A Convenient Preparation of 2,2′:6′,2″:6″,2‴-Quaterpyridine; The Crystal and Molecular Structures of 2,2′:6′,2″:6″,2‴-Quaterpyridine and Bis(acetonitrile)-(2,2′:6′,2″:6″,2‴-quaterpyridine)nickel(II) Hexafluorophosphate–Acetonitrile(1/1)†

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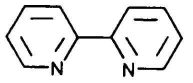
2,2′:6′,2″:6″,2‴-Quaterpyridine has been prepared in 40—45% yield by the nickel(0) coupling of a 6-halogeno-2,2′-bipyridine. The reaction initially yields a nickel(II) complex of 2,2′:6′,2″:6″,2‴-quaterpyridine which may be demetallated by treatment with NaCN. The crystal and molecular structures of 2,2′:6′,2″:6″,2‴-quaterpyridine [monoclinic, a = 6.348(1), b = 8.179(2), c = 14.894(3)Å, β = 100.15(1)°, space group $P2_1/n$, Z = 2] and bis(acetonitrile)-(2,2′:6′,2″:6″,2‴-quaterpyridine)nickel(II) hexafluorophosphate-acetonitrile (1/1) [monoclinic, a = 22.348(9), b = 11.504(5), c = 15.636(6) Å, β = 128.41 (2)°, space group $C2/c$, Z = 4] have been determined. The free ligand is essentially planar with transoid arrangements of the pyridyl rings as observed in 2,2′-bipyridine. The nickel complex is approximately octahedral with the 2,2′:6′,2″:6″,2‴-quaterpyridine occupying the equatorial sites; the Ni–N distances to the terminal pyridine rings are longer than those to the inner rings.

Although the co-ordination chemistry of 2,2′-bipyridine (L^1, bipy)[1] and 2,2′:6′,2″-terpyridine (L^2, terpy)[1,2] has been widely investigated, studies involving the higher oligopyridines are few in number.[2] We are currently making a systematic investigation of the co-ordination behaviour of the oligopyridines, and have recently demonstrated that the higher oligomers exhibit a range of bonding modes. Thus, bipy and terpy almost invariably form mononuclear complexes in which they act as chelating N$_2$ or N$_3$ donors respectively. In contrast, 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (L^3) forms mononuclear,[3] binuclear bridged,[4] and binuclear double-helical[5] complexes, whilst 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2‴‴-sexipyridine (L^4) gives binuclear double-helical species.[6] The relative size of the metal ion and the available bonding cavity of the ligand dictate the bonding mode adopted, and the ligand 2,2′:6′,2″:6″,2‴-quaterpyridine (L) occupies a pivotal position and is expected to form both mononuclear and binuclear complexes. In our investigations we have become aware of a need for reliable and easy syntheses of relatively large quantities of the ligands, and have recently described a convenient preparation of terpy.[7] In this paper we report a facile synthesis of L and the structural characterisation of the free ligand and of a nickel(II) complex.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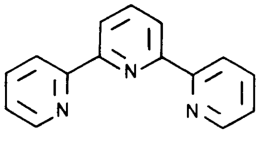
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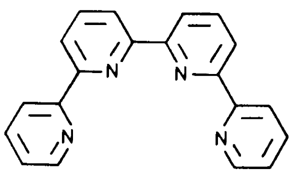
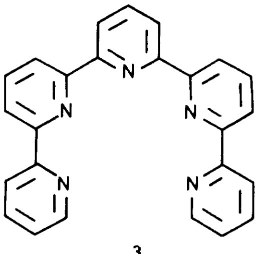

L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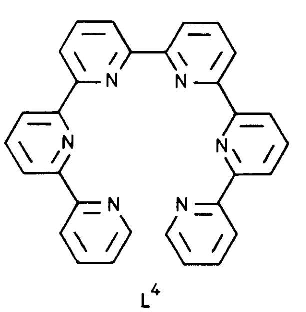
L^4

Experimental

Infra-red spectra were recorded in Nujol mull on a Perkin-Elmer 983 spectrometer, ^{1}H n.m.r. spectra on a Brüker WM250 spectrometer, and fast atom bombardment (f.a.b.) and electron impact (e.i.) mass spectra on Kratos MS50 and MS30 mass spectrometers respectively. 6-Bromo-2,2′-bipyridine and 6-chloro-2,2′-bipyridine were prepared from 2,2′-bipyridine by the literature methods,[8] and were recrystallised from methanol and dried over P_4O_{10} for 24 h before use. The complex [Ni(PPh$_3$)$_2$Cl$_2$] was prepared by the literature method.[9] Dimethylformamide was freshly purified[10] and deoxygenated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Atomic co-ordinates (× 10^4) For L

Atom	x	y	z
N(1)	132(2)	4 243(2)	1 681(1)
N(2)	588(2)	8 009(1)	493(1)
C(1)	1 202(3)	2 847(2)	1 869(1)
C(2)	3 141(3)	2 526(2)	1 626(1)
C(3)	4 030(3)	3 692(2)	1 153(1)
C(4)	2 942(3)	5 134(2)	932(1)
C(5)	1 007(2)	5 375(2)	1 212(1)
C(6)	−119(2)	6 927(2)	1 019(1)
C(7)	−2 028(3)	7 222(2)	1 381(1)
C(8)	−3 078(3)	8 685(2)	1 185(1)
C(9)	−2 292(3)	9 806(2)	639(1)
C(10)	−453(2)	9 426(2)	301(1)

Table 2. Bond lengths (Å) and bond angles (°) for L

N(1)–C(1)	1.333(2)	N(1)–C(5)	1.338(2)
N(2)–C(6)	1.335(2)	N(2)–C(10)	1.340(2)
C(1)–C(2)	1.369(3)	C(2)–C(3)	1.365(3)
C(3)–C(4)	1.377(2)	C(4)–C(5)	1.379(2)
C(5)–C(6)	1.485(2)	C(6)–C(7)	1.385(2)
C(7)–C(8)	1.375(2)	C(8)–C(9)	1.376(3)
C(9)–C(10)	1.387(2)	C(10)–C(10A)	1.482(3)
C(1)–N(1)–C(5)	117.3(2)	C(6)–N(2)–C(10)	118.5(1)
N(1)–C(1)–C(2)	123.9(2)	C(1)–C(2)–C(3)	118.4(2)
C(2)–C(3)–C(4)	119.1(2)	C(3)–C(4)–C(5)	119.1(2)
N(1)–C(5)–C(4)	122.2(1)	N(1)–C(5)–C(6)	116.4(1)
C(4)–C(5)–C(6)	121.3(1)	N(2)–C(6)–C(5)	116.5(1)
N(2)–C(6)–C(7)	122.6(1)	C(5)–C(6)–C(7)	120.9(1)
C(6)–C(7)–C(8)	118.5(2)	C(7)–C(8)–C(9)	119.5(2)
C(8)–C(9)–C(10)	118.8(1)	N(2)–C(10)–C(9)	122.1(1)
N(2)–C(10)–C(10A)	116.6(2)	C(9)–C(10)–C(10A)	121.3(2)

immediately before use. 2,2′-Bipyridine was used as supplied by Aldrich.

Preparation of 2,2′:6′,2″:6″,2‴-*Quaterpyridine.—From* 6-*bromo*-2,2′-*bipyridine.* A solution of $[Ni(H_2O)_6]Cl_2$ (3.80 g, 16 mmol) and PPh_3 (16.79 g, 64 mmol) in dimethylformamide (40 cm^3) was heated to 50 °C with stirring under an atmosphere of dry N_2. The resulting blue suspension was treated with zinc dust (1.05 g, 16 mmol) to produce a red-brown suspension; after 0.5 h a solution of 6-bromo-2,2′-bipyridine (1.88 g, 8 mmol) in dimethylformamide (15 cm^3) was added, and the mixture stirred for 2.5 h. After this period the reaction mixture contained a dark green material in suspension and was evaporated to dryness *in vacuo*. The residue was boiled with water (250 cm^3) for 4 h, after which the mixture was filtered. The green filtrate was treated with $[NH_4][PF_6]$ (5.22 g, 32 mmol) and cooled, to give a green precipitate. This was washed with water (3 × 20 cm^3) and dried to yield a green solid (1.80 g). This solid was heated to reflux for 5 h with a solution of NaCN (3.92 g) in methanol–water (19:1, 40 cm^3) to yield a turbid yellow suspension. This was cooled, diluted with water (150 cm^3), and the precipitate collected by filtration. After washing with water (3 × 20 cm^3) and recrystallisation from toluene, 2,2′:6′,2″:6″,2‴-quaterpyridine was obtained as a white crystalline solid (0.53 g, 43%, m.p. 221.5—222.5° °C) (Found: C, 77.5; H, 4.4; N, 17.9. $C_{20}H_{14}N_4$ requires C, 77.4; H, 4.6; N, 18.1%). E.i. mass spectrum. m/z 310 (P^+). I.r. (Nujol): 1 590w, 1 578m, 1 567s, 1 560m, 1 446w, 1 427s, 1 269w, 1 109w, 1 077w, 991w, and 769s cm^{-1}.

From 6-*chloro*-2,2′-*bipyridine.* A solution of $[Ni(PPh_3)_2Cl_2]$ (9.81 g, 15 mmol) and PPh_3 (8.4 g, 32 mmol) in dimethylformamide (70 cm^3) was heated to 50 °C with stirring under an atmosphere of dry N_2 and treated with zinc dust (2.1 g, 30 mmol) to produce a red-brown suspension; after 0.5 h a solution of 6-chloro-2,2′-bipyridine (2.86 g, 15 mmol) in dimethylformamide (15 cm^3) was added and the mixture stirred for 3 h. The reaction mixture was then poured into aqueous ammonia solution (150 cm^3, 7.5%) and the green solution extracted with $CHCl_3$ (3 × 100 cm^3). The aqueous solution was treated with $[NH_4][PF_6]$ (9.60 g, 60 mmol) to give a green precipitate. This was worked up as above to give 2,2′:6′,2″:6″,2‴-quaterpyridine (0.63 g, 27%).

Preparation of $[NiL(MeCN)_2][PF_6]_2\cdot MeCN$.—The green hexafluorophosphate salt obtained after the addition of ammonium hexafluorophosphate to the reaction mixture was dissolved in acetonitrile and diethyl ether vapour allowed to diffuse into the green solution so obtained. After 24 h green-brown dichroic crystals had been obtained which were dried *in vacuo* for 12 h to yield $[NiL(MeCN)_2][PF_6]_2\cdot 0.5MeCN$ (Found: C, 79.8; H, 2.9; N, 12.0. $C_{25}H_{21.5}F_{12}N_{6.5}NiP_2$ requires C, 79.9; H, 2.9; N, 12.0%). F.a.b. mass spectrum: m/z 368 ($[NiL]^+$) and 513 $\{[NiL(PF_6)]^+\}$. I.r. (KBr): 2 174w, 1 599s, 1 579s, 1 565m, 1 490s, 1 466s, 1 417s, 835vs, 775s, and 561s cm^{-1}.

X-*Ray Structural Determination of* 2,2′:6′,2″:6″,2‴-*Quaterpyridine.*—Colourless plates of the ligand were obtained by recrystallisation from methanol.

Crystal data. $C_{20}H_{14}N_4$, colourless plates, M = 310.38, monoclinic, a = 6.348(1), b = 8.179(2), c = 14.894(3) Å, β = 100.15(1)°, U = 761 Å^3, $F(000)$ = 324, space group $P2_1/n$ (non-standard setting of no. 34), Z = 2, D_c = 1.35 g cm^{-3}, D_m not measured, Mo-K_α radiation (λ = 0.710 73 Å), μ(Mo-K_α) = 0.8 cm^{-1}, Nicolet R3mV diffractometer.

Data collection and processing. A crystal having overall dimensions 0.76 × 0.70 × 0.05 mm was mounted on a glass fibre and used for the structure determination. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. The ω—2θ technique was used to measure 6 868 reflections (1 764 unique) in the range $5 \leqslant 2\theta \leqslant 55°$. Three standard reflections remeasured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects. There were 1 288 unique reflections with $I \geqslant 1.5\sigma(I)$. The structure was solved in the space group $P2_1/n$.

Structural analysis and refinement. All non-hydrogen atoms were obtained from the direct methods output. Least-squares refinement followed by Fourier synthesis led to the development of peaks due to hydrogen atoms in the molecule. The appearance of these peaks allows the unequivocal assignment of the nitrogen atoms in the structure. Final refinement was based on anisotropic C and N atoms, with H atoms accompanying idealised positions and assigned a common isotropic thermal parameter (U_{iso} = 0.08 Å^2). The final least-squares cycle included 109 parameters (only one half of a molecule was crystallographically unique) for 1 288 variables, and gave R = 0.048, R' = 0.053 and did not shift any parameter by more than 0.02 times its estimated standard deviation. Calculations were performed using SHELXTL+ [11] on a Microvax II computer. Positional co-ordinates are given in Table 1 and molecular dimensions in Table 2.

X-*Ray Structural Determination of* $[NiL(MeCN)_2][PF_6]_2\cdot MeCN$.—Dichroic green-brown blocks were obtained by the diffusion of diethyl ether vapour into an acetonitrile solution.

Crystal data. $C_{26}H_{23}F_{12}N_7NiP_2$, green-brown dichroic

Table 3. Atomic co-ordinates ($\times 10^4$) for $[NiL(MeCN)_2][PF_6]_2 \cdot MeCN$

Atom	*x*	*y*	*z*
Ni	5 000	472(1)	2 500
N(1)	5 308(2)	−886(3)	3 499(2)
N(2)	5 417(2)	1 302(3)	3 976(2)
C(1)	5 197(2)	−1 948(3)	3 097(3)
C(2)	5 436(3)	−2 911(4)	3 762(4)
C(3)	5 804(3)	−2 728(5)	4 847(4)
C(4)	5 936(3)	−1 620(5)	5 273(4)
C(5)	5 666(2)	−694(4)	4 554(3)
C(6)	5 723(2)	561(4)	4 824(3)
C(7)	6 057(3)	974(5)	5 866(3)
C(8)	6 065(3)	2 140(5)	6 033(4)
C(9)	5 730(3)	2 886(5)	5 159(4)
C(10)	5 428(2)	2 442(4)	4 156(3)
P(1)	1 568(1)	418(1)	7 796(1)
F(1)	2 353(2)	659(4)	8 952(3)
F(2)	803(3)	205(4)	6 618(3)
F(3)	1 965(6)	1 154(16)	7 371(8)
F(4)	2 023(9)	−655(11)	7 778(11)
F(5)	1 290(6)	1 555(10)	7 928(15)
F(6)	1 377(6)	−327(12)	8 370(10)
F(3A)	1 449(12)	1 662(10)	7 329(8)
F(4A)	1 055(9)	731(19)	8 149(11)
F(5A)	1 432(10)	−929(9)	7 935(10)
F(6A)	1 856(9)	−4(17)	7 226(14)
N(3)	6 109(2)	662(3)	3 002(3)
C(11)	6 712(2)	891(4)	3 394(3)
C(12)	7 507(2)	1 199(5)	3 897(4)
N(4)	2 109(8)	3 344(10)	3 788(12)
C(13)	2 354(4)	2 872(6)	4 554(6)

Table 4. Selected bond lengths (Å) and bond angles (°) for $[NiL(MeCN)_2][PF_6]_2 \cdot MeCN$

Ni–N(1)	2.004(3)	Ni–N(2)	2.106(4)
Ni–N(3)	2.095(4)	Ni–N(1A)	2.004(3)
Ni–N(2A)	2.106(4)	Ni–N(3A)	2.095(4)
N(1)–Ni–N(2)	78.2(1)	N(1)–Ni–N(3)	92.1(1)
N(2)–Ni–N(3)	85.8(1)	N(1)–Ni–N(1A)	77.6(2)
N(2)–Ni–N(1A)	155.7(1)	N(3)–Ni–N(1A)	97.3(2)
N(1)–Ni–N(2A)	155.7(1)	N(2)–Ni–N(2A)	126.0(2)
N(3)–Ni–N(2A)	88.8(1)	N(1A)–Ni–N(2A)	78.2(1)
N(1)–Ni–N(3A)	97.3(2)	N(2)–Ni–N(3A)	88.8(1)
N(3)–Ni–N(3A)	168.0(2)	N(1A)–Ni–N(3A)	92.1(1)
N(2A)–Ni–N(3A)	85.8(1)	Ni–N(1)–C(1)	118.4(3)
Ni–N(1)–C(5)	119.2(3)	Ni–N(2)–C(10)	127.8(3)
Ni–N(2)–C(6)	113.5(3)		

blocks, $M = 782.21$, monoclinic, $a = 22.348(9)$, $b = 11.504(5)$, $c = 15.636(6)$ Å, $\beta = 128.41(2)°$, $U = 3\ 150$ Å^3, $F(000) = 1\ 576$, space group $C2/c$ (no. 15), $Z = 4$, $D_c = 1.65$ g cm^{-3}, D_m not measured, Mo-K_α radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-K_α) = 8.2 cm^{-1}, Nicolet R3mV diffractometer.

Data collection and processing. A crystal having overall dimensions 0.35 × 0.40 × 0.65 mm was mounted on in a glass capillary and used for the structure determination. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 25 reflections taken from a rotation photograph and centred by the diffractometer. The ω—2θ technique was used to measure 4 687 reflections (3 571 unique) in the range $5 \leqslant 2\theta \leqslant 55°$. Three standard reflections remeasured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects. There were 2 760 unique reflections with $I \geqslant 1.5\sigma(I)$. The structure was solved and refined in the space group $C2/c$.

Structural analysis and refinement. The asymmetric unit contains one half of the cation, one $[PF_6]^-$ anion, and half of a disordered MeCN solvent lattice molecule. The Ni sits on a two-fold rotation axis and was located by direct methods. Alternating cycles of least-squares refinement and difference Fourier synthesis led to the identification of all non-hydrogen atoms. The $[PF_6]^-$ anion is disordered such that four equatorial F atoms occupy two sets of positions. The occupancy of each set was initially refined, but ultimately fixed at 45%:55% in the final cycles. A disordered MeCN molecule was also located in the lattice. The non-hydrogen atoms were refined anisotropically. Only the H atoms of the oligopyridine ligand were included in the final stages of refinement, and then their positions were idealised and they were assigned a common isotropic thermal parameter ($U_{iso} = 0.08$ Å^2). The final least-squares cycle included 258 parameters for 2 760 variables, and gave $R = 0.066$, $R' = 0.069$ and did not shift any parameter by more than 0.02 times its estimated standard deviation. The final difference Fourier synthesis was featureless with the largest peak 0.48 Å^{-3}. Calculations were performed using SHELXTL+ [11] on a Microvax II computer. Positional co-ordinates are given in Table 3 and molecular dimensions in Table 4.

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

Results and Discussion

2,2′:6′,2″:6″,2‴-Quaterpyridine was first reported by Burstall [12] in 1938, although it is likely that the compound had been previously prepared in trace quantities from the reaction of pyridine with iron(III) chloride.[13] The ligand was variously prepared by the oxidative dehydrogenation of 2,2′-bipyridine with iodine, iron(III) chloride, or ruthenium trichloride or by Ullmann reactions of 6-bromo-2,2′-bipyridine, mixtures of 6,6′-dibromo-2,2′-bipyridine and 6-bromopyridine, or mixtures of 6-bromo-2,2′-bipyridine and 2-bromopyridine. The route of choice was the reaction of 6-bromo-2,2′-bipyridine with copper powder, which was reported to give yields of 30%. We have found this reaction to give very variable yields dependent upon the nature of the copper used and the precise history of the 6-bromo-2,2′-bipyridine. We have previously developed metal-directed synthetic routes for the preparation of 2,2′:6′,2″-terpyridine [7] and 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2′′′′′-sexipyridine [6] and applied these to the synthesis of 2,2′:6′,2″:6″,2‴-quaterpyridine.

We investigated the use of nickel(0) reagents in the coupling of 6-halogeno-2,2′-bipyridines. Our initial approach was to adopt methodology utilising catalytic amounts of $[Ni(PPh_3)_n]$ [generated *in situ* from nickel(II)] and an excess of zinc.[14] However, such reactions did not yield any of the desired 2,2′:6′,2″:6″,2‴-quaterpyridine, but merely resulted in the formation of green nickel(II) complexes. This is a general problem that we have experienced with the preparation of nitrogen donor ligands by this route, and is due to the preferential formation of the nickel(II) complex of the newly formed chelating ligand. We have circumvented this by the use of stoicheiometric amounts of the nickel(0) reagents, generated *in situ* by zinc reduction of $[Ni(PPh_3)_2Cl_2]$ or $[Ni(H_2O)_6]Cl_2$ in dimethylformamide in the presence of an excess of PPh_3. We have found that yields are similar with the two nickel(II) precursor complexes, but we tend to prefer the use of $[Ni(PPh_3)_2Cl_2]$. We have also investigated the dependence of the coupling reaction upon the 6-halogeno-2,2′-bipyridine which is used. Our starting material of choice is 6-chloro-2,2′-

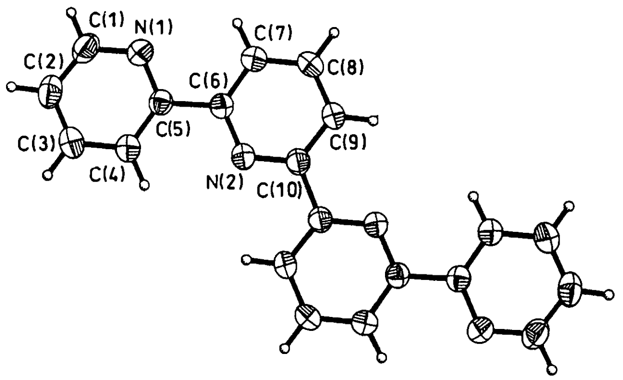


Figure 1. The crystal and molecular structure of 2,2′:6′,2″:6″,2‴-quaterpyridine showing the numbering scheme adopted

bipyridine, which is cheaper and easier to prepare than the 6-bromo analogue. However, yields from the coupling reaction using either of the nickel(II) precursor complexes were only in the 25—30% region, whereas yields in the range 40—45% were obtained with 6-bromo-2,2′-bipyridine. This reflects the usual pattern of reactivity observed in Ullmann reactions.[15]

The addition of zinc dust to a blue solution of $[Ni(PPh_3)_2Cl_2]$ or $[Ni(H_2O)_6]Cl_2$ in dimethylformamide containing PPh_3 results in the formation of a red-brown suspension of the nickel(0) complexes $[Ni(PPh_3)_n]$ (n = 3 or 4). Upon the addition of the 6-halogeno-2,2′-bipyridine the reaction mixture darkened, and after several hours a green suspension of a nickel(II) complex had been obtained. We have not fully characterised this species. Various methods of work-up may be employed, but the simplest involves removal of the dimethylformamide *in vacuo* followed by dissolution of the green residue in water. The green solution of nickel(II) complexes is treated with $[NH_4][PF_6]$ and the green precipitate collected. Treatment of this green solid with an excess of aqueous NaCN results in the formation of a suspension of 2,2′:6′,2″:6″,2‴-quaterpyridine in a yellow solution containing $[Ni(CN)_4]^{2-}$. Yields of the ligand were typically in the range of 40—45%.

Although the crystal structure of 2,2′-bipyridine has been determined,[16] the higher oligopyridines have been little investigated. The conformation of the free ligands has become of considerable interest to us in our studies of the binuclear double-helical complexes which they form.[3–5] In particular, we have been interested whether the higher oligopyridines adopt the planar transoid geometry exhibited by 2,2′-bipyridine.[16] Although the crystal structure of 2,2′:6′,2″-terpyridine does not appear to have been determined, we have described that of 4′-phenyl-2,2′:6′,2″-terpyridine, which is planar and exhibits two transoid interactions.[2] We have now determined the crystal and molecular structure of 2,2′:6′,2″:6″,2‴-quaterpyridine, and this is presented in Figure 1. The molecule is to all intents and purposes planar, with a mean deviation from the plane of 0.05 Å for all non-hydrogen atoms. The greatest individual deviation is seen for C(1) which lies 0.11 Å from the mean plane. The two terminal pyridyl rings are very slightly skewed with respect to the two central rings [torsion angle N(1)–C(5)–C(6)–C(7) 5.6°] whilst the two central rings are nearly coplanar [torsion angle N(2A)–C(10A)–C(10)–N(2) 0.4°]. All of the pyridyl rings adopt a transoid geometry with respect to the adjacent rings, as observed in 2,2′-bipyridine[16] and 4′-phenyl-2,2′:6′,2″-terpyridine.[2] This conformation is favoured by the minimising of the C(4)–C(7) and C(9)–C(9A) non-bonded interactions and also minimising nitrogen lone pair–lone pair and dipole–dipole interactions. The planar configuration maximises the delocalisation of the π-bonding system. All bond lengths and bond angles within the molecule closely resemble those observed in 2,2′-bipyridine.[16] The structure does not indicate the presence of any helical distortions in the free ligand. The packing of the 2,2′:6′,2″:6″,2‴-quaterpyridine molecules in the crystal lattice is presented in Figure 2. The molecules are arranged in stacks along the *a* axis, but the interplanar separation of 6.35 Å is such that there is no significant π–π interaction. This is in contrast to the short interplanar distances (3.5—3.7 Å) that we have observed in complexes of oligopyridines.[3–6]

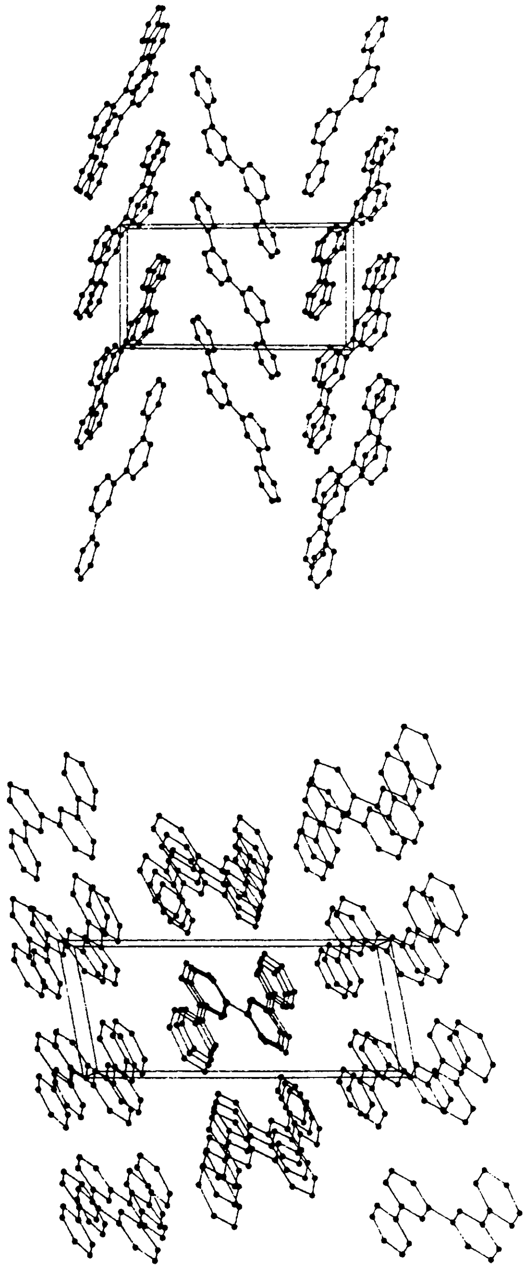


Figure 2. Crystal-packing diagrams showing the arrangement of 2,2′:6′,2″:6″,2‴-quaterpyridine molecules in the lattice along (*a*) the *a* axis and (*b*) the *b* axis

The ^1H n.m.r. correlation spectroscopy (COSY) spectra of a CD_3OD solution of $[H_2L]Cl_2$ [obtained from the reaction of L with either hydrochloric acid or chromium(III) chloride] are shown in Figure 3. The spectrum exhibits seven resonances, consistent with an average C_2 symmetry on the n.m.r. timescale. The COSY experiment allows unambiguous assignment of the spectrum (δ 9.05, H^6, d, J = 5.6; 8.19, H^5, dd, J = 5.6,

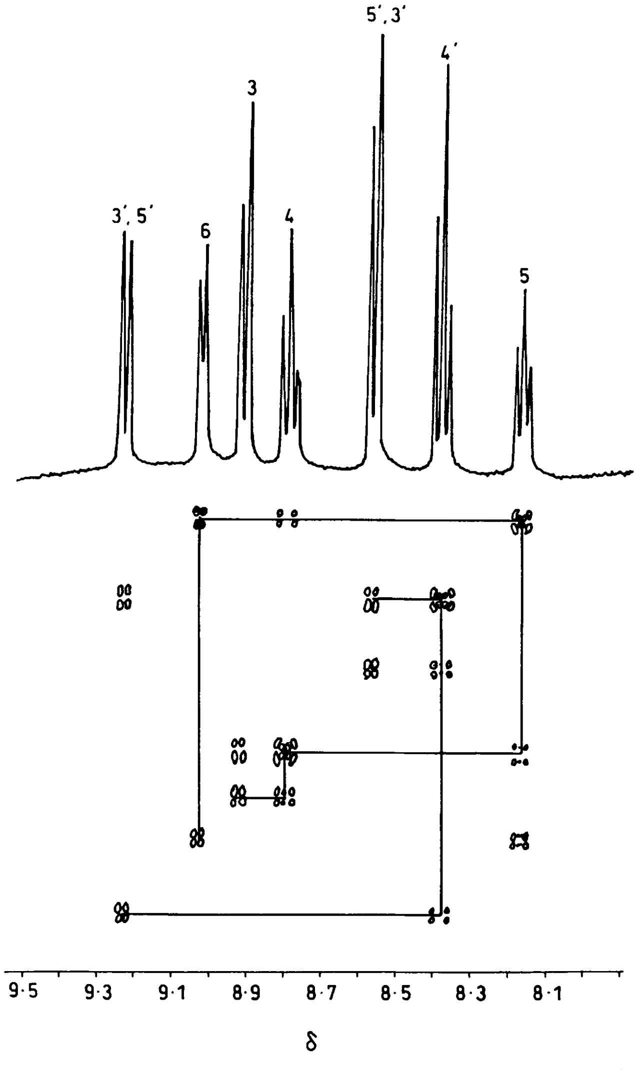


Figure 3. Double-quantum-filtered COSY and one-dimensional ^1H n.m.r. spectra of a CD_3OD solution of $[H_2L]Cl_2$

7.1; 8.81, H^4, t, J = 7.1; 8.94, H^3, d, J = 7.1; 9.25, $H^{3',5'}$, d, J = 7.1; 8.40, $H^{4'}$, t, J = 7.1; and 8.59, $H^{5',3'}$, d, J = 7.1 Hz). The unprotonated free ligand also exhibits seven resonances in its ^1H n.m.r. spectrum [$(CDCl_3)$ δ 8.70, H^6, d, J = 4.8; 7.34, H^5, dd, J = 4.8, 7.1; 7.87, H^4, t, J = 7.1; 8.47, H^3, d, J = 7.1; 8.66, $H^{3',5'}$, d, J = 7.1; 7.99, $H^{4'}$, t, J = 7.1; and 8.67, $H^{5',3'}$, d, J = 7. Hz]. In solution, it is most likely that the free ligand no longer adopts a planar configuration but favours an arrangement in which there is a twisting about the interannular bonds.

We have further investigated the green material which is initially precipitated from the reaction mixture by the addition of ammonium hexafluorophosphate. The f.a.b. mass spectrum of the crude green material exhibits peaks centred about m/z 368 ($[NiL]^+$) and 513 $\{[NiL(PF_6)]^+\}$. Microanalyses of the crude green product were inconsistent, but recrystallisation from hot water yielded material analysing as $[NiL(H_2O)_2][PF_6]_2$. Attempts to obtain good quality crystals from water were unsuccessful, but recrystallisation from acetonitrile by the diffusion of diethyl ether vapour into the solution resulted in the formation of X-ray quality crystals of a green-brown dichroic material analysing as $[NiL(MeCN)_2][PF_6]_2 \cdot 0.5MeCN$. This same complex may be obtained from the direct reaction of nickel(II) acetate with 2,2′:6′,2″:6″,2‴-quaterpyridine, followed

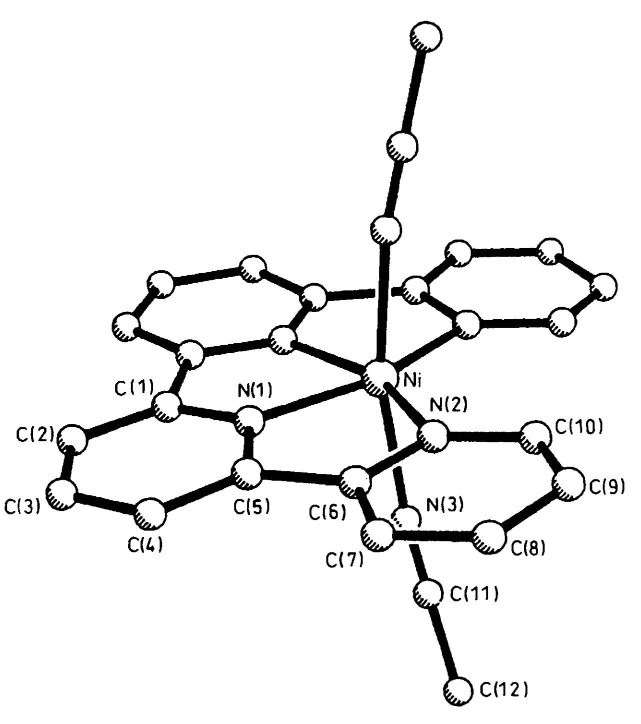
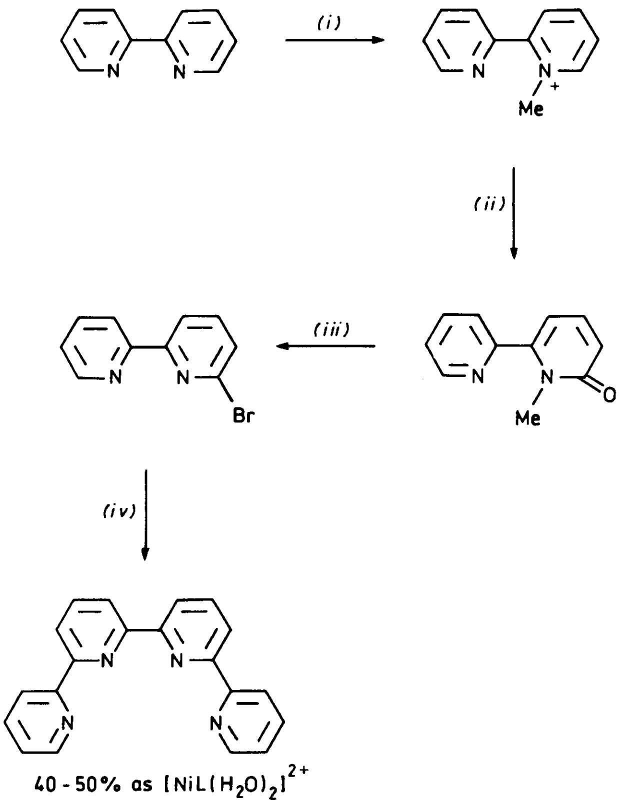


Figure 4. The crystal and molecular structure of the $[NiL(MeCN)_2]^{2+}$ cation in $[NiL(MeCN)_2][PF_6]_2 \cdot MeCN$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity

by treatment with ammonium hexafluorophosphate and recrystallisation from MeCN. This crystalline material also exhibited peaks centred about m/z 368 ($[NiL]^+$) and 513 $\{[NiL(PF_6)]^+\}$ in the f.a.b. mass spectrum. The complex is paramagnetic ($\mu_{eff.}$ 2.9, room temperature).

In order further to characterise this material we have determined its crystal and molecular structure. The structure of the $[NiL(MeCN)_2]^{2+}$ cation is presented in Figure 4, together with the numbering scheme adopted. The quadridentate ligand occupies the equatorial positions about a tetragonally distorted pseudo-octahedral nickel(II) centre, with the two axial sites occupied by the acetonitrile ligands. The bite of the 2,2′:6′,2″:6″,2‴-quaterpyridine ligand closely resembles that observed in 2,2′-bipyridine complexes [N(1)–Ni–N(2) 78.2(1), N(1)–Ni–N(1A) 77.6(2)°]. A consequence of this is a lengthening of the Ni–N(2) bonds [2.106(4) Å] with respect to the Ni–N(1) bonds [2.004(3) Å] to prevent undue strain across the transannular bond within the quadridentate ligand. As in the free ligand, the 2,2′:6′,2″:6″,2‴-quaterpyridine moiety is to all intents and purposes planar, with the mean deviation from the plane of all ligand non-hydrogen atoms being 0 09 Å and the greatest single deviation being 0.20 Å [C(9)]. Once again, this may be traced a slight twisting of the pyridyl rings, with the torsion angles N(1)–C(5)–C(6)–N(2) and N(1)–C(1)–C(1A)–N(1A) being 1.0 and 4.4° respectively. In contrast to the free ligand, the greatest skewing occurs between the two central pyridine rings rather than the central and the terminal rings. This distortion minimises non-bonded interactions between H(10) and H(10A). The distortion of the equatorial N_4 donor set results in a 'splaying out' of the quadridentate ligand, which is most simply observed in the angle N(2)–Ni–N(2A) of 126.0(2)°. This results in a co-ordination void which results in the two axial ligands 'falling' into the void, thus minimising electrostatic interactions between axial and equatorial Ni–N bonds. This is observed in the N(3)–Ni–N(3A) angle of 168.0(2)°. This pattern of bonding is reflected in the complexes $[CoL(H_2O)_2][NO_3]_2$,[17] $[CuL(H_2O)(NO_3)][NO_3] \cdot H_2O$,[17]



Scheme. (*i*) MeI; (*ii*) $[Fe(CN)_6]^{3-}$; (*iii*) PBr_3, $POBr_3$; (*iv*) $[Ni(PPh_3)_2Cl_2]$, PPh_3, dmf, Zn

and $[CoL(H_2O)(SO_3)][NO_3]\cdot H_2O$.[18] The complex $[NiL(MeCN)_2][PF_6]_2$ is electrochemically active, and the cyclic voltammogram of an acetonitrile solution ($[NBu^n{}_4][BF_4]$ supporting electrolyte, 100 mV s^{-1}) exhibits a reversible one-electron reduction ($E_a - E_p$ = 75 mV) *versus* an internal ferrocene–ferrocenium reference added at the end of the experiment ($E_a - E_p$ = 75 mV). The cyclic voltammogram also exhibits a number of other irreversible reduction processes between -1.5 and -1.9 V *vs* ferrocene–ferrocenium.

In conclusion, we have designed a convenient synthesis of 2,2′:6′,2″:6″,2‴-quaterpyridine *via* a nickel(II) complex. This synthetic approach is adaptable to substituted derivatives of 2,2′:6′,2″:6″,2‴-quaterpyridine. We have also demonstrated that 2,2′:6′,2″:6″,2‴-quaterpyridine (and presumably other linear oligopyridines) adopts a planar configuration with a transoid arrangement of adjacent rings, and have confirmed that $[NiLX_2]$ species possess an octahedral geometry, with the 2,2′:6′,2″:6″,2‴-quaterpyridine ligand occupying the four equatorial sites. We have no further interest in complexes of 2,2′:6′,2″:6″,2‴-quaterpyridine with first-row transition metals, but are currently investigating the interactions with second- and third-row transition elements and actinoids.

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