The Preparation and Co-ordination Chemistry of 2,2′:6′,2″-Terpyridine Macrocycles.† Part 3.[1] Transient Template Effects involving Dimethyltin(IV)

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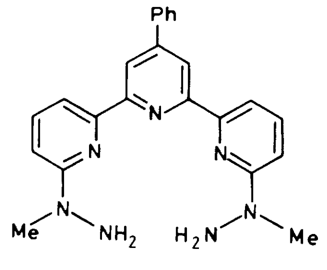
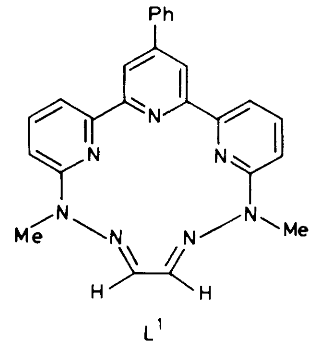
Complexes of a novel quinquedentate ligand L^1, which incorporates a 2,2′:6′,2″-terpyridine moiety, are prepared *via* template condensations about nickel(II) or manganese(II). The crystal and molecular structure of $[NiL^1(EtOH)_2][BF_4]_2$ shows the metal to be in a pentagonal-bipyramidal N_5O_2 environment. The free ligand L^1 may be obtained as its dication from template condensations in which there is a mismatch between the donor properties of the ligand and the acceptor properties of the metal ion. Thus $[H_2L^1][PF_6]_2$ may be isolated from the template condensation about Cr^{3+} or $[SnMe_2]^{2+}$. The crystal and molecular structure of $[H_2L^1][PF_6]_2$ is reported, and the origin of this novel template effect is discussed.

It is well established that transition metal ions[2] and Group 2A metal ions[3] may act as templates for the preparation of Schiff-base macrocyclic complexes. Typical experimental procedures have involved the reaction of a diamine with a dicarbonyl compound in the presence of an appropriate metal ion, when a macrocyclic complex is obtained. Such condensations have been applied to the synthesis of a wide range of Schiff-base macrocyclic complexes,[2-4] and provide the commonest synthetic procedure for the preparation of these compounds. It has been shown that complexes with Group 1B, 2A, 2B, and 4B metals are substitutionally labile, and may undergo facile transmetallation reactions on treatment with other metal ions.[3,5] This provides a method for the preparation of macrocyclic complexes of metal ions which do not act as templates for a particular condensation, but does not provide a completely general route, since it is not always possible to perform the template condensation in the presence of a suitable labile metal ion.

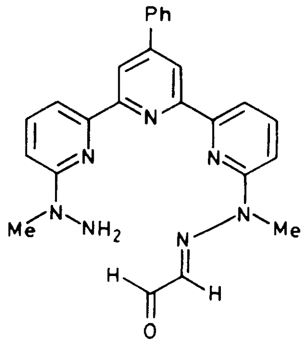
Our interest in the use of transition metal ions to modify the reactivity of a co-ordinated ligand led us to consider the effects of hole-size mismatch effects in macrocyclic chemistry. We have briefly described the condensation of 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine (L) with glyoxal in the presence of first-row transition metal ions (Scheme 1),[6] and a note has appeared discussing the electrochemistry and crystal structure of the macrocyclic complex $[NiL^1(EtOH)_2][BF_4]_2$.[1] In this paper we report the synthesis of the free macrocyclic ligand L^1 by a novel method involving the use of a *transient* template ion, the crystal and molecular structures of a salt of L^1 and its nickel(II) complex, and the preparation of a range of complexes of L^1 which are not available *via* template condensations.



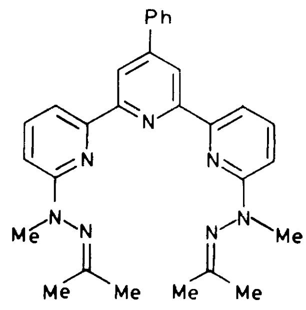
L



L^1



L^2



L^3

Results

Although complexes of 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine have been prepared with a wide range of transition metal and main-group metal ions,[6] the condensation depicted in Scheme 1 only proceeded in a satisfactory manner with nickel(II) or manganese(II) ions as the template. The only isolated products from the attempted template condensations using barium, calcium, strontium, cadmium, zinc, mercury(II), platinum(II), rhodium(III), ruthenium(III), iron(II), or copper(II) were 1 : 1 complexes with L.[7] In the case of cobalt(II), a product was obtained which was initially thought to be the desired $[CoL^1]^{2+}$ species, but the electrochemical behaviour was totally different from that of an authentic sample of $[CoL^1]^{2+}$ prepared from the free ligand (see below) and from that of the corresponding nickel(II) complex. The i.r. spectrum of the product exhibited strong N–H stretching frequencies and a band which may be assigned to a co-ordinated aldehyde stretching mode.[8] It is proposed that this compound has the pseudo-octahedral structure (1), although this structure must be regarded as speculative in the absence of crystallographic evidence. Attempts to convert this compound to the macrocyclic complex $[CoL^1]^{2+}$ were unsuccessful, and the compound was recovered unchanged after heating to reflux in ethanol, Bu^{n}OH, or Bu^{t}OH, or with benzene under Dean–Stark conditions. Attempts to dehydrate

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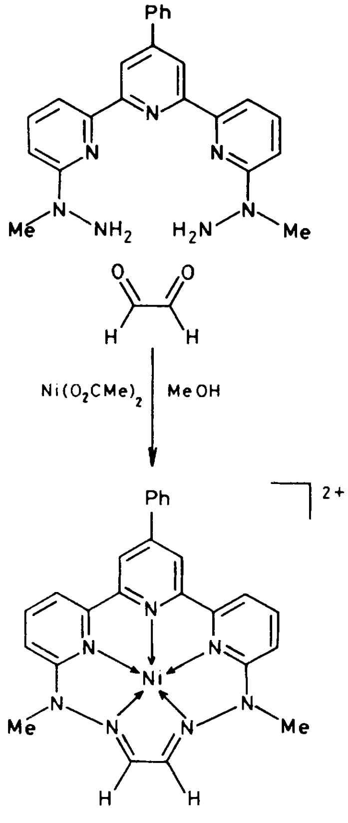
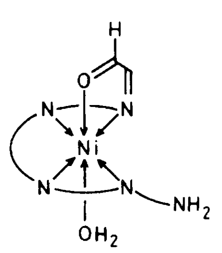
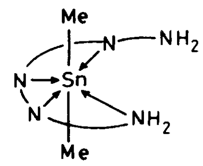
† *Supplementary data available* (No. SUP 56008, 9 pp.): thermal parameters, H-atom co-ordinates, bond angles involving hydrogen. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.



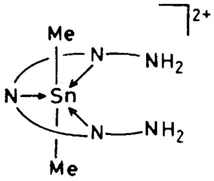
Scheme 1.



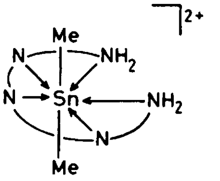
(1)



(2a)



(2b)



(2c)

the complex (1) by heating with 2,2-dimethoxypropane led to a transimination reaction, with the formation of the cobalt(II) complex of the dihydrazone ligand L^3.

The reaction of $[NiL]^{2+}$ with glyoxal in boiling methanol led to the quantitative formation of a deep yellow solution containing the complex ion $[NiL^1]^{2+}$. Treatment of this solution with $Na[BPh_4]$, $[NH_4][PF_6]$, or $[NBu^n_4][BF_4]$ led to the precipitation of the appropriate salt as a yellow solid. Recrystallisation of $[NiL^1(ROH)_2][BF_4]_2$ from ethanol gave *X*-ray quality crystals of $[NiL^1(EtOH)_2][BF_4]_2$ as yellow octahedra. Attempts to prepare macrocyclic complexes from the template condensation of $[NiL]^{2+}$ with butane-2,3-dione or benzil failed. 6,6″-Bis(α-methylhydrazino)-4′-phenyl-2,2′ : 6′,2″-terpyridine also reacted with glyoxal in the presence of a manganese(II) template, to form the complex ion $[MnL^1(ROH)_2]^{2+}$.

The dihydrazine ligand L reacted smoothly with $SnMe_2Cl_2$ in chlorobenzene, 1,2-dichloroethane, or chloroform to give a pale yellow salt. This salt was soluble in polar solvents (water, methanol, dimethyl sulphoxide, acetonitrile, or acetone) but was insoluble in chlorobenzene, chloroform, carbon tetrachloride, diethyl ether or tetrahydrofuran. On treatment of a methanolic solution of the salt with a methanolic solution of $Ag[ClO_4]$ *all* of the chloride was immediately precipitated as AgCl. The i.r. spectrum of the complex showed no indication of an Sn–Cl stretch in the region around 400 cm^{-1}.[8] Proton n.m.r. studies of a $(CD_3)_2SO$ solution of the complex indicated that the two methyl groups bonded to tin were equivalent on the n.m.r. time-scale, as were the two *N*-methyl groups and the two terminal pyridyl groups. The tin-bonded methyl groups exhibited low-intensity satellites due to coupling with the tin [^{117}Sn, 7.61%, $I = \frac{1}{2}$; ^{119}Sn, 8.58%, $I = \frac{1}{2}$; ^2J(Sn–H) = 111 (^{117}Sn), 116 Hz (^{119}Sn)].[9] These values are typical for a *trans* diaxial arrangement of the alkyl substituents.[10] Treatment of methanolic solutions of the salt with ammonium hexafluorophosphate led to the quantitative precipitation of the salts $[SnMe_2L][PF_6]Cl$ or $[SnMe_2L][PF_6]_2$, $(CD_3)_2SO$ solutions of which exhibited identical ^1H n.m.r. spectra to $(CD_3)_2SO$ solutions of the chloride. On the basis of these observations, we propose that the yellow complex is the ionic salt, $[SnMe_2L]Cl_2$, which possesses an octahedral, trigonal-bipyramidal, or pentagonal-bipyramidal structure, (2a)—(2c).

On heating a solution of $[SnMe_2L]Cl_2$ in methanol with glyoxal in the presence of a trace of acid, a cloudy orange suspension was obtained. Filtration through Celite, to remove the precipitated tin oxides, gave a clear orange filtrate, from which an orange solid was precipitated on addition of methanolic ammonium hexafluorophosphate. Elemental analysis of the precipitated solid indicated an empirical formula $C_{25}H_{21}F_{12}N_7P_2$, which is consistent with $[H_2L^1][PF_6]_2$ or a polymeric equivalent. The compound contained no tin, and was soluble in acetonitrile or Me_2SO. A 400-MHz ^1H n.m.r. spectrum of a $(CD_3)_2SO$ solution was consistent with the formulation $[H_2L^1][PF_6]_2$, and, in particular, no resonances attributable to an Sn–Me group were discernible. The mass spectrum of the salt showed a peak at *m/z* 419 which corresponds to the parent ion of the free macrocycle, L^1. We thus conclude that the product of the reaction is the free macrocycle L^1, as its bis(hexafluorophosphate) salt. When the reaction mixture was not treated with ammonium hexafluorophosphate, feathery needles of $[H_2L^1]Cl_2$ separated from the filtered solution. Recrystallisation of $[H_2L^1][PF_6]_2$ from methanol-acetonitrile led to *X*-ray quality red needles of the compound.

Treatment of a methanolic suspension of $[H_2L^1][PF_6]_2$ with a stoicheiometric quantity of nickel(II) acetate, manganese(II) acetate, or cobalt(II) acetate resulted in the formation of the appropriate macrocyclic complexes, isolated as the hexafluorophosphate salts, $[ML^1X_2][PF_6]_2$ (X = H_2O or MeOH). The yellow complex $[NiL^1(H_2O)_2][PF_6]_2$ and the pale yellow complex $[MnL^1(H_2O)_2][PF_6]_2$ were both identical in all respects to samples prepared *via* template condensations. The deep red cobalt(II) complex differed in a number of respects (i.r. spectra, electrochemistry, crystal form) from the previously isolated complex $[CoL^2][PF_6]_2$.

The reaction of 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′ : 6′,2″-terpyridine with glyoxal in either methanol, chloroform, or chlorobenzene in the presence of hydrochloric acid or hexafluorophosphoric acid also results in the formation of orange solutions, from which may be isolated the hexafluorophosphate salts. Although these materials analyse very similarly to the authentic compound $[H_2L^1][PF_6]_2$ obtained from the transient template reaction, they are very insoluble, exhibit broad i.r. spectra and only partially react with methanolic solutions of nickel(II) acetate. It was thus concluded that these products were partially polymeric. Weighing of the unreacted solid left after prolonged reaction with methanolic nickel(II) acetate at reflux indicated that the materials were probably about 50% polymeric and 50% macrocyclic in composition.

The reaction of trimethyltin(IV) chloride with L in chlorobenzene also proceeded smoothly to give a pale yellow solution from which a pale yellow solid was obtained upon the removal of the solvent *in vacuo*. Treatment of this solid with methanol followed by methanolic ammonium hexafluorophosphate led to demetallation, and the precipitation of $[H_2L][PF_6]_2$ as a hemihydrate.

The template condensation of L with glyoxal in the presence of methanolic $[Cr(H_2O)_6]Cl_3$ also proceeded smoothly, to give excellent yields of the free macrocycle.

Discussion

The template condensation of L with glyoxal in the presence of nickel(II) ions proceeds as expected to give the quinquedentate macrocyclic complex ion $[NiL^1(ROH)_2]^{2+}$. We have reported numerous related macrocyclic complexes containing 2,2′-bipyridine or 1,10-phenanthroline moieties,[11] and the formation of a pentagonal-bipyramidal N_5O_2-donor complex is fully in accord with our earlier results.[12] However, the isolation of the metal-free macrocyclic ligand as its dication from the chromium(III)- or dimethyltin(IV)-mediated reactions was unexpected, and requires further discussion. It is evident that the free macrocycle could arise from one of two limiting pathways, equations (i) and (ii) ($M^{n+} = Cr^{III}$ or $Sn^{IV}Me_2$).

$$[ML]^{n+} \rightleftharpoons L + M^{n+} \xrightleftharpoons{\text{glyoxal}} L^1 + M^{n+} \qquad \text{(i)}$$

$$[ML]^{n+} \xrightleftharpoons{\text{glyoxal}} [ML^1]^{n+} \rightleftharpoons L^1 + M^{n+} \qquad \text{(ii)}$$

Pathway (i) seems to be unlikely in this case, as L^1 is not formed in such high yield in the metal-free condensation of L with glyoxal, in which a considerable amount of polymer is formed. We are thus left with pathway (ii), in which some mismatch in the donor properties of the ligand and the acceptor properties of the metal ion results in an increased lability of the macrocyclic complex. If we consider the dimethyltin(IV) example, the complex $[SnMe_2L]Cl_2$ may be isolated, and is recovered unchanged from hot methanol solution. This indicates that there is no inherent mismatch between the dimethyltin(IV) ion and a planar N_5-donor set in O-donor solvents. We have recently determined the crystal and molecular structure of the complex $[SnMe_2L][PF_6]Cl$, and have shown it to possess the expected pentagonal-bipyramidal N_5C_2-donor set, with the five nitrogen atoms occupying the equatorial plane.[13] The mismatch must thus arise from the particular N_5-donor set in the macrocycle, L^1, such that the enhanced lability of the $[SnMe_2L^1]^{2+}$ complex ion renders it both thermodynamically and kinetically unstable with respect to L^1 and $[SnMe_2]^{2+}$ (and so ultimately to SnO_2). We consider that this enhanced lability of the dimethyltin(IV) complex arises from the reduction in hole size which occurs on passing from the open-chain quinquedentate ligand, L, to the macrocyclic ligand, L^1.

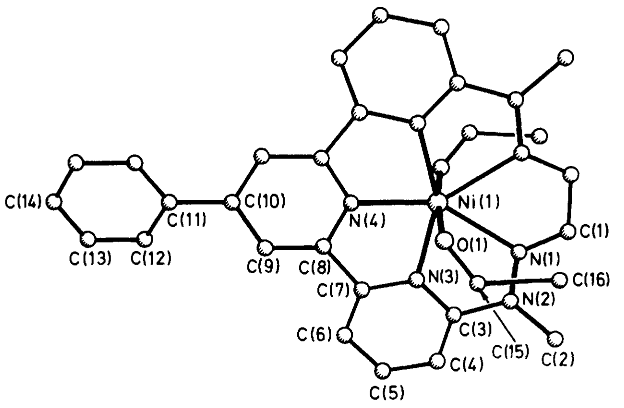


Figure 1. The molecular structure of the cation $[NiL^1(EtOH)_2]^{2+}$, showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity

The hole size of the macrocyclic ligand L^1 (as defined by the radius of the best-fit circle described through the five nitrogen donor atoms) is determined to be 2.12 Å for the free macrocycle and 2.10 Å for the nickel(II) complex. In contrast, the hole size for the open-chain ligand, L, as determined from the crystal structure analysis of $[SnMe_2L][PF_6]Cl$, is 2.32 Å, which is considerably larger than that of the macrocycle. The reduction in hole size upon cyclisation may be traced to the drawing together of the terminal $-NH_2$ nitrogen atoms, with a reduction in the non-bonded N–N distance of 0.62 Å, from 3.22 to 2.60 Å. The net effect is to impose an N_5-donor set on the metal ion which would require extremely short Sn–N bonds. The presence of the axial methyl groups prevents the metal atom from moving out of the equatorial plane, with resultant lengthening of the Sn–N bonds. Thus, whilst the ultimate origin of this transient template effect is thermodynamic (the formation of insoluble tin oxides), the local origin is kinetic, in the enhanced lability of the dimethyltin(IV) macrocyclic complex arising from a hole-size mismatch.

In the case of the chromium-mediated reaction, the origin of the transient template effect is not so readily determined, although it is undoubtedly thermodynamic in origin (*i.e.* an octahedral O_6 environment is thermodynamically more favourable than a planar pentagonal N_5 or pentagonal-bipyrimidal N_5O_2 environment). This behaviour has been observed in the template synthesis of free ligands from the reaction of 3-ethoxyacrylaldehyde with $NC(H_2N)C{=}C(NH_2)CN$ in the presence of chromium(III) sulphate [14] and in the preparation of a range of quinquedentate Schiff-base macrocycles incorporating 2,2′-bipyridine or 1,10-phenanthroline,[15] and we are presently undertaking a systematic study of the role of small, highly polarising cations in template syntheses.

Structure of $[NiL^1(EtOH)_2][BF_4]_2$.—The discrete $[NiL^1(EtOH)_2]^{2+}$ cation lies on a crystallographic two-fold axis which passes through the atoms N(1), N(4), C(10), C(11), and C(14). The cation geometry is illustrated in Figure 1, along with the numbering scheme adopted. The hydrogen atoms have been omitted for clarity. The final fractional atomic co-ordinates are presented in Table 1. Associated bond lengths, bond angles, and details of least-squares planes are given in Tables 2—4 respectively. The *X*-ray analysis confirms the presence of the seven-co-ordinate pentagonal-bipyramidal nickel(II) centre. The N_5-donor set of atoms which define vertices of the equatorial plane are coplanar (maximum deviation from the least-squares plane 0.01 Å) and the nickel atom is located

Table 1. Atomic co-ordinates ($\times 10^4$) for $[NiL^1(EtOH)_2][BF_4]_2$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	0	2 439(1)	2 500	C(10)	0	−320(3)	2 500
C(1)	−257(3)	4 215(2)	1 945(3)	C(11)	0	−1 180(3)	2 500
N(1)	−470(2)	3 551(2)	1 526(3)	C(12)	−593(8)	−1 587(2)	1 718(4)
N(2)	−932(2)	3 450(2)	511(3)	C(13)	−600(4)	−2 388(3)	1 720(5)
C(2)	−1 129(4)	4 094(3)	−249(4)	C(14)	0	−2 786(4)	2 500
N(3)	−730(2)	2 161(2)	952(4)	C(15)	1 613(8)	2 924(7)	1 159(9)
C(3)	−1 096(3)	2 680(2)	209(4)	C(16)	1 868(6)	3 939(5)	1 242(7)
C(4)	−1 621(3)	2 458(2)	−790(4)	O(1)	1 281(3)	2 500(3)	1 877(3)
C(5)	−1 752(3)	1 689(2)	−993(4)	B(1)	−2 380(5)	5 715(3)	1 552(6)
C(6)	−1 374(3)	1 151(2)	−242(4)	F(1)	−2 516(3)	6 293(2)	2 267(3)
C(7)	−865(3)	1 403(2)	734(3)	F(2)	−1 505(3)	5 815(2)	1 212(4)
N(4)	0	1 279(2)	2 500	F(3)	−2 400(3)	5 018(2)	2 043(3)
C(8)	−418(3)	892(2)	1 614(3)	F(4)	−3 072(4)	5 757(2)	709(3)
C(9)	−425(3)	100(2)	1 586(3)				

Table 2. Selected bond lengths (Å) for $[NiL^1(EtOH)_2][BF_4]_2$ *

Ni(1)–N(1)	2.324(3)	C(8)–C(9)	1.377(5)	Ni(1)–N(3)	2.104(3)	C(6)–C(7)	1.389(6)
Ni(1)–N(4)	2.015(4)	C(9)–C(10)	1.409(5)	Ni(1)–O(1)	2.084(4)	N(4)–C(8)	1.350(4)
C(1)–C(1′)	1.463(8)	C(11)–C(12)	1.390(5)	C(1)–N(1)	1.284(5)	C(10)–C(11)	1.494(8)
N(2)–C(2)	1.462(6)	C(13)–C(14)	1.382(6)	N(1)–N(2)	1.345(5)	C(12)–C(13)	1.391(6)
N(3)–C(3)	1.341(5)	C(15)–C(16)	1.800(15)	N(2)–C(3)	1.399(5)	C(15)–O(1)	1.293(12)
C(3)–C(4)	1.406(6)	B(1)–F(2)	1.384(9)	N(3)–C(7)	1.351(5)	B(1)–F(1)	1.369(7)
C(5)–C(6)	1.374(6)	B(1)–F(4)	1.333(8)	C(4)–C(5)	1.366(6)	B(1)–F(3)	1.357(7)
C(7)–C(8)	1.477(5)						

* The primed atoms are related to the unprimed atoms by the symmetry operation $-x, y, \frac{1}{2} - z$.

Table 3. Selected bond angles (°) for $[NiL^1(EtOH)_2][BF_4]_2$ *

N(1)–Ni(1)–N(3)	69.5(1)	C(3)–C(4)–C(5)	118.1(4)	N(1)–Ni(1)–N(4)	146.2(1)	C(4)–C(5)–C(6)	120.7(4)
N(1)–Ni(1)–N(3′)	137.1(1)	C(5)–C(6)–C(7)	118.8(4)	N(1)–Ni(1)–N(1′)	67.7(2)	N(3)–C(7)–C(6)	121.5(4)
N(1)–Ni(1)–O(1)	88.3(1)	N(3)–C(7)–C(8)	113.8(3)	N(1)–Ni(1)–O(1′)	86.8(1)	C(6)–C(7)–C(8)	124.8(4)
N(3)–Ni(1)–N(4)	76.7(1)	Ni(1)–N(4)–C(8)	119.8(2)	N(3)–Ni(1)–N(3′)	153.4(2)	C(7)–C(8)–N(4)	113.3(3)
N(3)–Ni(1)–N(1′)	137.1(1)	C(8)–N(4)–C(8′)	120.4(4)	N(3)–Ni(1)–O(1)	91.4(1)	N(4)–C(8)–C(9)	121.3(4)
N(3)–Ni(1)–O(1′)	90.0(1)	C(7)–C(8)–C(9)	125.5(4)	N(4)–Ni(1)–N(3′)	76.7(1)	C(9)–C(10)–C(9′)	117.7(5)
N(4)–Ni(1)–N(1′)	146.2(1)	C(8)–C(9)–C(10)	119.7(4)	N(4)–Ni(1)–O(1)	92.9(1)	C(9)–C(10)–C(11)	121.2(2)
O(1)–Ni(1)–O(1′)	174.2(2)	C(10)–C(11)–C(12)	120.5(3)	N(1)–C(1)–C(1′)	116.0(2)	C(11)–C(12)–C(13)	120.5(4)
Ni(1)–N(1)–C(1)	120.2(3)	C(12)–C(11)–C(12′)	118.9(5)	Ni(1)–N(1)–N(2)	116.3(2)	C(13)–C(14)–C(13′)	120.0(6)
C(1)–N(1)–N(2)	123.5(3)	C(12)–C(13)–C(14)	120.0(5)	N(1)–N(2)–C(2)	121.7(3)	O(1)–C(15)–C(16)	127.4(9)
N(1)–N(2)–C(3)	114.6(3)	Ni(1)–O(1)–C(15)	135.1(5)	C(2)–N(2)–C(3)	123.3(3)	F(1)–B(1)–F(2)	108.6(5)
Ni(1)–N(3)–C(3)	124.4(3)	F(1)–B(1)–F(3)	110.6(6)	Ni(1)–N(3)–C(7)	116.4(3)	F(1)–B(1)–F(4)	108.0(5)
C(3)–N(3)–C(7)	119.2(3)	F(2)–B(1)–F(3)	109.0(5)	N(2)–C(3)–N(3)	115.2(3)	F(2)–B(1)–F(4)	110.9(6)
N(2)–C(3)–C(4)	123.1(4)	F(3)–B(1)–F(4)	109.9(5)	N(3)–C(3)–C(4)	121.8(4)		

* The primed atoms are related to the unprimed atoms by the symmetry operation $-x, y, \frac{1}{2} - z$.

in the cavity of the macrocycle. The co-ordinated ethanol molecules occupy the axial sites.

The nickel atom is coplanar with the N_5 least-squares plane and the O(1)–Ni(1)–O(1′) bond angle is 174.2(2)°, and so the geometry about the nickel atom may be regarded as a slightly distorted pentagonal bipyramid. Interatomic distances indicate that the tetrafluoroborate anions are not co-ordinated. The unco-ordinated nitrogen atoms N(2) and N(2′) are planar sp^2 hybridised (the sum of the bond angles around these atoms is 359.6°) and deviate from the least-squares plane by 0.015 Å.

The Ni–N distances fall in the range 2.01—2.23 Å; the long Ni–N(imine) [2.324(3) Å] and the shorter Ni–N(terminal pyridine) [2.104(3) Å] and Ni–N(central pyridine) [2.015(4) Å] are consistent with the bond lengths found in other related nickel(II) macrocyclic complexes.[6] Angles subtended by adjacent nitrogen-donor atoms at the nickel(II) centre are in the range 68—77°, and the bond angle of 76.7° formed by adjacent nitrogen donors of the terpyridyl moiety is consistent with the short Ni–N(4) bond.

The phenyl ring makes an angle of 14.9° with the plane of the central pyridine ring, whilst the pyridine rings are inclined at an angle of 3°. The separation between H(6) and H(9) is 2.174 Å, whilst the separation between H(9) and H(12) of 1.958 Å is significantly shorter than the sum of the van der Waals radii, and possibly represents a compromise between a coplanar arrangement of the phenyl ring giving maximum conjugation, and a perpendicular arrangement minimising the H ··· H van der Waals interactions.

Structure of $[H_2L^1][PF_6]_2$.—The 15 atoms that make up the periphery of the macrocyclic ring (Figure 2) are essentially coplanar (maximum deviation from the least-squares plane 0.04 Å), whilst the deviation of any nitrogen from the N_7 least-squares plane is not more than 0.03 Å. The sums of bond angles around N(2) and N(6) are 359.9 and 359.5° respectively, indicating that they are sp^2 hybridised.

The N(1)–C(1) and N(7)–C(25) bond lengths [1.284(18) and 1.321(18) Å respectively] are identical within the e.s.d.s and indicate multiple bond order, whilst the N(1)–N(2) [1.398(16)

Table 4. Least-squares planes for $[NiL^1(EtOH)_2][BF_4]_2$. The equation of each plane is given in direct space by $Px + Qy + Rz = S$, where x, y, and z are the atomic fractional co-ordinates

Plane	Atoms	*P*	*Q*	*R*	*S*
1	N(1)—N(4)	13.300	0.082	−6.192	−1.537
	[Ni(1), 0.010; N(1), 0.000; N(2), 0.016; N(3), 0.000; N(4), 0.000]				
2	N(3), C(3)—C(7)	12.951	−0.387	−6.703	−1.666
	[N(3), −0.002; C(3), 0.002; C(4), 0.001; C(5), −0.003; C(6), 0.004; C(7), 0.004]				
3	N(4), C(8)—C(10)	13.229	0.020	−6.194	−1.548
	[N(4), 0.002; C(8), −0.003; C(9), 0.003; C(10), −0.0016]				
4	C(11)—C(14)	−11.401	0.010	8.744	2.184
	[C(11), 0.001; C(12), −0.002; C(13), 0.002; C(14), −0.001]				

Angles between planes (°): 1—2, 3.2; 1—3, 0.2; 1—4, 15.0; 2—3, 3.1; 2—4, 12.2; 3—4, 14.9

Table 5. Atomic co-ordinates (× 10^4) for $[H_2L^1][PF_6]_2$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
C(1)	8 934(17)	198(11)	6 876(5)	C(21)	10 710(17)	3 516(11)	4 959(5)
N(1)	8 248(14)	−303(9)	6 514(4)	C(22)	10 967(17)	3 456(10)	5 448(5)
N(2)	7 350(15)	−1 233(9)	6 579(4)	C(23)	10 391(15)	2 592(10)	5 687(4)
C(2)	7 162(18)	−1 708(11)	7 055(5)	N(6)	10 534(14)	2 384(9)	6 181(4)
N(3)	7 012(12)	−1 047(8)	5 751(3)	C(24)	11 199(18)	3 175(11)	6 542(5)
C(3)	6 729(16)	−1 656(10)	6 147(5)	N(7)	9 815(15)	1 465(9)	6 311(4)
C(4)	5 919(17)	−2 588(11)	6 093(5)	C(25)	9 753(18)	1 170(12)	6 773(5)
C(5)	5 316(18)	−2 890(12)	5 644(5)	P(1)	8 878(5)	3 653(3)	3 252(1)
C(6)	5 578(17)	−2 242(11)	5 218(5)	F(1)	10 481(11)	4 101(8)	3 044(4)
C(7)	6 446(15)	−1 317(10)	5 282(4)	F(2)	9 818(12)	2 661(7)	3 498(3)
N(4)	7 792(12)	266(8)	5 068(3)	F(3)	9 129(13)	4 300(6)	3 743(3)
C(8)	6 942(15)	−573(9)	4 911(4)	F(4)	7 933(12)	4 647(6)	3 010(3)
C(9)	6 437(16)	−741(10)	4 419(4)	F(5)	8 624(12)	2 988(6)	2 770(3)
C(10)	6 989(15)	28(9)	4 072(4)	F(6)	7 260(12)	3 191(7)	3 454(4)
C(11)	7 902(15)	884(9)	4 236(4)	P(2)	3 892(5)	−3 871(3)	3 989(2)
C(12)	8 263(15)	971(10)	4 742(4)	F(7)	4 376(23)	−4 346(12)	4 506(3)
C(13)	6 505(16)	−121(10)	3 535(4)	F(7′)	5 392(27)	−4 251(25)	4 319(10)
C(14)	5 515(16)	−932(10)	3 366(4)	F(8)	3 342(15)	−2 758(5)	4 183(4)
C(15)	5 181(18)	−1 074(11)	2 876(5)	F(9)	5 546(10)	−3 241(11)	4 013(6)
C(16)	5 769(18)	−428(11)	2 542(5)	F(9′)	3 096(38)	−3 823(26)	4 501(6)
C(17)	6 784(18)	419(12)	2 690(5)	F(10)	4 410(15)	−4 946(5)	3 750(4)
C(18)	7 140(17)	558(11)	3 185(5)	F(11)	2 232(11)	−4 454(11)	4 069(6)
N(5)	9 544(13)	1 800(8)	5 439(3)	F(11′)	4 691(40)	−3 599(25)	3 492(6)
C(19)	9 221(15)	1 888(9)	4 934(4)	F(12)	3 304(23)	−3 398(12)	3 481(3)
C(20)	9 803(16)	2 740(10)	4 692(5)	F(12′)	2 250(22)	−3 777(26)	3 677(11)

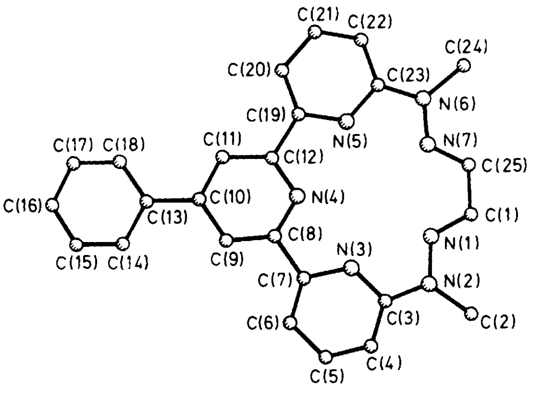


Figure 2. The molecular structure of the cation $[H_2L^1]^{2+}$, showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity

Å] and N(6)–N(7) [1.352(16) Å] distances suggest that there is some overlap of the filled *p* orbitals on N(2) or N(6) with the π orbitals of the imine moiety, The C(1)–C(25) distance [1.430(20) Å] is indicative of a carbon–carbon bond order of greater than one, and the distances between the other atoms of the periphery (excluding the aromatic ring bond distances) tend to suggest that the macrocycle represents a delocalised system.

The terpyridine moiety of the macrocycle is subject to van der Waals interactions between neighbouring hydrogen atoms: in particular the non-bonded distances associated with H(9) are 2.089 Å to H(6) and 1.933 Å to H(14), and for H(11) the distances are 1.905 Å to H(18) and 2.152 Å to H(20). The last interaction would be greater but for the twisting of the phenyl ring so as to minimise steric interactions. This accounts for the observed dihedral angle of 5.7° between the phenyl group and the central pyridine ring. The methyl groups are also subject to van der Waals interactions, which are minimised by the deviation of the methyl groups from the least-squares N_7 plane. Hole-size calculations based on the circle described by the five donor atoms show no significant differences between the two structures, 2.12 Å for the free macrocycle and 2.10 Å for the nickel(II) complex.

Experimental

Infrared spectra were recorded as Nujol mulls supported between potassium bromide discs using Perkin-Elmer 257 or 457 spectrometers, over the range 400—4 000 cm⁻¹. ^1H N.m.r. spectra were recorded using Varian CFT-20, Bruker

Table 6. Bond lengths (Å) for $[H_2L^1][PF_6]_2$

C(1)–N(1)	1.284(18)	N(5)–C(19)	1.400(15)	C(1)–C(25)	1.430(20)	N(5)–C(23)	1.378(16)
N(1)–N(2)	1.398(16)	C(19)–C(20)	1.358(18)	N(2)–C(2)	1.446(17)	C(20)–C(21)	1.412(18)
N(2)–C(3)	1.374(16)	C(21)–C(22)	1.347(18)	N(3)–C(3)	1.354(15)	C(22)–C(23)	1.364(18)
N(3)–C(7)	1.386(14)	C(23)–N(6)	1.374(16)	C(3)–C(4)	1.354(19)	N(6)–C(24)	1.490(17)
C(4)–C(5)	1.360(19)	N(6)–N(7)	1.352(16)	C(5)–C(6)	1.444(20)	N(7)–C(25)	1.321(18)
C(6)–C(7)	1.373(18)	P(1)–F(1)	1.559(10)	C(7)–C(8)	1.452(17)	P(1)–F(2)	1.601(9)
N(4)–C(8)	1.327(15)	P(1)–F(3)	1.577(8)	N(4)–C(12)	1.328(15)	P(1)–F(4)	1.601(9)
C(8)–C(9)	1.407(16)	P(1)–F(5)	1.568(8)	C(9)–C(10)	1.441(17)	P(1)–F(6)	1.569(11)
C(10)–C(11)	1.377(17)	P(2)–F(7)	1.570(11)	C(10)–C(13)	1.516(16)	P(2)–F(7′)	1.570(25)
C(11)–C(12)	1.407(16)	P(2)–F(8)	1.570(9)	C(12)–C(19)	1.481(17)	P(2)–F(9)	1.570(11)
C(13)–C(14)	1.374(18)	P(2)–F(9′)	1.570(20)	C(13)–C(18)	1.398(18)	P(2)–F(10)	1.569(9)
C(14)–C(15)	1.368(18)	P(2)–F(11)	1.570(11)	C(15)–C(16)	1.328(20)	P(2)–F(11′)	1.570(23)
C(16)–C(17)	1.403(20)	P(2)–F(12)	1.570(11)	C(17)–C(18)	1.385(19)	P(2)–F(12′)	1.570(22)

Table 7. Bond angles (°) for $[H_2L^1][PF_6]_2$

N(1)–C(1)–C(25)	117.6(13)	C(22)–C(23)–N(6)	127.3(12)	C(1)–N(1)–N(2)	122.0(11)	C(23)–N(6)–C(24)	122.5(11)
N(1)–N(2)–C(2)	122.4(10)	C(23)–N(6)–N(7)	113.6(10)	N(1)–N(2)–C(3)	113.2(10)	C(24)–N(6)–N(7)	123.4(10)
C(2)–N(2)–C(3)	124.3(11)	N(6)–N(7)–C(25)	121.8(11)	C(3)–N(3)–C(7)	122.6(10)	C(1)–C(25)–N(7)	117.8(13)
N(2)–C(3)–N(3)	113.5(11)	F(1)–P(1)–F(2)	92.1(5)	N(2)–C(3)–C(4)	126.3(12)	F(1)–P(1)–F(3)	92.3(6)
N(3)–C(3)–C(4)	120.2(11)	F(1)–P(1)–F(4)	88.1(5)	C(3)–C(4)–C(5)	119.9(13)	F(1)–P(1)–F(5)	88.4(5)
C(4)–C(5)–C(6)	120.7(13)	F(1)–P(1)–F(6)	179.1(6)	C(5)–C(6)–C(7)	118.0(12)	F(2)–P(1)–F(3)	90.1(5)
N(3)–C(7)–C(6)	118.6(11)	F(2)–P(1)–F(4)	179.6(4)	N(3)–C(7)–C(8)	113.3(10)	F(2)–P(1)–F(5)	89.0(5)
C(6)–C(7)–C(8)	128.0(11)	F(2)–P(1)–F(6)	87.8(5)	C(8)–N(4)–C(12)	118.5(9)	F(3)–P(1)–F(4)	89.5(5)
C(7)–C(8)–N(4)	116.4(10)	F(3)–P(1)–F(5)	178.9(5)	C(7)–C(8)–C(9)	119.5(11)	F(3)–P(1)–F(6)	88.6(6)
N(4)–C(8)–C(9)	124.0(11)	F(4)–P(1)–F(5)	91.4(4)	C(8)–C(9)–C(10)	116.2(11)	F(4)–P(1)–F(6)	91.9(5)
C(9)–C(10)–C(11)	119.5(10)	F(5)–P(1)–F(6)	90.7(6)	C(9)–C(10)–C(13)	118.6(10)	F(7)–P(2)–F(8)	95.9(7)
C(11)–C(10)–C(13)	122.0(11)	F(7)–P(2)–F(9)	88.2(9)	C(10)–C(11)–C(12)	118.1(11)	F(7)–P(2)–F(10)	89.0(7)
N(4)–C(12)–C(11)	123.6(11)	F(7)–P(2)–F(11)	83.4(9)	N(4)–C(12)–C(19)	116.5(10)	F(7)–P(2)–F(12)	176.7(10)
C(11)–C(12)–C(19)	119.9(11)	F(7′)–P(2)–F(9′)	81.0(14)	C(10)–C(13)–C(14)	123.0(11)	F(7′)–P(2)–F(11′)	102.7(15)
C(10)–C(13)–C(18)	119.8(11)	F(7′)–P(2)–F(12′)	166.0(16)	C(14)–C(13)–C(18)	117.1(11)	F(8)–P(2)–F(9)	78.2(7)
C(13)–C(14)–C(15)	121.2(12)	F(8)–P(2)–F(10)	175.1(6)	C(14)–C(15)–C(16)	122.0(13)	F(8)–P(2)–F(11)	96.2(7)
C(15)–C(16)–C(17)	119.7(13)	F(8)–P(2)–F(12)	83.0(7)	C(16)–C(17)–C(18)	118.5(13)	F(9)–P(2)–F(10)	101.8(7)
C(13)–C(18)–C(17)	121.5(12)	F(9)–P(2)–F(11)	169.4(8)	C(19)–N(5)–C(23)	119.9(10)	F(9)–P(2)–F(12)	94.5(9)
C(12)–C(19)–N(5)	111.4(10)	F(9′)–P(2)–F(11′)	165.2(17)	C(12)–C(19)–C(20)	129.4(11)	F(9′)–P(2)–F(12′)	96.0(14)
N(5)–C(19)–C(20)	119.2(11)	F(10)–P(2)–F(11)	84.6(7)	C(19)–C(20)–C(21)	118.8(12)	F(10)–P(2)–F(12)	92.1(7)
C(20)–C(21)–C(22)	122.1(13)	F(11)–P(2)–F(12)	93.7(9)	C(21)–C(22)–C(23)	118.6(12)	F(11′)–P(2)–F(12′)	83.7(15)
N(5)–C(23)–C(22)	121.2(11)			N(5)–C(23)–N(6)	111.5(11)		

Table 8. Least-squares planes for $[H_2L^1][PF_6]_2$. The equation for each plane is given in direct space by $Px + Qy + Rz = S$, where x, y and z are the atomic fractional co-ordinates

Plane	Atoms	P	Q	R	S
1	N(1)—N(7)	6.895	−6.602	−4.585	2.884
	[N(1), 0.017; N(2), −0.019; N(3), 0.005; N(4), −0.011; N(5), 0.014; N(6), −0.029; N(7), 0.022]				
2	N(3), C(3)—C(7)	7.052	−6.154	−4.952	2.736
	[C(3), −0.015; C(4), 0.014; C(5), −0.003; C(6), −0.006; C(7), 0.005; N(3), 0.006]				
3	N(4), C(8)—C(12)	6.932	−6.561	−4.128	3.142
	[C(8), 0.019; C(9), −0.017; C(10), 0.004; C(11), 0.008; C(12), −0.008; N(4), −0.006]				
4	N(5), C(19)—C(23)	7.033	−6.188	−5.063	2.829
	[N(5), 0.016; C(19), −0.011; C(20), −0.006; C(21), 0.018; C(22), −0.012; C(23), −0.005]				
5	C(13)—C(18)	6.592	−7.449	−2.552	3.475
	[C(13), 0.001; C(14), −0.005; C(15), 0.005; C(16), −0.002; C(17), −0.002; C(18), 0.003]				

Angles between planes (°): 1—2, 2.4; 1—3, 1.0; 1—4, 2.3; 1—5, 6.1; 2—3, 2.6; 2—4, 0.3; 2—5, 8.3; 3—4, 2.7; 3—5, 8.3; 4—5, 8.3

WM 250, or Bruker WH 400 spectrometers. The ligand L was prepared as described in ref. 6. Glyoxal was used in 40% w/v aqueous solution as supplied by Aldrich Chemical Co. Unless otherwise stated, all preparations were carried out in air, using reagent grade solvents and reactants.

Template Condensation with Nickel(II).—$Ni(O_2CMe)_2 \cdot 4H_2O$ (32 mg, 0.126 mmol) and L (50 mg, 0.126 mmol) were warmed in methanol (30 cm^3) to give a pale green solution. Glyoxal (0.02 cm^3, 0.138 mmol) and concentrated hydrochloric acid (1 drop) were added, and the solution heated to reflux for 3 h. The orange solution was cooled and treated with a methanolic solution of $Na[BPh_4]$ (900 mg), to give yellow microcrystalline platelets of $[NiL^1(H_2O)_2][BPh_4]_2 \cdot 1.5H_2O$ (Found: C, 74.4; H, 5.7; N, 8.0. Calc. for $C_{73}H_{68}B_2N_7NiO_{3.5}$: C, 74.3; H, 5.8; N, 8.3%). Treatment of the solution with methanolic $[NH_4][PF_6]$ or NaI instead of $Na[BPh_4]$ led to the precipitation of $[NiL^1(H_2O)_2][PF_6]_2 \cdot MeOH$ (Found: C, 37.0; H, 3.6; N, 11.85. Calc. for $C_{26}H_{29}F_{12}N_7NiO_3P_2$: C, 37.4; H, 3.5; N, 11.7%) or $[Ni(MeOH)_2L^1]I_2$ (Found: C, 40.45; H, 3.5; N, 12.1. Calc. for $C_{27}H_{29}I_2N_7NiO_2$: C, 40.7; H, 3.6; N, 12.3%) respectively.

Template Condensation with Manganese(II).—$Mn(O_2CMe)_2 \cdot 4H_2O$ (31 mg, 0.126 mmol) and L (50 mg, 0.126 mmol) were heated in methanol (30 cm^3) to give a clear yellow solution. Glyoxal (0.02 cm^3, 0.138 mmol) was added, and the mixture heated to reflux for 14 h, after which $Na[BPh_4]$ (900 mg) was added. On cooling, yellow crystals of $[MnL^1(H_2O)_2][BPh_4]_2$ slowly separated (Found: C, 76.2; H, 6.0; N, 8.8. Calc. for $C_{73}H_{65}B_2MnN_7O_2$: C, 76.3; H, 5.7; N, 8.5%).

Attempted Template Condensation with Cadmium(II).—$Cd(O_2CMe)_2{\cdot}2H_2O$ (34 mg, 0.126 mmol) in water (10 cm^3) was added to a hot suspension of L (50 mg, 0.126 mmol) in methanol (30 cm^3). The mixture was heated to reflux to give a clear yellow solution (10 min) and treated with glyoxal (0.02 cm^3, 0.138 mmol). The resultant solution was heated to reflux for 2 h, cooled and treated with ammonium hexafluorophosphate, when a yellow precipitate of $[CdLCl][PF_6]{\cdot}5.5H_2O$ (Found: C, 38.5; H, 3.5; N, 13.4. Calc. for $C_{23}H_{26}CdClF_6N_7O_{1.5}P$: C, 38.9; H, 3.6; N, 13.7%) was obtained.

Attempted Template Condensation with Iron(II).—$FeCl_2{\cdot}4H_2O$ (28 mg, 0.141 mmol) and L (56 mg, 0.141 mmol) were heated in methanol (20 cm^3) for 10 min to give a purple solution. Glyoxal (0.023 cm^3, 0.141 mmol) was added, and the solution heated to reflux for 1 h. The hot solution was treated with $[NBu^n{}_4][BF_4]$ and allowed to cool, when green irridescent crystals of $[FeLCl][BF_4]{\cdot}H_2O$ separated (Found: C, 46.4; H, 4.1; N, 16.3. Calc. for $C_{23}H_{25}BClF_4FeN_7O$: C, 46.5; H, 4.2; N, 16.5%).

Attempted Template Condensation with Silver(I).—$Ag[ClO_4]$ (33mg, 0.15 mmol) and L (59.2 mg, 0.15 mmol) were warmed in methanol (20 cm^3) to give a pale yellow suspension On warming this turned brown, and after 2 h at reflux, a silver mirror had appeared on the flask. Exactly similar behaviour occurred when glyoxal was added immediately after mixing the reactants.

Attempted Template Condensation with Cobalt(II).—$Co(O_2CMe)_2{\cdot}4H_2O$ (138 mg, 0.554 mmol) and L (220 mg, 0.554 mmol) were heated to reflux in methanol (20 cm^3) to give a red solution. $[HOC(SO_3Na)]_2{\cdot}H_2O$ (139 mg, 0.554 mmol) and water (8 cm^3) were added, and the solution heated to reflux for 20 h, with the occasional addition of concentrated hydrochloric acid (0.05 cm^3 portions) to maintain a clear solution. The orange solution so obtained was filtered to remove a small amount of black solid, and treated with $[NH_4][PF_6]$ (1 g). On standing, orange needles of $[CoL^2(H_2O)][PF_6]_2$ separated (Found: C, 37.5; H, 3.5; N, 12.0. Calc. for $C_{25}H_{26}CoF_{12}N_7O_2P_2$: C, 37.3; H, 3.2; N, 12.2%). Recrystallisation from methanol gave orange needles of the methanol complex $[CoL^2(MeOH)][PF_6]_2{\cdot}2H_2O$ (Found: C, 36.5; H, 3.6; N, 11.5. Calc. for $C_{26}H_{31}CoF_{12}N_7O_4P_2$: C, 36.5; H, 3.6; N, 11.5%). The same products were obtained when glyoxal was substituted for its sodium hydrogensulphite adduct.

Attempted Condensations of L *with Butane*-2,3-*dione or Benzil*.—The reaction of L with butane-2,3-dione in the presence of nickel(II) acetate led to the quantitative formation of $[NiL(H_2O)_2][BF_4]_2$. Similarly, the products of the attempted reaction of L with benzil in the presence of $Ni(O_2CMe)_2{\cdot}4H_2O$, $Co(O_2CMe)_2{\cdot}4H_2O$, $FeCl_2{\cdot}4H_2O$, $CrCl_3{\cdot}6H_2O$, $Ag[ClO_4]$, or $Mn(O_2CMe)_2{\cdot}4H_2O$ were $[NiL(H_2O)_2][PF_6]_2$, $[CoL(H_2O)_2][BF_4]_2$, $[FeLCl][BF_4]{\cdot}H_2O$, $[CrL(H_2O)_2][PF_6]_2Cl$, silver metal, or $[MnL(H_2O)_2][PF_6]_2$ respectively.

Preparation of $[SnMe_2L]Cl_2$.—Dimethyltin(IV) chloride (220 mg, 1 mmol) was added in one portion to a boiling solution of L (397 mg, 1 mmol) in chlorobenzene (20 cm^3). The solution was maintained at reflux for 2 h, after which a copious yellow precipitate had formed. This was collected by filtration, washed with chloroform (20 cm^3) and diethyl ether (20 cm^3) and dried *in vacuo* to give $[SnMe_2L]Cl_2{\cdot}0.75H_2O$ as a pale yellow solid (85%) (Found: C, 47.7; H, 5.1; N, 15.4. Calc. for $C_{25}H_{30.5}Cl_2N_7O_{0.75}Sn$: C, 47.6; H, 4.85; N, 15.55%). Treatment of a solution of $[SnMe_2L]Cl_2$ in methanol with ammonium hexafluorophosphate led to the precipitation of $[SnMe_2L][PF_6]_2$ as a pale yellow solid (Found: C, 35.7; H, 3.7; N, 11.6. Calc. for $C_{25}H_{29}F_{12}N_7P_2Sn$: C, 35.9; H, 3.45; N, 11.75%).

Preparation of $[H_2L^1][PF_6]_2$.—*Method* 1. $[SnMe_2L]Cl_2$ (78 mg, 0.126 mmol) was dissolved in methanol (20 cm^3), and the pale yellow solution so obtained treated with glyoxal (0.02 cm^3, 0.126 mmol) and hydrochloric acid (0.05 cm^3), and heated to reflux for 1 h. The turbid orange suspension so obtained was filtered hot through Celite to remove tin oxides, and the filtrate was treated with methanolic $[NH_4][PF_6]$ solution to give an orange precipitate of $[H_2L^1][PF_6]_2$ (Found: C, 47.1; H, 3.5; N, 13.8. Calc. for $C_{25}H_{23}F_{12}N_7P_2$: C, 42.2; H, 3.2; N, 13.8%).

Method 2. $CrCl_3{\cdot}6H_2O$ (34 mg, 0.126 mmol) and L (50 mg, 0.126 mmol) were heated to reflux in methanol (30 cm^3) to give an orange solution. Glyoxal (0.02 cm^3, 0.126 mmol) was added, followed by one drop of concentrated HCl, and the solution was then heated to reflux for 14 h. The solution was filtered from a small amount of a red solid which had precipitated, treated with ammonium hexafluorophosphate (0.5 g) and cooled, to give an orange precipitate of $[H_2L^1][PF_6]_2$.

Preparation of $[NiL^1(H_2O)_2][PF_6]_2$.—$[H_2L^1][PF_6]_2$ (100 mg, 0.14 mmol) and $Ni(O_2CMe)_2{\cdot}4H_2O$ (35 mg, 0.14 mmol) were heated to reflux in methanol (35 cm^3) for 4 h, to give a yellow solution. Treatment with ammonium hexafluorophosphate or sodium tetraphenylborate led to the precipitation of nickel(II) complexes identical to those obtained from the template condensation about nickel(II). The complex $[MnL^1(H_2O)_2][PF_6]_2$ was similarly prepared from the free macrocycle and manganese(II) acetate.

Preparation of $[CoL^1(H_2O)_2]X_2$.— $Co(O_2CMe)_2{\cdot}4H_2O$ (35 mg, 0.14 mmol) and $[H_2L^1][PF_6]_2$ (100 mg, 0.14 mmol) were heated to reflux in methanol (30 cm^3) for 2.5 h to give a clear orange solution. The hot solution was treated with sodium tetraphenylborate and allowed to cool, when orange needles of $[CoL^1(H_2O)_2][BPh_4]_2{\cdot}H_2O$ separated (Found: C, 74.9; H, 5.8; N, 8.8. Calc. for $C_{73}H_{67}B_2CoN_7O_3$: C, 74.9; H, 5.7; N, 8.4%). Treatment of the orange solution with ammonium hexafluorophosphate rather than sodium tetraphenylborate led to the precipitation of the complex $[CoL^1(H_2O)_2][PF_6]_2{\cdot}MeOH$ (Found: C, 37.3 H, 3.7; N, 11.5. Calc. for $C_{26}H_{29}CoF_{12}N_7O_3P_2$: C, 37.3; H, 3.5; N, 11.7%).

X-*Ray Crystallography*.—*Structure of* $[NiL^1(EtOH)_2][BF_4]_2$.Yellow rhombohedral crystals were deposited from ethanol. The crystals were stable in air and several were mounted on glass fibres; a crystal having overall dimensions *ca.* 0.31 × 0.31 × 0.27 mm was used for the structure determination. The space group and unit-cell dimensions were derived from preliminary Weissenberg (Cu-K_α) photography.

The crystal was mounted on a Syntex $P2_1$ four-circle diffractometer, and accurate unit-cell dimensions were obtained from angular measurements of 15 strong reflections in the range $40 < 2\theta < 50°$. A total of 2 773 intensity data were recorded using graphite-monochromated Cu-K_α radiation in the range $3.0 < 2\theta < 125.0°$ using a 96-step ω–2θ scan technique; scan speeds varied from 2.5 to 29.3° min^{-1}. Reflections for which the intensity was less than 30 counts s^{-1} in a preliminary 1-s prescan were measured at the slowest speed. Two check reflections which were monitored periodically showed no significant variation in intensity.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 476 azimuthal scan data from 30 independent reflections was applied. Transmission factors ranged from 0.048 to 0.003 for the full data set. Lorentz and polarisation corrections were applied, the data were profile fitted,[16] and equivalent reflections averaged to give 1 944 unique observed intensities [$F > 3\sigma(F)$].

Crystal data. $C_{29}H_{33}B_2F_8N_7NiO_2$, $M = 743.93$, monoclinic, $a = 14.271(3)$ $b = 17.365(5)$, $c = 12.364(4)$ Å, $\beta = 98.03(3)°$, $U = 3\,033.95$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.629$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 8.09 cm^{-1}, $F(000) = 764$, space group $C2/c$ from systematic absences and successful refinement.

The crystal structure was initially solved in the space group Cc since the first stages of the structure determination in $C2/c$ proved unfruitful. The structure was solved using non-centrosymmetric tangent expansion techniques with subsequent Fourier difference syntheses. When all non-hydrogen atoms had been successfully located it was noticed that the two halves of the molecule were related by a two-fold axis; the space group was changed to $C2/c$ by applying a translation to all the atomic co-ordinates. This space group has the special position $(0,y,\frac{1}{4})$ and a two-fold axis of symmetry. Atoms lying on this two-fold axis had their x and z co-ordinates fixed at 0 and $\frac{1}{4}$ respectively, and were assigned an occupancy factor of 0.5. Anisotropic thermal parameters were introduced for all the non-hydrogen atoms, with the exception of the carbon atoms associated with the co-ordinated ethanol molecules.

The methyl and aromatic ring protons were constrained to lie, in geometrically idealised positions, 1.08 Å from the relevant carbon atoms, with the exception of the hydrogen atom lying in the two-fold axis, the methyl groups being treated as rigid bodies. Each type of hydrogen atom was assigned a common isotropic thermal parameter. The hydrogen atoms associated with the co-ordinated ethanol molecules were not located. The tetrafluoroborate anions are ordered.

The structure was refined by blocked-cascade least-squares methods. In the final stages of refinement, a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.0008|F|^2]$ was introduced, since this reduced the dependence of $w\Delta^2$ on $|F|$ and sinθ. The final residuals converged to $R[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.068$ and $R'[= \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|] = 0.077$. A final difference synthesis showed no significant regions of electron density.

Structure of $[H_2L^1][PF_6]_2$. Crystals of the diprotonated macrocycle hexafluorophosphate salt were obtained from methanol–acetonitrile as orange-red blocks. The crystals were air-stable, and several were mounted on glass fibres using epoxy-resin. A crystal having overall dimensions *ca.* 0.37 × 0.33 × 0.28 mm was used for the structure determination. The space group and unit-cell dimensions were derived from preliminary Weissenberg (Cu-K_α) photography. The crystal was mounted on a Syntex $P2_1$ four-circle diffractometer, and accurate unit-cell dimensions were obtained from angular measurements of 15 strong reflections in the range $40 < 2\theta < 50°$. A total of 2 675 intensity data were recorded using graphite-monochromated Cu-K_α radiation in the range $3.0 < 2\theta < 120°$ using a 96-step ω–2θ scan technique; scan speeds varied from 2.5 to 29.3° min^{-1}. Reflections for which the intensity was less than 7 counts s^{-1} in a preliminary 1-s pre-scan were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation in intensity.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 460 azimuthal scan data from 34 independent reflections was applied. Transmission factors ranged from 1.000 to 0.627 for the full data set. Lorentz and polarisation corrections were applied, the data were profile fitted,[17] and equivalent reflections averaged to give 2 011 unique observed reflections [$F > 5\sigma(F)$].

Crystal data. $C_{25}H_{23}F_{12}N_7P_2$, $M = 711.44$, monoclinic, $a = 8.199(2)$, $b = 12.592(4)$, $c = 27.399(12)$ Å, $\beta = 92.32(2)°$, $U = 2\,820.21$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.676$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 22.88 cm^{-1}, $F(000) = 1\,440$, space group $P2_1/c$ from systematic absences.

The majority of the atoms of the macrocyclic ring were located by multisolution Σ^2 sign expansion, and the remaining non-hydrogen atoms were located from subsequent Fourier difference syntheses. One of the hexafluorophosphate anions was disordered, and in the refinement it was treated as two interlocking octahedra of fluorine atoms surrounding the central phosphorus atom. In each octahedron, the P–F distances were fixed at 1.570(1) Å; the occupancies of the fluorine atoms were refined as k and $(1 - k)$. Finally, k converged to a value of 0.665(7).

All of the disordered fluorine atoms were assigned a common isotropic thermal parameter. The methyl and aromatic ring hydrogen atoms were constrained to positions 1.08 Å from the relevant carbon atoms, and each type was assigned a common isotropic thermal parameter. The protons in the macrocyclic cavity were not located. Anisotropic thermal parameters were introduced for the nitrogen atoms, and for the phosphorus and fluorine atoms of the ordered anion. The structure was refined by blocked full-matrix least-squares methods until convergence was achieved. In the final stages of refinement, a weighting scheme of the form $w = 18.6725/[\sigma^2(F) + 0.0002|F|^2]$ was introduced, since this reduced the dependence of $w\Delta^2$ on $|F|$ and sin θ.

The final residuals were $R = 0.119$ and $R'[=\Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|] = 0.130$. A final difference synthesis showed no significant regions of electron density. The final atomic fractional co-ordinates (non-hydrogen atoms) are presented in Table 5. The molecular structure of the dication is illustrated in Figure 2, along with the numbering scheme adopted. The hydrogen atoms have been omitted for clarity. Tables 6—8 list the bond lengths, bond angles, and details of least-squares planes respectively. The X-ray analysis confirms the presence of the free macrocyclic ligand.

Computations were made using the SHELX program [18] on the University of Cambridge IBM 370/165 computer. Neutral-atom scattering factors were taken from ref. 19, and were corrected for both parts of the anomalous dispersion.

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