyl)-2,2′ : 4′,2″-terpyridine, the purple acetonitrile solutions of [Fe(ttpy)$_2$][PF$_6$]$_2$ were miscible with toluene, and separation of the by-product proved unsuccessful. We were able successfully to isolate the by-product by repeatedly washing the purple [Fe(ttpy)$_2$][PF$_6$]$_2$ precipitate with toluene, and then combining the washings. This modified procedure still yielded reasonable amounts of 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine. It is then easily converted into the reactive bromomethyl derivative.[2]

Metal complexes of L

These are obtained from reactions of the appropriate stoichiometric amounts of L and the hydrated metal(II) nitrate salts in ethanol, followed by the addition of hexafluorophosphoric acid to a suspension of the resulting metal(II) complex nitrate salts in ethanol and water (1 : 1). It was the production of seemingly intractable nitrate salts of the metal(II) complexes that prompted us to redissolve them in dilute HPF$_6$ and recrystallize them from that medium. It is not surprising that under these conditions the resulting complexes, [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ and [Ni(H$_2$L)$_2$][PF$_6$]$_6$, are isolated with partial protonation of the 1,4,7-triazacyclononane macrocyclic subunit. This procedure led to the isolation of two copper(II) complexes from the same reaction mixture, the crystalline turquoise [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ and an intractable purple powder. Attempts to characterize this latter material by elemental analysis and mass spectroscopy proved unsuccessful. The UV/VIS spectrum of each complex is consistent with the given formulations. The copper(II) complex shows a broad d–d band at 680 nm ($\varepsilon = 120$ dm^3 mol^{-1} cm^{-1}) in the visible region, and does not allow a distinction to be made between either five- or six-co-ordination in solution. The UV/VIS spectrum of the nickel(II) complex shows a broad d–d band at 800 nm ($\varepsilon = 37.4$ dm^3 mol^{-1} cm^{-1}) and a very broad shoulder of lower intensity around 550 nm. In the UV region there are two intense bands at 330 ($\varepsilon = 3.87 \times 10^4$) and 291 nm ($5.77 \times 10^4$ dm^3 mol^{-1} cm^{-1}). The visible spectrum is very similar to that reported for [Ni(terpy)$_2$]$^{2+}$ (λ_{max} 785 nm, ε 32.3 dm^3 mol^{-1} cm^{-1}).[11] The presence of coordinated water molecules in [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ is confirmed by a broad O–H band in the infrared spectrum at 3000 cm^{-1}.



Scheme 1 (i) thf, r.t. 24 h; (ii) water, 100 °C, 3.5 h; (iii) KOH (20 mol. equivalents), EtOH·water (3 : 1), 100 °C, 48 h.

Cyclic voltammetry of millimolar solutions of the [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ and [Ni(H$_2$L)$_2$][PF$_6$]$_6$·H$_2$O complexes in aqueous solution were run in the scan range −1.0 to +1.0 V (*vs.* SCE). A reversible one electron process (Fig. 1) was observed at −0.445 V (*vs.* SCE, $\Delta E_p = 80$ mV) for [Ni(H$_2$L)$_2$][PF$_6$]$_6$ and is attributed to the Ni^{II}–Ni^{I} redox couple. Two irreversible waves, a cathodic and an anodic one electron process, were observed for [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$. The irreversible cathodic process at −0.6 V (*vs.* SCE) is attributed to the one electron reduction of [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ to the copper(I) species, and its subsequent rearrangement within the co-ordination sphere. The solvolysis of the copper(I) species and its resulting disproportionation to aqueous copper(II) and elemental copper was not observed. The irreversible anodic process at −0.355 V (*vs.* SCE) is related to the cathodic process and may be the oxidation of the rearranged copper(I) species to copper(II) followed by its rearrangement back to [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$.

Crystal structure

To gain further insight into the structure of the copper(II) complex, the crystal structure of [Cu(HL)(H$_2$O)$_2$][PF$_6$]$_3$ was determined (Fig. 2). The cation geometry is approximately trigonal bipyramidal, where two water molecules and the central pyridyl nitrogen atom of ligand L occupy the three sites of the equatorial plane and the two axial sites of the polyhedron are occupied by each terminal pyridyl nitrogen atom of

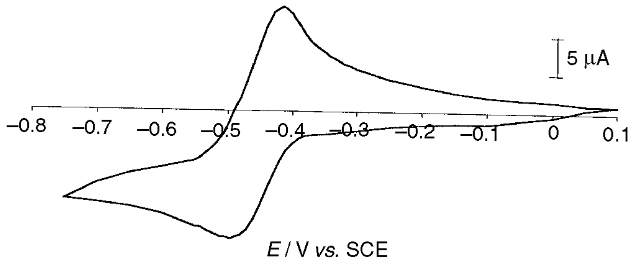


Fig. 1 Cyclic voltammogram of $[Ni(H_2L)_2][PF_6]_6{\cdot}H_2O$ in water at a platinum working electrode (0.1 mol dm^{-3} $NaClO_4$ supporting electrolyte; 20 °C) at scan rate 50 mV s^{-1} *vs.* SCE.

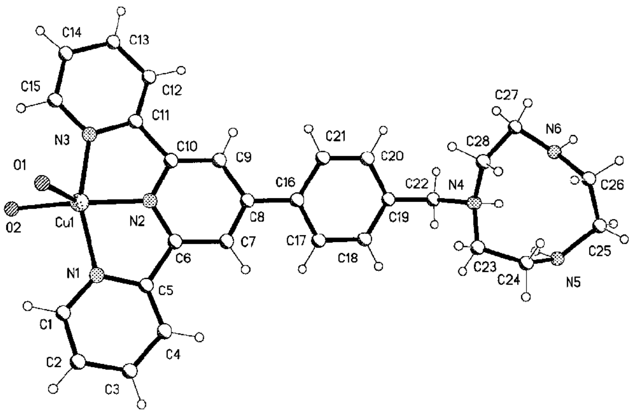


Fig. 2 Crystal structure of the $[Cu(HL)(H_2O)_2]^{3+}$ ion showing the atomic numbering.

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu(HL)(H_2O)_2]^{3+}$ ion

Cu1–N1	2.062(7)	Cu1–O1	2.201(6)
Cu1–N2	1.914(6)	Cu1–O2	1.999(5)
Cu1–N3	1.989(7)		
N2–Cu1–N1	79.7(3)	O2–Cu1–O1	87.3(2)
N2–Cu1–N3	79.4(3)	O2–Cu1–N3	95.4(3)
N3–Cu1–N1	158.9(3)	O2–Cu1–N1	101.7(3)
N2–Cu1–O1	119.8(2)	N3–Cu1–O1	96.4(2)
N2–Cu1–O2	152.7(2)	N1–Cu1–O1	96.6(2)

L. The N–Cu–N angles are lower than those required for an idealized trigonal bipyramid by about 10°, presumably as a consequence of the restricted ligand bite. The equatorial Cu–N2 bond distance of 1.914(6) Å is significantly shorter than the the two axial Cu–N distances (mean 2.026(3) Å). As is usual in complexes formed with terpy the ligand remains planar, and the bond lengths and angles the terpy makes with the Cu^{II} are similar to those found in other mono(terpyridyl)copper(II) complexes.[12–14] The plane of the Cu1, O1 and O2 atoms is at 88.6(2)° to the best fit plane through Cu1 and the terpy subunit. There is also very little deviation of the Cu–O bond lengths from those found in related compounds.[12–14] However, in contrast to other mono(terpyridyl)copper(II) complexes, the cation $[Cu(HL)(H_2O)_2]^{3+}$ adopts a trigonal bipyramidal rather than a square pyramidal geometry. A distortion in the direction of a trigonal bipyramidal geometry for fivefold co-ordination is expected for weaker ligands such as H_2O. Indeed, the geometry of complexes of the type $[Cu(terpy)X_2]$, where X^- is I^-, Br^- or NCS^-, lies between trigonal bipyramidal and square pyramidal in what is known as "reverse" geometry.[15,16] In the present case, distortions from a regular trigonal bipyramidal geometry are evident from the N1–Cu–N3, O2–Cu–N2, and O1–Cu–O2 bond angles of 158.9(3), 152.7(2), and 87.3(2)° respectively.

The phenyl ring is not coplanar with the terpyridyl fragment, but is twisted about the interannular bond such that its plane makes an angle of 24.2(3)° with the plane of the central pyridyl ring. This twist simultaneously maximizes both van der Waals H···H repulsion and π overlap, and minimizes π conjugation and non-bonded H···H contacts between the *ortho* protons of the phenyl ring and those of the central pyridyl ring.

The triazacyclononane subunit of the complex adopts a conformation where all the electron lone pairs of the ring nitrogen atoms are pointing in the same direction (endodentate). The torsion angles of N4–C23–C24–N5, N5–C25–C26–N6, and N6–C27–C28–N4 ethyl linkages are −49(1), −62(1), and −43(1)° respectively, and are indicative of *gauche* conformation. The solid state structure of $[Cu(HL)(H_2O)_2][PF_6]_3$ illustrates that the conformation of the triazacyclononane subunit of the complex is ideally suited for facial co-ordination to another transition metal ion. Recent work has exploited the contrasting co-ordination modes of the ligand L by forming the heterobinuclear heteroleptic complex $[Ru(ttpy)\{LNi(SCN)_3\}]$-SCN, where the heteroleptic *mer*-$[Ru(ttpy)_2]^{2+}$ fragment is covalently linked by the CH_2 spacer to the *fac*-tris(thiocyanato)triazacyclononanenickelate(II) fragment. One envisages that the heterotrinuclear homoleptic complex $[Ru\{LNi(SCN)_3\}_2]$ could also be synthesized, and it is towards this end, and the production of more extended oligomeric species based on the successful coupling of two 9N3 fragments of L with nickel(II) and other first-row transition metal ions, that our future work is directed.

Acknowledgements

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References

1 V. Balzani (Editor), *Supramolecular Photochemistry*, Reidel, Dordrecht, 1987.
2 F. Scandola, M. T. Indelli, C. Chiorboli and C. A. Bignozzi, *Top. Curr. Chem.*, 1990, **158**, 73.
3 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.
4 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1995, 1615.
5 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7692.
6 J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230.
7 N. W. Alcock, A. J. Clarke, W. Errington, A. M. Josceanu, P. Moore, S. C. Rawle, P. Sheldon, S. M. Smith and M. L. Turonek, *Supramolecular Chem.*, 1996, **6**, 281.
8 G. R. Weisman, D. J. Vachon, V. B. Johnson and D. A. Gronbeck, *J. Chem. Soc., Chem. Commun.*, 1987, 886.
9 E. C. Constable, M. D. Ward and S. Corr, *Inorg. Chim. Acta*, 1988, **141**, 201; B. Whittle, S. R. Batten, J. C. Jeffrey, L. H. Rees and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1996, 4249.
10 G. M Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
11 R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.
12 R. Allmann, S. Kremer and D. Kucharzcyk, *Inorg. Chim. Acta*, 1984, 85, L19.
13 T. Rojo, R. Cortes, L. Lezama, J. L. Mesa, J. Via and M. I. Arriortua, *Inorg. Chim. Acta*, 1989, **165**, 91.
14 I. Castro, J. Fuas, M. Julve and M. Philoche-Levisalles, *Transition Met. Chem.*, 1992, **17**, 263.
15 M. I. Arriortua, J. L. Mesa, T. Rojo, T. Debaerdemaeker, D. Beltran-Porter, H. Stratemeier and D. Reinen, *Inorg. Chem.*, 1988, **27**, 2976.
16 A. Kutoglu, R. Allmann, J.-V. Folgado, M. Atanasov and D. Reinen, *Z. Naturforsch.*, *Teil B*, 1991, **46**, 1193.

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