Macrocyclic Polyphosphane Ligands. Cobalt(II) and Nickel(II) Complexes of (4*RS*, 7*RS*, 13*RS*, 16*RS*)-Tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane and Crystal Structure of the Nickel Dibromide Complex †

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The chiral configuration of the title diastereoisomer, δ-L^1, has been ascertained by the *X*-ray crystal structure of its nickel complex $[Ni(\delta\text{-}L^1)]Br_2\cdot5.5H_2O$. The complex crystallises in the monoclinic space group $P2_1/n$ with $a = 17.375(5)$, $b = 15.047(5)$, $c = 16.122(5)$ Å, $\beta = 90.33(4)°$, and $Z = 4$. Least-squares refinement gives $R = 0.066$ for the 1 881 observed reflections. The nickel atom is five-co-ordinated by one sulphur and four phosphorus atoms of the macrocycle according to a distorted trigonal-bipyramidal geometry. The stereochemistry of some cobalt(II) and nickel(II) complexes of this ligand are investigated in the solution and in the solid state by electronic spectroscopy.

Macrocyclic polyphosphane ligands are actively studied at present.[1] As part of our systematic program to investigate the co-ordinative ability of macrocyclic ligands we have recently reported the synthesis and ligational behaviour of macrocycles of type 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane ($C_{12}H_{24}P_4E_2Ph_4$), which contain four phosphane groups and two different donor atoms (E = S, NPr, or O) (Figure 1).[2-5] Due to the chiral nature of the phosphane groups, these compounds can occur as five diastereoisomers which are interconvertible at elevated temperature ($t_{\frac{1}{2}} \approx 7$ min at 140 °C) but are quite stable at room temperature. The five diastereoisomers of the P_4O_2 derivative exhibit a markedly different co-ordinative behaviour in their cobalt(II) and nickel(II) complexes. A nearly planar arrangement of the four phosphorus atoms occurs in metal complexes and two, one, or none ethereal oxygens of the macrocycle are co-ordinated to these metals according to the steric demands of each isomer.

As far as the P_4S_2 macrocycle is concerned, all five diastereoisomers have been isolated and the chiral configuration of the α and β isomers (Figure 1) definitely ascertained by ^{31}P n.m.r. spectroscopy and *X*-ray crystallography, respectively.[5] The cobalt(II) and nickel(II) complexes of the above two isomers display square-pyramidal MP_4S chromophores for the α isomer and MP_4S_2 chromophores with the β isomer. Here we describe the synthesis and characterisation of some cobalt(II) and nickel(II) complexes of another diastereoisomer, δ-L^1 (Figure 1; E = S). The *X*-ray analysis of $[Ni(\delta\text{-}L^1)]Br_2\cdot5.5H_2O$ is reported and discussed by comparison with the known structures of relevant [ML] complexes.

Results and Discussion

The present diastereoisomer, δ-L^1, readily forms low-spin 1 : 1 complexes of cobalt(II) and nickel(II) with bromide and tetraphenylborate anions. In order to ascertain both the chiral configuration of this isomer and the stereochemistry of its nickel complex, the crystal structure of $[Ni(\delta\text{-}L^1)]Br_2\cdot5.5H_2O$ has been determined by an *X*-ray analysis. The structure consists of $[Ni(\delta\text{-}L^1)]^{2+}$ cations, bromide anions, and interposed water molecules (Figure 2). The configurations of the four chiral phosphorus atoms are (4*RS*,7*RS*,13*RS*,16*RS*), thus justifying its designation as the δ isomer (Figure 1) for the present diastereoisomer. The nickel atom is five-co-ordinated, being linked to the four phosphorus atoms and to a sulphur atom of the macrocyclic ligand. The metal–ligand bond distances appear to be normal (see Table 1). The other sulphur atom of the ligand is not linked to the metal, the Ni $\cdots$ S(1) distance being 3.592 Å. The co-ordination polyhedron is best described in terms of a distorted trigonal bipyramidal geometry, whose apices are occupied by P(1) and P(4). A slight distortion towards a square-pyramidal geometry may, however, be observed from the angular values around the nickel atom. Following this point of view, the S(2) atom is in the apical position.

The compounds $[Ni(\delta\text{-}L^1)]X_2$ (X = Br or BPh_4) show ligand-field spectra with bands at 19 600 and 25 000 cm^{-1}, irrespective of the nature of the counter ions. When dissolved in methyl cyanide these complexes show bands at 19 700 (ε = 1 485) and 25 700 cm^{-1} (ε = 1 485 dm^3 mol^{-1} cm^{-1}), no significant spectral change being apparent. Therefore, a distorted trigonal-bipyramidal stereochemistry holds for the present nickel complexes in solution also.

As far as the cobalt complexes are concerned, their ligand-field spectra show essentially the same transition pattern both in solution and in the solid state (Figure 3). In methyl cyanide, bands are found at 10 500 (ε = 40), 15 700 (ε = 80), and 25 000 cm^{-1} (ε = 3 200 dm^3 mol^{-1} cm^{-1}). They differ significantly from those of octahedral and square-planar low-spin configurations, but closely resemble those of five-co-ordinate low-spin complexes.[6] In fact, it has been shown that trigonal-bipyramidal and square-pyramidal cobalt(II) complexes show rather similar electronic spectra. They differ essentially in the relative intensities of the absorption band at *ca.* 15 500 cm^{-1} to that at *ca.* 7 000 cm^{-1}, the former one being the highest for trigonal-bipyramidal geometries and the low-

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† *Supplementary data available* (No. SUP 23850, 15 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

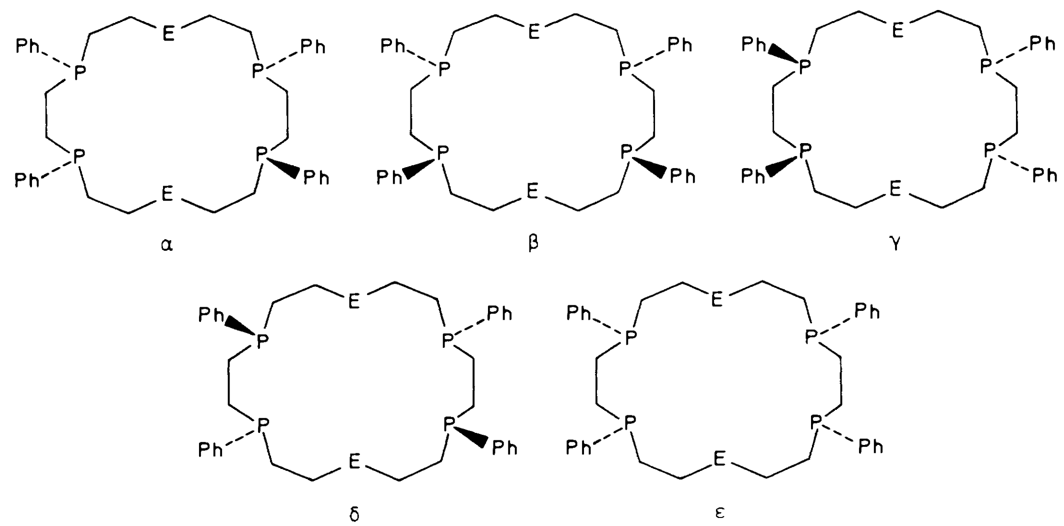

Figure 1. The five diastereoisomers of L [E = S (L¹), O (L²), or NPr (L³)]

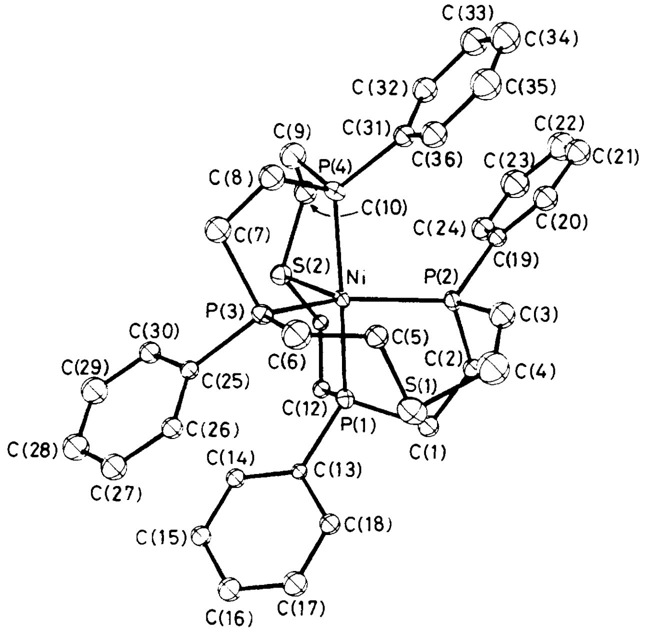

Figure 2. ORTEP drawing of the complex cation $[Ni(\delta\text{-}L^1)]^{2+}$ with the atom labelling scheme

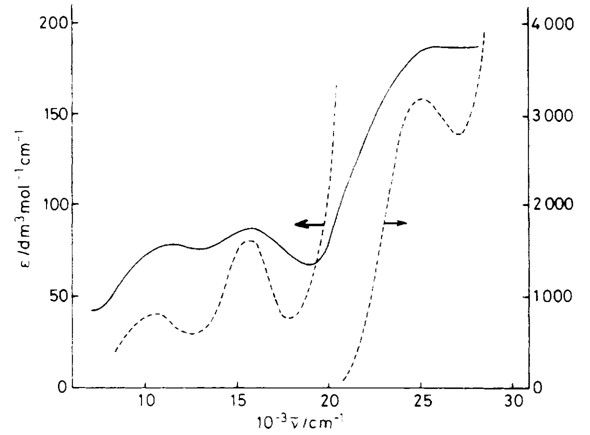

Figure 3. Electronic spectra of $[Co(\delta\text{-}L^1)][BPh_4]_2\cdot 2Me_2CO$: (——) solid state, arbitrary scale; (— — —) in MeCN

est for square-pyramidal geometries.[7] With the present $[Co(\delta\text{-}L^1)]^{2+}$ complexes, the spectral data fit more closely the trigonal-bipyramidal pattern. We assign, therefore, to these cobalt complexes a stereochemistry similar to that of the nickel derivatives.

It is interesting to compare the co-ordination geometries of $[M(\delta\text{-}L^1)]^{2+}$ ions (M = Co or Ni) with that of the cobalt complex containing the isochiral analogue δ-L². An *X*-ray structure determination showed that this ethereal macrocycle acts as a sexidentate ligand, the cobalt atom being *trans*-octahedrally co-ordinated by the four phosphorus atoms and the two ethereal oxygens of the macrocycle.[3] The P–O–P moieties in the $[Co(\delta\text{-}L^2)]^{2+}$ ion adopt meridional co-ordination which is mandatory when the phosphorus atoms of these moieties have the same chiralities and a nearly planar arrangement of the four phosphorus atoms occurs.[2,3]

In fact, in $[Ni(\delta\text{-}L^1)]^{2+}$ the moiety P(1)C(12)C(11)S(2)-C(10)C(9)P(4) adopts a meridional configuration but, in contrast to $[Co(\delta\text{-}L^2)]^{2+}$, the other chain P(2)C(3)C(4)S(1)C(5)-C(6)P(3) brings the sulphur atom away from the co-ordination polyhedron and decreases the P(2)–Ni–P(3) angle from 180° to 137.6(2)°. The planar arrangement of the four phosphorus atoms no longer occurs and the stereochemistry of the metal atom is well described as five-co-ordinated trigonal bipyramidal. As has been shown, the same stereochemistry holds for the cobalt derivatives.

The difference in stereochemistry with the above P_4S_2 *versus* P_4O_2 macrocycles can probably be attributed to the high energies of d^7 and d^8 low-spin configurations in regular octahedral co-ordination. Due to the antibonding character of the d_{z^2}* orbital, six-co-ordinate compounds can occur only with strongly elongated octahedral stereochemistry or with ' weak ' axial donors. Both conditions apply to the six-co-ordinate $[Co(\delta\text{-}L^2)]^{2+}$ ion where the two weak ethereal oxygens occupy axial positions at rather long bond distances (2.32 Å, *cf.* 2.0—2.1 Å for normal Co–O bond distances).

Further comparisons can be made with the co-ordination behaviour of the β diastereoisomers of macrocycles L toward cobalt(II) and nickel(II). With $[Co(\beta\text{-}L^2)]^{2+}$, an octahedral geometry is observed, the Co–O bond distances being rather

Table 1. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for $[Ni(\delta\text{-}L^1)]Br_2\cdot5.5H_2O$

(*i*) Bond distances

Ni–P(1)	2.234(6)	P(2)–C(2)	1.843(18)	P(4)–C(9)	1.844(19)	C(1)–C(2)	1.526(21)
Ni–P(2)	2.241(5)	P(2)–C(3)	1.811(18)	P(4)–C(31)	1.809(14)	C(3)–C(4)	1.492(33)
Ni–P(3)	2.250(6)	P(2)–C(19)	1.827(14)	S(1)–C(4)	1.850(33)	C(5′)–C(6)	1.400(37)
Ni–P(4)	2.216(6)	P(3)–C(6)	1.871(21)	S(1)–C(5′)	1.863(38)	C(5″)–C(6)	1.378(39)
Ni–S(2)	2.350(5)	P(3)–C(7)	1.828(18)	S(1)–C(5″)	1.849(4)	C(7)–C(8)	1.490(22)
P(1)–C(1)	1.813(17)	P(3)–C(25)	1.813(13)	S(2)–C(10)	1.850(18)	C(9)–C(10)	1.428(22)
P(1)–C(12)	1.830(15)	P(4)–C(8)	1.820(19)	S(2)–C(11)	1.794(16)	C(11)–C(12)	1.528(19)
P(1)–C(13)	1.825(12)						

(*ii*) Bond angles

P(1)–Ni–P(2)	85.5(2)	Ni–P(2)–C(19)	123.7(4)	Ni–S(2)–C(10)	100.5(6)
P(1)–Ni–P(3)	100.1(2)	C(2)–P(2)–C(3)	104.5(9)	Ni–S(2)–C(11)	100.6(6)
P(1)–Ni–P(4)	169.8(2)	C(2)–P(2)–C(19)	101.6(7)	C(10)–S(2)–C(11)	107.9(8)
P(1)–Ni–S(2)	84.8(2)	C(3)–P(2)–C(19)	100.4(8)	P(1)–C(1)–C(2)	108.2(12)
P(2)–Ni–P(3)	137.6(2)	Ni–P(3)–C(6)	115.8(7)	P(2)–C(2)–C(1)	109.9(13)
P(2)–Ni–P(4)	95.7(2)	Ni–P(3)–C(7)	107.4(7)	P(2)–C(3)–C(4)	121.1(19)
P(2)–Ni–S(2)	118.6(2)	Ni–P(3)–C(25)	122.6(4)	S(1)–C(4)–C(3)	118.2(23)
P(3)–Ni–P(4)	85.9(2)	C(6)–P(3)–C(7)	102.3(9)	S(1)–C(5′)–C(6)	113.4(25)
P(3)–Ni–S(2)	103.8(2)	C(6)–P(3)–C(25)	105.8(7)	S(1)–C(5″)–C(6)	115.4(28)
P(4)–Ni–S(2)	85.7(2)	C(7)–P(3)–C(25)	99.9(7)	P(3)–C(6)–C(5′)	117.8(21)
Ni–P(1)–C(1)	110.5(6)	Ni–P(4)–C(8)	109.0(6)	P(3)–C(6)–C(5″)	123.3(24)
Ni–P(1)–C(12)	106.2(5)	Ni–P(4)–C(9)	106.8(7)	P(3)–C(7)–C(8)	108.4(14)
Ni–P(1)–C(13)	127.9(4)	Ni–P(4)–C(31)	126.6(5)	P(4)–C(18)–C(7)	112.9(15)
C(1)–P(1)–C(12)	105.0(8)	C(8)–P(4)–C(9)	101.1(9)	P(4)–C(9)–C(10)	112.3(15)
C(1)–P(1)–C(13)	103.7(7)	C(8)–P(4)–C(31)	102.9(7)	S(2)–C(10)–C(9)	106.7(15)
C(12)–P(1)–C(13)	101.2(7)	C(9)–P(4)–C(31)	107.7(8)	S(2)–C(11)–C(12)	105.8(11)
Ni–P(2)–C(2)	107.9(6)	C(4)–S(1)–C(5′)	105.8(16)	P(1)–C(12)–C(11)	114.5(11)
Ni–P(2)–C(3)	116.4(7)	C(4)–S(1)–C(5″)	145.1(18)		

Table 2. Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for $[Ni(\delta\text{-}L^1)]Br_2\cdot5.5H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	−245(2)	1 853(2)	2 507(2)	C(18)	−1 443(6)	−386(10)	3 890(8)
Br(1)	2 368(2)	1 017(2)	249(2)	C(19)	−511(9)	4 046(10)	3 338(9)
Br(2)	2 818(2)	4 408(2)	1 300(3)	C(20)	179(9)	4 161(10)	3 771(9)
P(1)	−405(3)	1 005(4)	3 631(4)	C(21)	473(9)	5 013(10)	3 896(9)
P(2)	−860(4)	2 907(4)	3 229(4)	C(22)	78(9)	5 751(10)	3 588(9)
P(3)	−529(4)	862(4)	1 507(4)	C(23)	−612(9)	5 636(10)	3 155(9)
P(4)	121(4)	2 739(4)	1 486(4)	C(24)	−907(9)	4 783(10)	3 030(9)
S(1)	−2 254(4)	1 298(5)	2 583(5)	C(25)	−259(6)	−300(11)	1 576(9)
S(2)	1 076(4)	1 634(5)	2 754(4)	C(26)	−791(6)	−993(11)	1 540(9)
C(1)	−1 044(13)	1 544(14)	4 360(15)	C(27)	−542(6)	−1 872(11)	1 600(9)
C(2)	−901(13)	2 544(15)	4 319(14)	C(28)	240(6)	−2 058(11)	1 696(9)
C(3)	−1 854(13)	3 110(17)	2 944(17)	C(29)	773(6)	−1 365(11)	1 732(9)
C(4)	−2 541(24)	2 405(29)	3 034(33)	C(30)	523(6)	−486(11)	1 672(9)
C(5′)	−2 050(26)	1 496(32)	1 465(32)	C(31)	−237(7)	3 845(12)	1 271(9)
C(5″)	−2 167(30)	655(34)	1 611(35)	C(32)	239(7)	4 579(12)	1 398(9)
C(6)	−1 547(16)	871(17)	1 122(18)	C(33)	−12(7)	5 426(12)	1 172(9)
C(7)	9(14)	1 182(16)	582(16)	C(34)	−740(7)	5 539(12)	818(9)
C(8)	−21(15)	2 168(16)	502(16)	C(35)	−1 217(7)	4 804(12)	691(9)
C(9)	1 180(14)	2 802(19)	1 536(16)	C(36)	−965(7)	3 958(12)	917(9)
C(10)	1 468(14)	2 696(16)	2 361(15)	O(1)	−1 622(10)	2 746(12)	6 608(11)
C(11)	1 103(12)	1 672(14)	3 866(12)	O(2)	3 193(11)	1 407(13)	3 221(12)
C(12)	530(11)	968(14)	4 157(13)	O(3)	2 965(11)	2 453(13)	4 685(12)
C(13)	−692(6)	−160(10)	3 674(8)	O(4)	2 061(11)	3 109(14)	−220(13)
C(14)	−143(6)	−825(10)	3 561(8)	O(5)	2 398(24)	4 248(28)	3 522(26)
C(15)	−344(6)	−1 715(10)	3 666(8)	O(6)	2 257(24)	4 668(28)	3 027(26)
C(16)	−1 096(6)	−1 941(10)	3 882(8)	O(7)	2 008(16)	3 812(20)	4 534(18)
C(17)	−1 645(6)	−1 276(10)	3 994(8)				

long (2.35 Å).[2] For the nickel analogue, an *X*-ray structure determination is not available and spectroscopic data are inconclusive from a stereochemical point of view.[2] On the other hand, an *X*-ray investigation showed the $[Ni(\beta\text{-}L^1)]^{2+}$ ion to display strongly elongated octahedral geometry, the Ni–S distances being as long as 2.942(2) Å.[5] On the basis of the electronic spectra an octahedral geometry was assigned to the cobalt analogue also. With the six-co-ordinate complexes of the β diastereoisomers the P–E–P moieties adopt *fac* configurations, which allow long M–E distances even with a planar arrangement of the four phosphorus atoms. On the contrary, with a *mer* configuration of the P–E–P moieties long M–E distances can occur only if the P–M–P angle decreases. This apparently prevents the occurrence of elongated octahedral co-ordination for the $[M(\delta\text{-}L^1)]^{2+}$ complexes and leads to more stable five-co-ordinate structures.

Experimental

Synthesis of the Cobalt(II) *and Nickel*(II) *Complexes.*—All cobalt complexes were prepared under a nitrogen atmosphere. The yields of the recrystallised complexes were in the range 70—80%. The ligand δ-L^1 was prepared by the method previously described [m.p. 144—145 °C; $\delta(^{31}P) = -21.06$ p.p.m.].[5]

$[M(\delta\text{-}L^1)][BPh_4]_2\cdot nMe_2CO$ (M = Co, $n = 2$; M = Ni; $n = 0$). A solution of $M[BF_4]_2\cdot 6H_2O$ (0.2 mmol) and $Na[BPh_4]$ (0.5 mmol) in ethanol–acetone (15 cm^3, 1 : 1 v/v) was added to a solution of the ligand (0.2 mmol) in dichloromethane (10 cm^3). The resulting solution was evaporated to *ca.* 10 cm^3 and left overnight. Crystals separated which were filtered off, washed with ethanol–light petroleum, and dried *in vacuo* (Found: C, 73.3; H, 6.8. Calc. for $C_{90}H_{96}B_2CoO_2P_4S_2$: C, 73.1; H, 6.55%. Found: C, 74.1; H, 6.6. Calc. for $C_{84}H_{84}B_2NiP_4S_2$: C, 74.1; H, 6.2%).

$[M(\delta\text{-}L^1)]Br_2\cdot nH_2O$ (M = Co, $n = 2$; M = Ni, $n = 5.5$). A solution of MBr_2 (0.2 mmol) in water (5 cm^3) was added dropwise to a solution of the ligand (0.2 mmol) in acetone–dichloromethane (20 cm^3, 1 : 1 v/v). The resulting solution was evaporated to *ca.* 5 cm^3. On standing overnight, crystals separated which were filtered off, washed with ethanol–diethyl ether (1 : 2 v/v), and dried *in vacuo* (Found: C, 46.7; H, 5.2. Calc. for $C_{36}H_{48}Br_2CoO_2P_4S_2$: C, 47.0; H, 5.25%. Found: C, 43.8; H, 5.8. Calc. for $C_{36}H_{55}Br_2NiO_{5.5}P_4S_2$: C, 44.0; H, 5.65%).

Crystal Data.—$C_{36}H_{55}Br_2NiO_{5.5}P_4S_2$, $M = 982.39$, monoclinic, space group $P2_1/n$, $a = 17.375(5)$, $b = 15.047(5)$, $c = 16.122(5)$ Å, $\beta = 90.33(4)°$, $U = 4\,214.89$ Å^3, $Z = 4$, $D_c = 1.548$ g cm^{-3}, $F(000) = 2\,020$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 26.235$ cm^{-1}.

Data Collection.—The crystal used for data collection had dimensions 0.20 × 0.25 × 0.50 mm. Intensity data were collected on an automatic computer-controlled diffractometer (Philips PW 1 100), equipped with a graphite monochromator, using Mo-K_α radiation. All reflections with $5 \leqslant 2\theta \leqslant 40°$ were measured using the ω—2θ scan technique with a scan speed of 0.07° s^{-1} in a variable range of $(0.70 + 0.30\tan\omega)°$ across the peak. Three standard reflections were measured every 120 min during data collection, but no significant variation was noticed. The intensity data were corrected for Lorentz and polarization effects; the standard deviations $\sigma(I)$ were estimated as described elsewhere [8] with an instability factor of 0.03. A reflection was considered unobserved if the net intensity, I, was $<3\sigma(I)$. Of the 2 715 total reflections 1 881 had intensity $>3\sigma(I)$. An absorption correction was applied by a numerical method. Atomic scattering factors for non-hydrogen atoms were taken from ref. 9, those for hydrogen atoms from ref. 10. Corrections for anomalous dispersion effects were also applied.[11]

Structure Determination and Refinement.—The position of the nickel and of some phosphorus and sulphur atoms were obtained from a three-dimensional Patterson synthesis. Successive F_o and ΔF Fourier syntheses showed the positions of all non-hydrogen atoms, including the oxygen atoms of the solvent water molecules. On the basis of the heights of electron-density peaks on the oxygen atoms, different population parameters were assigned to these atoms, *i.e.* 1 to the atoms O(1)—O(4) and 0.5 to the atoms O(5)—O(7). These population parameters were confirmed by the successive refinements. The C(5) atom, which has a distorted array, has been found in two different positions, C(5′) and C(5″), each having a population parameter of 0.5. The structure was refined using the full-matrix least-squares method of the SHELX program.[12] The minimised function was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms of the macrocycle were introduced in calculated positions, with an overall temperature factor $U = 0.05$ Å^2 and were not refined. Their positions were varied in every cycle on the basis of the shift of the carbon atom (the C–H distance was fixed at 1.08 Å). Isotropic temperature factors were used for carbon and oxygen atoms, and anisotropic temperature factors for nickel, bromine, phosphorus, and sulphur atoms. Phenyl groups were refined as rigid bodies, with the assumption of D_{6h} symmetry for the rings. The final conventional R factor was 0.066. The R' factor, defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, was 0.061. A final ΔF Fourier synthesis did not show any unusual features. The final atomic co-ordinates are presented in Table 2.

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