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The coordination chemistry of 4′-phenyl-2,2′:6′,2″-terpyridine; the synthesis, crystal and molecular structures of 4′-phenyl-2,2′:6′,2″-terpyridine and bis(4′-phenyl-2,2′:6′,2″-terpyridine)nickel(II) chloride decahydrate

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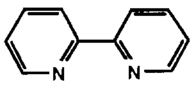
Abstract

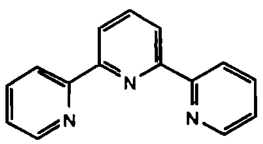
The convenient preparation and the structural characterisation of the terdentate ligand 4′-phenyl-2,2′:6′,2″-terpyridine (crystallographic data: space group *Pbcn*, $a=11.801(1)$, $b=12.177(3)$, $c=10.976(3)$ Å, $Z=4$, 1192 reflections with $F \geqslant 3\sigma(F)$, $R=0.0556$) is described. The three pyridyl rings adopt approximately planar *transoid* configurations about the interannular C–C bonds, whilst the phenyl ring adopts an angle of 10.9° with respect to the central pyridyl ring. A range of 1:1 and 2:1 complexes of this ligand with transition metals has been prepared, and the compound $[NiL_2]Cl_2 \cdot 10H_2O$ (L=4′-phenyl-2,2′:6′,2″-terpyridine) has been structurally characterised (crystallographic data: space group $P\bar{1}$, $a=10.340(2)$, $b=12.690(2)$, $c=19.822(4)$ Å, $Z=2$, 5926 reflections with $F \geqslant 4\sigma(F)$, $R=0.0583$). The complex possesses a distorted octahedral structure with two approximately planar terdentate L ligands; the phenyl groups now adopt angles of ≈17° with respect to the central pyridyl rings.

Introduction

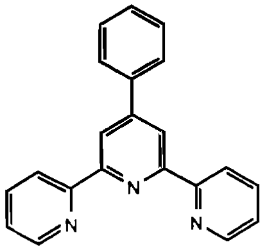
Polydentate ligands containing N-donor heterocyclic rings have played an important role in the development of coordination chemistry, and continue to be of widespread interest. Particular attention has centred upon complexes of the diimine ligands, 2,2′-bipyridine (bipy) and 2,2′:6′,2″-terpyridine (terpy) [1–3], although more recently the coordination chemistry of the higher homologues has been shown to be of very considerable interest [4, 5]. Although the coordination chemistry of 2,2′:6′,2″-terpyridine is well studied [2], the behaviour of substituted derivatives has been little investigated. The electrochemical and photophysical properties of complexes of 4′-phenyl-2,2′:6′,2″-terpyridine with iron(II) [6–8], cobalt(II) [6–8], manganese(II) [9, 10], chromium(III) [9, 10] and ruthenium(II) [11] have been described. In this paper we describe a facile preparation of 4′-phenyl-2,2′:6′,2″-terpyridine (L) and some of its coordination properties, together with the crystal and molecular structures of the free ligands and the nickel(II) complex $[NiL_2]Cl_2 \cdot 10H_2O$.



bipy



terpy



HL

Experimental

Infrared spectra were recorded in compressed KBr pellet on a Perkin-Elmer 983 spectrometer; ^{1}H NMR

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spectra were recorded on Brüker WM250 or AM400 spectrometers. Mass spectra were recorded on a Kratos MS50 mass spectrometer. 2-Acetylpyridine was used as suppled by Aldrich.

Synthesis of 3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione

2-Acetylpyridine (25 cm^3, 0.22 mol) was added dropwise to a stirred emulsion of benzaldehyde (11.5 cm^3, 0.11 mol) in ethanol (100 cm^3) and aqueous sodium hydroxide solution (150 cm^3, 1.5 M). The mixture was then stirred for 24 h at room temperature, after which period the precipitate was collected by filtration. The white solid was washed with ethanol (50 cm^3) and recrystallised from ethanol–dimethyl formamide (1:1) to yield white crystals of 3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione (35.2 g, 96%). Melting point (m.p.) 175–160 °C. *Anal.* Found: C, 76.4; H, 5.3; N, 8.4. Calc. for $C_{21}H_{18}N_2O_2$: C, 76.3; H, 5.5; N, 8.5%. MS *m/z* 330. IR ν(CO) 1698 cm^{-1}. ^{1}H NMR, CDCl$_3$, δ, 8.64, 2H, ddd, $J=4.5$, 1.8, 1.0 Hz, $H_{6,6''}$; 7.95, 2H, ddd, $J=7.6$, 1.2, 1.0 Hz, $H_{3,3''}$; 7.78, 2H, ddd, $J=7.6$, 7.8, 1.76 Hz, $H_{4,4''}$; 7.43, 2H, ddd, $J=8.8$, 4.5, 1.2 Hz, $H_{5.5''}$; 7.38, 2H, phenyl; 7.24, 2H, phenyl; 7.13, 1H, phenyl; 4.16, 1H, tt, $J=6.8$, 7.4 Hz, methine; 3.64, 2H, dd, $J=17.6$, 6.8 Hz, methylene; 3.77, dd, $J=17.6$, 7.44 Hz, methylene.

Synthesis of $[ML_2]^{2+}$ salts (M=Mn, Fe, Co, Ni, Cu or Zn)

A solution of the appropriate metal chloride or acetate (0.2 mmol) in methanol (50 cm^3) was heated to reflux with 4′-phenyl-2,2′:6′,2″-terpyridine (0.124 g, 0.4 mmol) for 10 min, after which period a methanolic solution of $[NH_4][PF_6]$ or $Na[BF_4]$ was added. In each case, a microcrystalline precipitate of the appropriate hexafluorophosphate or tetrafluoroborate salt was obtained on standing. This was collected by filtration, washed with cold methanol (2×10 cm^3) and diethyl ether (2×50 cm^3) and dried *in vacuo*. Yields were in the range of 60–80%. In the case of the halides, if the $[NH_4][PF_6]$ or $Na[BF_4]$ was not added the chloride could be obtained in crystalline form upon concentration. Recrystallisation of the halides from water yielded hydrates.

Synthesis of $[MLCl_2]$ (M=Mn, Cu, or Zn)

A solution of the appropriate metal chloride (0.4 mmol) in methanol (25 cm^3) was heated to reflux with 4′-phenyl-2,2′:6′,2″-terpyridine (0.124 g, 0.4 mmol) for 30 min. The zinc complex precipitated from solution over this period, whilst it was necessary to concentrate the solutions to obtain the manganese or copper compounds. The precipitates were washed with methanol (2×5 cm^3) and diethyl ether (2×25 cm^3) and dried *in vacuo*. Yields were in the range 55–80%.

Synthesis of $[MLCl_2]$ (M=Ni or Co)

A solution of the appropriate metal chloride (0.4 mmol) and sodium chloride (0.234 g, 4 mmol) in aqueous methanol (1:1, 50 cm^3) was heated to reflux with 4′-phenyl-2,2′:6′,2″-terpyridine (0.124 g, 0.4 mmol) for 3 h. The complexes were obtained upon concentration. The precipitates were washed with water (10 cm^3) and diethyl ether (2×25 cm^3) and dried *in vacuo* (60%).

X-ray crystallography of 4′-phenyl-2,2′:6′,2″-terpyridine

A colourless crystal obtained from methanol was mounted on a glass fibre. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Enraf Nonius CAD4) following procedures described previously [12]. Pertinent crystallographic data are given in Table 1. Lattice dimensions were verified by preliminary Weissenberg photography. Intensity data, gathered by the 2θ–ω method, were reduced by routine procedures. Calculations were carried out using the program SHELX [13] on the University of Cambridge IBM 370/165 computer. Empirical absorption corrections were applied.

All the non-hydrogen atoms were located by direct methods and refined anisotropically. Hydrogen atoms

TABLE 1. Crystal data for L

Formula	$C_{21}H_{15}N_3$
Formula weight	309.37
Space group	*Pbcn*
a (Å)	11.801(1)
b (Å)	12.177(3)
c (Å)	10.976(3)
V (Å^3)	1577
Z	4
$F(000)$	648
D_{calc} (g/cm^3)	1.302
Crystal size (mm)	0.7×0.7×0.5
μ(Cu Kα) (cm^{-1})	5.33
Data collection instrument	Enraf Nonius CAD4
Radiation	Cu Kα ($\lambda=1.5418$ Å)
Orientation reflections: no., range (2θ)	25, $40° \leqslant 2\theta \leqslant 60°$
Data collection range	$6.0° \leqslant 2\theta \leqslant 130.0°$
Temperature (°C)	20
No. unique data	1620
Total with $F \geqslant 3\sigma(F)$	1192
R[a]	0.0556
R'[b]	0.0452
Weighting scheme	$w=0.0125/[\sigma^2F+0.001F^2]$
Largest peak (e/Å^3)	0.19

[a] $R=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$. [b] $R'=\Sigma w^{1/2}[|F_o|-|F_c|]/\Sigma w^{1/2}|F_o|$.

were placed in idealised positions with a fixed isotropic thermal parameter, $U=0.08$ Å. The final difference Fourier map had no peaks larger than 0.2 e/Å^3. Positional parameters are presented in Table 2 and bond distances and bond angles are given in Table 3.

X-ray crystallography of bis(4'-phenyl-2,2':6',2"-terpyridine) nickel(II) chloride decahydrate

A orange block obtained by recrystallisation from water was mounted in a glass capillary tube containing a small amount of the mother liquor from the recrystallisation. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Syntex P2$_1$) following procedures described previously [14]. Pertinent crystallographic data are given in Table 4. Lattice dimensions were verified by preliminary Weissenberg photography. Intensity data, gathered by the 2θ-ω method, were reduced by routine procedures. Calculations were carried out using the program SHELX [13] on the University of Cambridge IBM 370/165 computer. Empirical absorption corrections were applied.

TABLE 2. Positional parameters ($\times 10^4$) and their e.s.d.s for L

	x	y	z
N(1)	1734(1)	−1372(1)	5103(2)
C(1)	2301(2)	−733(2)	5940(2)
C(2)	2396(2)	375(2)	5937(2)
C(3)	1885(2)	968(2)	5029(2)
C(4)	1288(2)	388(2)	4158(2)
C(5)	1229(2)	−778(2)	4224(2)
N(2)	0	−853(2)	2500
C(6)	584(1)	−1450(2)	3319(2)
C(7)	613(2)	−2625(2)	3341(2)
C(8)	0	−3242(2)	2500
C(9)	0	−4506(2)	2500
C(10)	458(2)	−5114(2)	3456(2)
C(11)	452(2)	−6283(2)	3458(2)
C(12)	0	−6870(3)	2500

TABLE 3. Bond distances (Å) and bond angles (°) for L

N(1)–C(1)	1.343(2)	N(1)–C(5)	1.342(2)
C(1)–C(2)	1.370(3)	C(2)–C(3)	1.368(3)
C(3)–C(4)	1.382(3)	C(4)–C(5)	1.379(3)
C(5)–C(6)	1.494(2)	N(2)–C(6)	1.346(2)
C(6)–C(7)	1.388(2)	C(7)–C(8)	1.393(2)
C(8)–C(9)	1.492(4)	C(9)–C(10)	1.388(2)
C(10)–C(11)	1.380(3)	C(11)–C(12)	1.374(3)
C(1)–N(1)–C(5)	117.1(2)	N(1)–C(1)–C(2)	123.9(2)
C(1)–C(2)–C(3)	118.3(2)	C(2)–C(3)–C(4)	119.3(2)
C(3)–C(4)–C(5)	119.0(2)	N(1)–C(5)–C(4)	122.3(2)
N(1)–C(5)–C(6)	116.2(2)	C(4)–C(5)–C(6)	121.5(2)
C(6)–N(2)–C(6')	116.9(2)	C(5)–C(6)–N(2)	116.4(2)
C(5)–C(6)–C(7)	120.4(2)	N(2)–C(6)–C(7)	123.3(2)
C(6)–C(7)–C(8)	119.8(2)	C(7)–C(8)–C(7')	117.0(3)
C(7)–C(8)–C(9)	121.5(1)	C(8)–C(9)–C(10)	121.1(1)
C(10)–C(9)–C(10')	117.8(3)	C(9)–C(10)–C(11)	121.0(2)
C(10)–C(11)–C(12)	120.4(2)	C(11)–C(12)–C(11')	119.4(3)

TABLE 4. Crystal data for $[NiL_2]Cl_2 \cdot 10H_2O$

Formula	$C_{42}H_{50}Cl_2N_6NiO_{10}$
Formula weight	748.36
Space group	$P\bar{1}$
a (Å)	10.340(2)
b (Å)	12.690(2)
c (Å)	19.822(4)
α (°)	104.47(2)
β (°)	92.57(2)
γ (°)	116.28(1)
V (Å^3)	2247.77
Z	2
F(000)	972
D_{calc} (g/cm^3)	1.105
Crystal size (mm)	$0.5\times0.3\times0.3$
μ(Cu Kα) (cm^{-1})	21.31
Data collection instrument	Syntex P2$_1$
Radiation	Cu Kα ($\lambda=1.5418$ Å)
Orientation reflections:	
no., range (2θ)	15, $50°\leq2\theta\leq60°$
Data collection range	$3.0°\leq2\theta\leq125.0°$
Temperature (°C)	20
No. unique data	6920
Total with $F\geq4\sigma(F)$	5926
R^a	0.0583
R'^b	0.0663
Weighting scheme	$w=0.0125/\sigma^2F+0.001F^2]$
Largest peak (e/Å^3)	0.67

$^aR=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$. $^bR'=\Sigma w^{1/2}[|F_o|-|F_c|]/\Sigma w^{1/2}|F_o|$.

All the non-hydrogen atoms were located by direct methods and refined anisotropically. Hydrogen atoms were placed in idealised positions with a fixed isotropic thermal parameter, $U=0.08$ Å. The final difference Fourier map had no peaks larger than 0.7 e/Å^3. Positional parameters are presented in Table 5 and bond distances and bond angles are given in Table 6.

Results and discussion

The desired ligand, 4'-phenyl-2,2':6',2"-terpyridine was prepared by a Krohnke-type synthesis (Scheme 1) [15]. The reaction of two equivalents of 2-acetylpyridine with one equivalent of benzaldehyde in stirred alkaline aqueous alcoholic medium results in the precipitation of 3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione as a white solid in good yield (96%). This intermediate dione was fully characterised on the basis of elemental analysis, mass spectroscopy

TABLE 5 Positional parameters ($\times 10^4$) and their e s d s for $[NiL_2]Cl_2$ $10H_2O$

	x	y	z
Ni(1)	2722(1)	2827	2499
N(1)	1781(3)	3870(2)	2211(1)
C(1)	1411(4)	3888(3)	1562(2)
C(2)	884(4)	4672(3)	1421(2)
C(3)	801(5)	5489(3)	1988(2)
C(4)	1206(4)	5491(3)	2664(2)
C(5)	1687(4)	4663(3)	2760(2)
N(2)	2653(3)	3764(2)	3427(1)
C(6)	2115(4)	4555(3)	3456(2)
C(7)	1946(4)	5166(3)	4090(2)
C(8)	2331(4)	4942(3)	4702(2)
C(9)	2940(4)	4139(3)	4659(2)
C(10)	3073(4)	3561(3)	4011(2)
C(11)	2115(4)	5539(3)	5387(2)
C(12)	1869(5)	6559(3)	5455(2)
C(13)	1652(5)	7118(4)	6088(2)
C(14)	1680(5)	6694(5)	6658(2)
C(15)	1919(6)	5728(6)	6609(2)
C(16)	2113(5)	5107(5)	5969(2)
N(3)	3586(3)	2164(2)	3195(1)
C(17)	3629(4)	2651(3)	3882(2)
C(18)	4116(4)	2282(3)	4402(2)
C(19)	4560(5)	1390(4)	4215(2)
C(20)	4488(5)	888(4)	3521(2)
C(21)	3999(4)	1298(3)	3023(2)
N(4)	718(3)	1201(2)	2277(1)
C(22)	−311(4)	891(3)	2684(2)
C(23)	−1587(4)	−180(3)	2492(2)
C(24)	−1821(4)	−966(3)	1848(2)
C(25)	−756(4)	−671(3)	1425(2)
C(26)	505(4)	418(3)	1654(2)
N(5)	2820(3)	1929(2)	1564(1)
C(27)	1731(4)	821(3)	1253(2)
C(28)	1814(4)	161(3)	612(2)
C(29)	3046(4)	643(3)	297(2)
C(30)	4149(4)	1807(3)	633(2)
C(31)	3999(4)	2431(3)	1262(2)
C(32)	3210(4)	−40(3)	−374(2)
C(33)	2348(5)	−1304(3)	−617(2)
C(34)	2518(5)	−1941(4)	−1236(2)
C(35)	3520(5)	−1339(4)	−1630(2)
C(36)	4367(5)	−112(4)	−1403(2)
C(37)	4222(5)	538(3)	−774(2)
N(6)	4739(3)	4079(2)	2291(1)
C(38)	5078(4)	3696(3)	1670(2)
C(39)	−6281(4)	4430(3)	1421(2)
C(40)	−7155(4)	5617(3)	1811(2)
C(41)	−6791(4)	6008(3)	2436(2)
C(42)	−5585(4)	5227(3)	2662(2)
Cl(1)	190(1)	3235(1)	9450(1)
Cl(2)	4746(2)	2144(2)	6268(1)
O(1)	7731(3)	3891(3)	−19(1)
O(2)	7978(5)	1487(3)	7988(2)
O(3)	5726(4)	2217(4)	7817(2)
O(4)	7537(5)	1887(3)	5859(2)
O(5)	5458(4)	3804(3)	−881(2)
O(6)	3300(4)	3632(3)	32(2)
O(7)	−1871(6)	−2186(5)	4205(2)
O(8)	−351(5)	−959(5)	5623(2)
O(9)	7501(6)	428(4)	4576(3)
O(10)	−583(5)	1536(6)	6746(3)

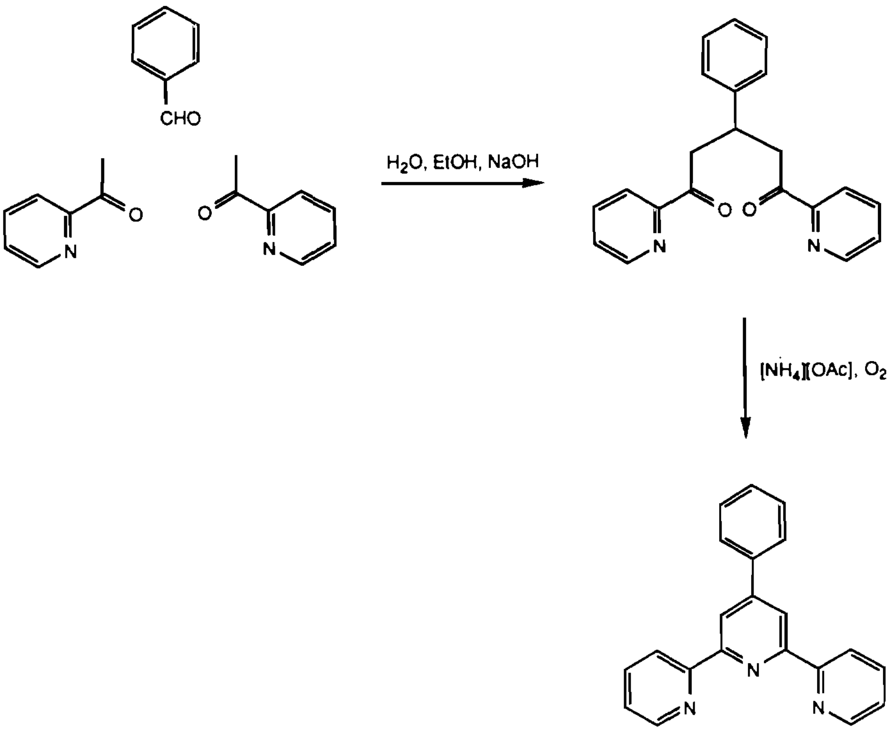
TABLE 6 Bond distances (Å) and bond angle (°) within the coordination sphere for $[NiL_2]Cl_2$ $10H_2O$

Ni(1)–N(1)	2 108(4)	Ni(1)–N(2)	1 986(3)
Ni(1)–N(3)	2 114(3)	Ni(1)–N(4)	2 118(2)
Ni(1)–N(5)	1 987(3)	Ni(1)–N(6)	2 115(3)
N(1)–Ni(1)–N(2)	78 3(1)	N(1)–Ni(1)–N(3)	156 1(1)
N(1)–Ni(1)–N(4)	94 4(1)	N(1)–Ni(1)–N(5)	100 8(1)
N(1)–Ni(1)–N(6)	88 4(1)	N(2)–Ni(1)–N(3)	77 8(1)
N(2)–Ni(1)–N(4)	103 6(1)	N(2)–Ni(1)–N(5)	178 5(1)
N(2)–Ni(1)–N(6)	100 5(1)	N(3)–Ni(1)–N(4)	90 0(1)
N(3)–Ni(1)–N(5)	103 0(1)	N(3)–Ni(1)–N(6)	97 1(1)
N(4)–Ni(1)–N(5)	77 6(1)	N(4)–Ni(1)–N(6)	155 8(1)
N(5)–Ni(1)–N(6)	78 2(1)	Ni(1)–N(1)–C(1)	126 6(3)
Ni(1)–N(1)–C(5)	113 9(2)	Ni(1)–N(2)–C(6)	119 2(2)
Ni(1)–N(2)–C(10)	120 1(3)	Ni(1)–N(3)–C(17)	114 1(3)
Ni(1)–N(3)–C(21)	126 7(2)	Ni(1)–N(4)–C(22)	127 0(2)
Ni(1)–N(4)–C(26)	114 3(2)	Ni(1)–N(5)–C(27)	119 8(2)
Ni(1)–N(5)–C(31)	119 4(2)	Ni(1)–N(6)–C(38)	114 3(2)
Ni(1)–N(6)–C(42)	127 0(2)		

(P^+, m/z 330) and NMR spectroscopy The compound exhibits an absorption in its infrared spectrum at 1698 cm^{-1}, which may be assigned to the conjugated carbonyl groups The reaction of this dione with boiling ethanolic ammonium acetate in air results in the formation of a dark coloured solution, from which crystals of 4'-phenyl-2,2' 6',2"-terpyridine separate upon cooling Recrystallisation from ethanol yields pale yellow blocks of the ligand (47%) The compound exhibits a parent ion at m/z 309, and the infrared spectrum shows no absorptions between 1602 and 1900 cm^{-1}, indicating the complete loss of the carbonyl functionality

The ^{1}H NMR spectrum of the ligand is shown in Fig 1(a) There are no resonances observed below δ7 0, which is conclusive evidence that the product of the reaction is the fully aromatised pyridine, rather than the intermediate dihydropyridine The low field region of the spectrum consists of a singlet (δ8 75) and two doublets showing further coupling (δ8 74, 8 69), which may be assigned to $H_{3',5'}$, $H_{6,6''}$ and $H_{3,3''}$, respectively The downfield shifts of these protons may be traced to deshielding by adjacent pyridyl or phenyl rings The assignments indicated have been confirmed by homonuclear decoupling experiments The ^{13}C NMR spectrum is shown in Fig 1(b), and is fully in accord with the fully aromatised structure rather than that of a dihydropyridine

Although the molecular structure of 2,2'-bipyridine has been determined [16], there is very little structural data for higher oligopyridines We were particularly interested in the relative orientations of the pyridyl and phenyl rings in L, and accordingly determined the solid state structure of the compound The molecular structure of the 4'-phenyl-2,2' 6',2"-terpyridine is presented in Fig 2 The molecule lies



Scheme 1.

on a crystallographic two-fold axis which passes through N(2), C(8), C(9) and C(12). The three pyridyl rings are all approximately coplanar, making an interannular angle with the central ring of 5.7°, with a *transoid* arrangement about each interannular C–C bond. This is in accord with the *transoid* configuration observed in the crystal structures of 2, 2′-bipyridine [16] and 2,2′:6′,2″:6″,2‴-quaterpyridine [5]. The C–C and C–N distances within the aromatic rings are normal and within the range 1.344 ± 0.002 and 1.370 ± 0.013 Å, respectively. The interannular C–C bonds also closely resemble those seen in 2,2′-bipyridine [16] and 2,2′:6′,2″:6″,2‴-quaterpyridine [5] with lengths of 1.439 ± 0.001 Å.

The phenyl ring is not coplanar with the terpyridyl fragment, but is twisted about the interannular bond such that the plane of the phenyl ring makes an angle of 10.9° with the plane of the central pyridyl ring. This represents a compromise between a coplanar arrangement in which π-conjugation and non-bonded H–H contacts between the *ortho* protons of the phenyl ring and $H_{3',5'}$ are maximised, and one in which the two rings are perpendicular, in which both H–H contacts and π-overlap are minimised. The non-bonded distance H(7)–H(10) observed (1.937 Å) is still within the sum of the van der Waals radii of the two atoms. The two terminal pyridyl rings are also twisted about the interannular C–C bonds, and interplanar angles of 8.2° are made with the central pyridine ring.

The free ligand is electrochemically active, and the cyclic voltammogram of an acetonitrile solution ($[^nBu_4N][BF_4]$ supporting electrolyte) shows a reversible one electron reduction centred at −2.3 V versus Ag/Ag^+. Chemical reduction with sodium amalgam or controlled potential electrolysis at −2.5 V resulted in the formation of a purple solution of the radical anion, but this was a very short-lived species and we were unable to record the ESR spectrum.

The interactions of the new ligand with first row transition metals (Mn^{2+}–Zn^{2+}) were investigated. Two series of complexes were obtained, depending upon the ratio of L to metal used, and upon the presence of coordinating anions. With an excess of L the complex ions $[ML_2]^{2+}$ were obtained, whereas with lower amounts of L or in the presence of a coordinating halide, species of stoichiometry $[MLX_2]$ were obtained. This behaviour parallels that previously reported for 2,2′:6′,2″-terpyridine [2]. The reaction of L with $MCL_2 \cdot nH_2O$ (M = Mn, Cu or Zn) in methanolic solution results in the formation species of stoichiometry ($MLCl_2$), which could be obtained by concentration of the solution. The corresponding cobalt(II) and nickel(II) complexes could only be obtained if the reaction was conducted in the presence

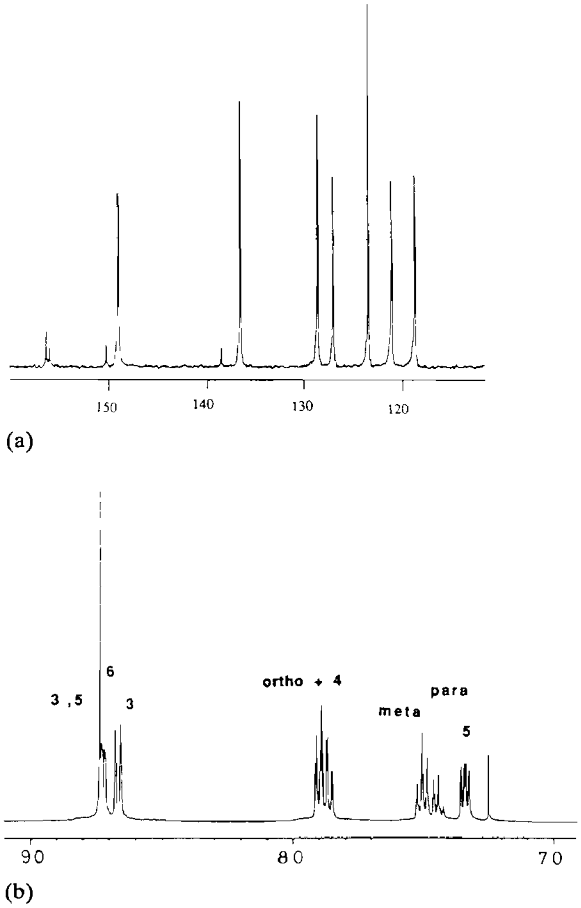


Fig 1 (a) ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) and (b) $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz observe, $CDCl_3$, 25 °C) of 4'-phenyl-2,2' 6',2'-terpyridine showing the assignments

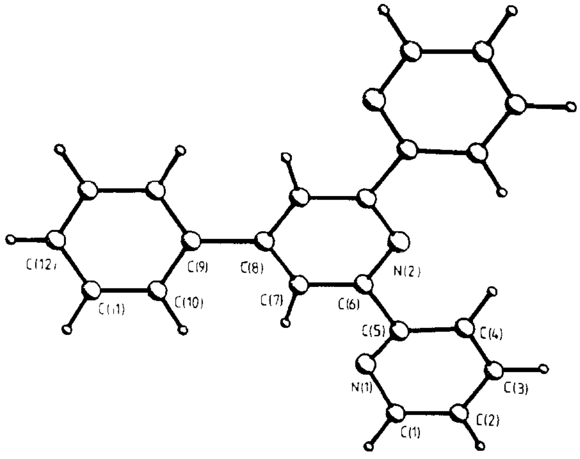


Fig 2 Crystal and molecular structure of 4'-phenyl-2,2' 6',2"-terpyridine showing the numbering scheme adopted

of an excess of sodium chloride In the absence of the sodium chloride, the complexes $[ML_2]Cl_2$ were obtained Analytical data for these complexes is presented in Table 7 We believe that these 1 1 complexes possess structures which are strictly analogous to those of the 2,2' 6',2"-terpyridine analogues We thus assign five coordinate structures to the complexes $[MnLCl_2]$ [17], $[CoLCl_2]$ [18] $[CuLCl_2]$ [19] and $[ZnLCl_2]$ [20], and the structure $[NiL_2][NiCl_4]$ to the nickel complex [21] Recrystallisation of the cobalt or nickel complexes from methanol in the absence of added halide resulted in the formation of $[ML_2]^{2+}$ salts The reaction of $[M(PPh_3)_2Cl_2]$ (M = Co, Ni or Zn) with L in benzene resulted in the formation of 1 1 adducts apparently similar to those obtained from the direct reaction of the appropriate halide with L In no case was a mixed ligand complex with both L and a phosphine coordinated to the metal obtained

The interaction of the metal halides with two or more equivalents of L in methanol results in the formation of the complex ions $[ML_2]^{2+}$ (M = Mn, Fe, Co, Ni, Cu or Zn), which are conveniently isolated from solution as their hexafluorophosphate or tetrafluoroborate salts Microanalytical data for these compounds is also presented in Table 7 These complexes are all distorted octahedral species with local D_{2d} symmetry about the metal The crystal structures of $[Fe(terpy)_2]^{2+}$ [22], $[Co(terpy)_2]^{2+}$ [23], $[Ni(terpy)_2]^{2+}$ [24] and $[Cu(terpy)_2]^{2+}$ [25] salts have been described

Recrystallisation of $[NiL_2]Cl_2$ (obtained directly from the reaction of nickel chloride with L or from

TABLE 7 Microanalytical data for the compounds

Compound	Found (calc) (%)		
	C	H	N
L	81 2(81 5)	5 0(4 9)	13 4(13 6)
$[MnLCl_2]$	57 8(58 0)	3 3(3 5)	9 6(9 7)
$[CoLCl_2]$	57 5(57 4)	3 7(3 4)	9 6(9 6)
$[NiLCl_2]$	57 1(57 4)	3 4(3 4)	9 4(9 6)
$[CuLCl_2]$	55 5(56 8)	3 3(3 4)	9 2(9 5)
$[ZnLCl_2]$	56 8(56 6)	3 4(3 4)	9 3(9 4)
$[MnL_2][BF_4]_2$	59 5(59 5)	3 5(3 6)	9 8(9 9)
$[MnL_2]Cl[PF_6]$ H_2O	56 3(56 7)	3 4(3 8)	9 3(9 4)
$[FeL_2][BF_4]_2$ $2H_2O$	57 3(57 0)	3 4(3 9)	9 5(9 5)
$[FeL_2][PF_6]_2$ $2H_2O$	50 4(50 4)	3 2(3 4)	8 2(8 4)
$[CoL_2][BF_4]_2$	58 3(59 3)	3 6(3 6)	9 7(9 9)
$[CoL_2][PF_6]_2$	51 6(52 1)	3 2(3 2)	8 6(8 7)
$[NiL_2][BF_4]_2$	59 1(59 3)	3 4(3 6)	9 7(9 9)
$[NiL_2][PF_6]_2$	52 2(52 2)	3 1(3 1)	8 7(8 7)
$[CuL_2][BF_4]_2$ $2H_2O$	56 6(56 6)	3 2(3 8)	9 3(9 4)
$[CuL_2][PF_6]_2$	51 6(51 9)	2 9(3 1)	8 5(8 6)
$[ZnL_2][PF_6]_2$	51 5(51 8)	3 0(3 1)	8 6(8 7)
$[ZnL_2][BF_4]_2$	58 2(58 8)	3 4(3 5)	9 7(9 8)

the 1:1 adduct) from water results in the formation of the decahydrate, and we have determined the crystal and molecular structure of $[NiL_2]Cl_2 \cdot 10H_2O$. The molecular structure of the $[NiL_2]^{2+}$ cation is presented in Fig. 3. The nickel is in the expected distorted octahedral geometry, with each of the terdentate ligands occupying three *meridionally* arranged coordination sites. The nickel–nitrogen bond lengths show the expected pattern for a complex of 2,2′:6′,2″-terpyridine [2], with short contacts to the central ring (1.986–1.987 Å) and longer contacts to the terminal rings (2.108–2.118 Å). These bond lengths to the terminal rings very closely resemble those observed in $[Ni(terpy)_2][PF_6]_2$ (2.136, 2.125, 2.107, 2.114 Å), but the bond to the nitrogen atom of the central pyridine ring is significantly shorter than those of 2.016 and 2.009 to those in the central ring in $[Ni(terpy)_2][PF_6]_2$ (2.016, 2.009 Å) [24]. This we attribute to a greater π-bonding component with the 4′-phenyl substituted ligand. The configuration of the ligands closely resembles that observed in other complexes of 2,2′:6′,2″-terpyridine, with resulting bite angles in the range 77.6–78.3°. The terminal pyridine rings are not coplanar with the central ring and form interannular angles within the range 3.9–8.2°, very similar to those observed in the free ligand. However, the phenyl rings are slightly more twisted about the interannular C–C bond, and angles of 16.7 and 17.8° are observed. This is associated with a slight shortening of these bonds (1.485(5) and 1.483(5) Å) with respect to the free ligand (1.492(4) Å). This presumably represents a purely electrostatic effect associated with the positively charged metal centre, as the greater degree of twisting is expected to reduce π-overlap and lengthen the bond. There is an extensive hydrogen bonding network involving the lattice water molecules and the halide counterions.

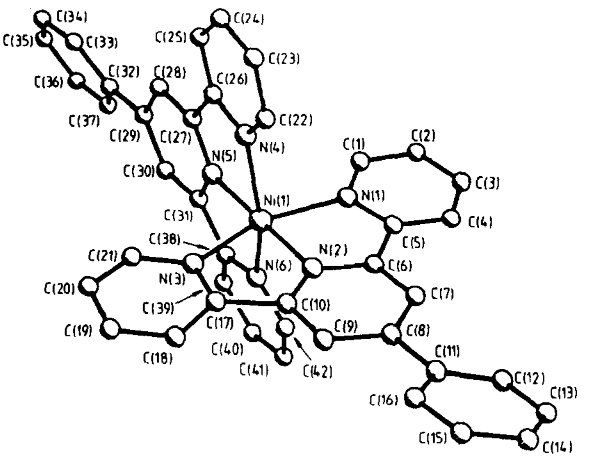


Fig. 3. Crystal and molecular structure of the $[NiL_2]^{2+}$ cation in bis(4′-phenyl-2,2′:6′,2″-terpyridine)nickel(II) chloride decahydrate showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.

Supplementary material

Tables of anisotropic displacement parameters, hydrogen atom coordinates, remaining bond lengths and angles and least-squares planes are available from the authors.

Acknowledgement

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References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem., 12* (1969) 135.
2 E. C. Constable, *Adv. Inorg. Chem. Radiochem., 30* (1986) 69.
3 E. C. Constable, *Adv. Inorg., 34* (1989) 1.
4 E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.,* (1987) 1600; E. C. Constable and J. M. Holmes, *Inorg. Chim. Acta, 126* (1987) 187; M. Barley, E. C. Constable, S. A. Corr, M. G. B. Drew, R. C. S. McQueen, J. C. Nutkins and M. D. Ward, *J. Chem. Soc., Dalton Trans.,* (1988) 2655; E. C. Constable, M. G. B. Drew, G. Forsyth and M. D. Ward, *J. Chem. Soc., Chem. Commun.,* (1988) 1450; E. C. Constable, M. G. B. Drew, G. Forsyth and M. D. Ward, *Polyhedron, 8* (1989) 2551; E. C. Constable, M. D. Ward and D. A. Tocher, *J. Am. Chem Soc., 112* (1990) 1256; *J. Chem. Soc., Chem. Commun.,* (1990) 621; E. C. Constable, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc., 112* (1990) 4590.
5 E. C. Constable, S. M. Elder, J. A. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.,* (1990) 1010.
6 J. M. Rao, M. C. Hughes and D. J. Macero, *Inorg. Chim. Acta, 16* (1976) 231.
7 D. H. Wilkins and G. F. Smith, *Anal. Chim. Acta, 9* (1953) 338.
8 J. M. Rao, D. J. Macero and M. C. Hughes, *Inorg. Chim. Acta, 41* (1980) 221.
9 J. M. Rao, M. C. Hughes and D. J. Macero, *Inorg. Chim. Acta, 18* (1976) 127.
10 M. C. Hughes, D. J.. Macero and J. M. Rao, *Inorg. Chim. Acta, 49* (1981) 241.
11 M. L. Stone and G. A. Crosby, *Chem. Phys. Lett., 79* (1981) 169; S. F. Agnew, M. L. Stone and G. A. Crosby, *Chem. Phys. Lett., 85* (1982) 57.
12 M. B. Hursthouse, R. A. Jones, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc., 101* (1979) 4128.
13 G. M. Sheldrick, *SHELX,* crystallographic computing package, University of Cambridge, U.K., 1976.
14 E.C. Constable, J. Lewis, M. C. Liptrot and P. R. Raithby, *J. Chem. Soc., Dalton Trans.,* (1984) 2177.

15 F. Krohnke, *Synthesis,* (1976) 1.

16 L. L. Merritt, Jr. and E. D. Schroeder, *Acta Crystallogr., 9* (1956) 801; K. Nakatsu, H. Yoshioka, M. Matsui, S. Koda and S. Ooi, *Acta Crystallogr., Sect. A, 28* (1972) S24; M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress and W. H. Woodruff, *J. Am. Chem. Soc., 103* (1981) 4945.

17 C. M. Harris, T. N. Lockyer and N. C. Stephenson, *Aust. J. Chem., 19* (1966) 1741; J. S. Judge, W. M. Reiff, G. M. Intille, P. Ballway and W. A. Baker, Jr., *J. Inorg. Nucl. Chem., 29* (1967) 1711.

18 A. Bakac, R. Marcec and M. Orhanovic, *Inorg. Chem., 15* (1977) 3133.

19 D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.,* (1956) 594; C. M. Harris, T. N. Lockyer and N. C. Stephenson, *Aust. J. Chem., 19* (1966) 1741; W. Henke, S. Kremer and D. Reinen, *Inorg. Chem., 22* (1983) 2858; T. Rojo, M. Vlasse and D. Beltran-Porter, *Acta Crystallogr., Sect. C, 39* (1983) 194; F. J. Ruiz, J. L. Mesa, T. Rojo and M. I. Arriortua, *J. Appl. Crystallogr., 16* (1983) 430.

20 D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.,* (1956) 594; J. E. Douglas and C. J. Wilkins, *Inorg. Chim. Acta, 3* (1969) 635; F. W. B. Einstein and B. R. Penfold, *Acta Crystallogr., 20* (1966) 924; M. Vlasse, T. Rojo and D. Beltran-Porter, *Acta Crystallogr., Sect. C, 39* (1983) 560.

21 C. M. Harris and T. N. Lockyer, *Aust. J. Chem., 23* (1970) 1703.

22 A. T. Baker and H. A. Goodwin, *Aust. J. Chem., 38* (1985) 207.

23 B. N. Figgis, E. S. Kucharski and A. H. White, *Aust. J. Chem., 36* (1983) 1527, 1537, 1563; W. Henke and S. Kremer, *Inorg. Chim. Acta, 65* (1982) L115; E. N. Maslen, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.,* (1974) 1803; C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.,* (1976) 7.

24 M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain and J. P. Declerq, *Bull. Soc. Chim. Belg., 91* (1982) 337.

25 R. Allmann, W. Henke and D. Reinen, *Inorg. Chem., 17* (1978) 378; M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain and J. P. Declercq, *Acta Crystallogr., Sect. B, 38* (1982) 1323; M. Mathew and G. J. Palenik, *J. Coord. Chem., 1* (1971) 243.