Macrocyclic Polyphosphane Ligands: Synthesis and Characterisation of Three Diastereoisomers of 5,8,16,19-Tetraphenyl-1,12-Dithia-5,8,16,19-tetraphosphacyclodocosane and the *X*-Ray Crystal Structure † of a Dinuclear Nickel(II) Complex of the β Isomer

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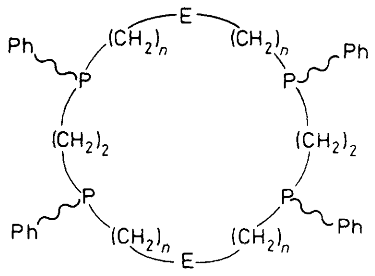
The macrocycle 5,8,16,19-tetraphenyl-1,12-dithia-5,8,16,19-tetraphosphacyclodocosane, L^3, has been synthesised in 13% yield. Three of the five possible diastereoisomers are isolated and one of them (β) is used to form cobalt(II) and nickel(II) complexes with 1 : 1 and 2 : 1 metal–ligand ratios. The compound $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot MeOH$ crystallises in the orthorhombic space group *Pbca* with $a = 17.791(4)$, $b = 20.993(4)$, $c = 22.758(5)$ Å, and $Z = 4$. Least-squares refinement gave $R = 0.092$, for the 917 observed reflections. The cation $[Ni_2Br_2(\beta\text{-}L^3)]^{2+}$ contains two nickel atoms in a slightly distorted square-planar environment related by a crystallographic centre of symmetry. Each nickel atom is co-ordinated by two phosphorus and one sulphur atoms of the macrocycle and by one bromide ion. The Ni ··· Ni separation within the cation is 5.13 Å. The stereochemistries of some cobalt(II) and nickel(II) complexes of $\beta\text{-}L^3$ have been investigated in solution and in the solid state by electronic and ^{31}P n.m.r. spectroscopy, and by magnetic measurements.

In recent years, much interest has been devoted to macrocyclic polyphosphane ligands.[1] Our systematic studies on tetraphospha macrocycles, containing two additional donors, have dealt with a number of rings of the type L, where $n = 2$, E = O,[2-4] S,[5,6] or N–Pr.[7,8] Due to chirality of the phosphane groups five diastereoisomers are possible (Figure 1), all of which have been isolated in a pure state for E = O and S. The co-ordination behaviour of these ligands towards cobalt(II) and nickel(II) appears to be related markedly to the mutual chirality of the phosphane groups and to the nature of the E donor atoms, on the one hand, and to the nature of the metal ion on the other. The denticity of the ligand, as well as the geometry of the complexes, is variable. Thus, with the macrocycle L^1 ($n = 2$, E = O), both the β and δ isomers give *trans*-octahedral cobalt(II) complexes with facial [2] and meridional [3] arrangements of the P ··· O ··· P moieties, respectively. On the contrary, a square-pyramidal geometry is exhibited by $[Co(\alpha\text{-}L^1)]^{2+}$ (ref. 2) and a square-planar one by $[Ni(\varepsilon\text{-}L^1)]^{2+}$.[4] Such behaviour has been rationalised in terms of the mutual chiralities of the phosphane groups in the P ··· O ··· P chains.[2,3] On the other hand, $\delta\text{-}L^2$ ($n = 2$, E = S) gives cobalt(II) and nickel(II) complexes with trigonal-bipyramidal structure, one sulphur atom being unco-ordinated.[6]

As part of the above research we now investigate the effect of ring size on the co-ordination behaviour of such macrocycles in their 1 : 1 metal–ligand complexes as well as their ability to form dinuclear complexes. In this paper we report the synthesis of the macrocycle L^3 ($n = 3$, E = S) and the separation of three of its five diastereoisomers. For the β isomer we report the preparation and properties of some complexes with cobalt(II) and nickel(II) and the *X*-ray structure determination of $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot MeOH$.



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Results and Discussion

Synthesis of the Macrocycle and Separation of Diastereoisomers.—The macrocycle L^3 has been synthesised by a one-pot reaction between equimolar amounts of bis(3-chloropropyl) sulphide and the dilithium salt of 1,2-bis(phenylphosphino)ethane. The main products of this reaction, however, are polymeric materials from which the isomeric mixture of L^3 can be separated with an overall yield of *ca.* 13%.

The isolation of the single diastereoisomers in the pure state is a lengthy process based on fractional crystallisation of the isomeric mixture as well as ion-exchange chromatography of their nickel salts. The isolation process can be effectively monitored by ^{31}P n.m.r. spectroscopy. So far only three out of the five isomers have been obtained as pure substances. The remaining two isomers (γ, ε) have been identified both in the crude reaction mixture and in the material resulting from the thermal isomerisation of the pure isomers in boiling *o*-xylene. They show $^{31}P\text{-}\{^1H\}$ chemical shifts of −22.0 and −22.30 p.p.m.

The structural assignments of the three diastereoisomers are based on *X*-ray data as well as on ^{31}P n.m.r. spectroscopy. Our previous studies on the diastereoisomers of L^1, L^2 and also L^4 ($n = 2$, E = N–Pr) proved that the resonances of *RR* or *SS*

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† *Supplementary data available* (No. SUP 56002, 11 pp.): thermal parameters, structure factors. See Instructions for Authors, *J Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

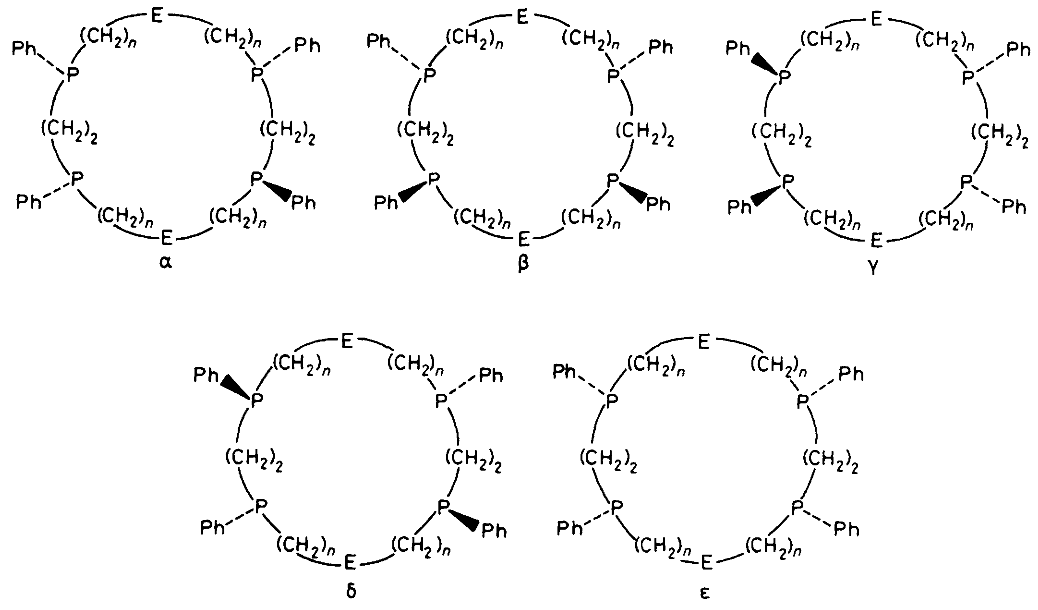

Figure 1. The five diastereoisomers of L^3

Table 1. Analytical and physical data for some complexes of β-L^3

Compound	Colour	Analysis (%)[a]		Λ[b]/Ω^{-1} cm^2 mol^{-1}	Electronic spectra,[c] ν/cm^{-1}	^{31}P N.m.r. spectra[d]		
		C	H			δ_A	δ_B	J_{AB}
[Co(β-L^3)][BF_4]$_2$	Orange	49.9	5.5	166 (MeOH)	Solid: 6 300, 8 600, 14 100, 20 800 (sh)			
		(50.4)	(5.50)		MeOH: 13 700 (40), 20 800 (410)			
[Co(β-L^3)][$CoBr_4$]	Green	40.9	4.6	152 (dmf)	Solid: 7 000, 8 300, 14 900, 24 700			
		(41.45)	(4.50)					
[Ni(β-L^3)][BF_4]$_2$	Yellow	51.0	5.8	139 (dmf)	Solid: 26 700 (sh)[e], 18 500, 24 700[f]	56.4[g]		
		(50.4)	(5.50)		MeOH: 18 500 (450), 24 200 (1 500)			
[Ni_2Br_2(β-L^3)]Br_2	Orange	41.1	4.7	153 (MeOH)	Solid: 23 500	72.9	62.2	58[h]
		(41.5)	(4.55)		MeOH: 23 300 (2 000)			
[Ni_2Cl_2(β-L^3)][BPh_4]$_2$	Yellow	68.6	6.0	101 (dmf)	Solid: 24 400	69.7	61.0	63[i]
		(68.3)	(6.00)		dmf: 23 200 (2 350)			
[Ni_2Br_2(β-L^3)][BPh_4]$_2$	Orange	64.5	6.1	135 (dmf)	Solid: 23 500	70.5	64.6	58[j]
		(64.6)	(5.65)		dmf: 23 000 (2 000)			

[a] Calculated values are given in parentheses. [b] Molar conductance values for *ca.* 10^{-3} mol dm^{-3} solutions at 20 °C. Solvents are given in parentheses (dmf = *N,N*-dimethylformamide). [c] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] Chemical shifts (δ) in p.p.m., coupling constants (*J*) in Hz. [e] Yellow form. [f] Red form. [g] In MeCN. [h] In MeOH. [i] In dmf. [j] In Me_2SO.

pairs of the phosphorus atoms in the P–CH_2CH_2–P moieties are deshielded with respect to those of the *RS* pairs (0.9—1.5 p.p.m.).[2-7] Inspection of Figure 1 shows that the four phosphorus atoms are non-equivalent in the α isomer, whereas they are all equivalent in the other four isomers. Thus, four resonances are expected for the α isomer, two falling at distinctly lower fields (*RR* or *SS* pairs) than the other two (*RS* pairs). This is the case for one of the isolated isomers (−20.83, −20.88, and one resonance of twice relative intensity at −22.20 p.p.m.) which is accordingly assigned the α configuration. The other two isolated isomers exhibit lower-field ^{31}P-{^{1}H} singlets (δ – 20.83 and −20.96 p.p.m.) and should possess *RR* or *SS* P–CH_2CH_2–P moieties. They should be assigned, therefore, one of the two configurations β or δ of Figure 1. As a matter of fact, the *X*-ray crystal structure determination on a nickel complex of the isomer showing the singlet at −20.83 p.p.m. (see later) has ascertained that it is the β isomer only. Thus the remaining isolated isomer, exhibiting the resonance at −20.96 p.p.m., has tentatively to be assigned the δ configuration.

Cobalt(II) *and Nickel*(II) *Complexes of* β-L^3.—Cobalt(II) and nickel(II) complexes are readily formed with β-L^3 which are of the 1 : 1 type with non-co-ordinating anions ([BF_4]$^-$, [BPh_4]$^-$) and of the 2 : 1 type in the presence of co-ordinating halide anions (Cl^-, Br^-) (Table 1).

In order to ascertain both the configuration of the β isomer and the co-ordination geometry of its dinickel complex, the crystal structure of [Ni_2Br_2(β-L^3)][BPh_4]$_2$·MeOH has been determined by an *X*-ray analysis (Tables 2 and 3, Figure 2).

The structure of the compound consists of [Ni_2Br_2(β-L^3)]$^{2+}$ cations and [BPh_4]$^-$ anions. Figure 2 shows a stereoscopic view of the cation which contains two nickel atoms in a slightly distorted square-planar environment. Each nickel atom is co-ordinated by two phosphorus and one sulphur atoms of the macrocycle and by one bromide ion. The two

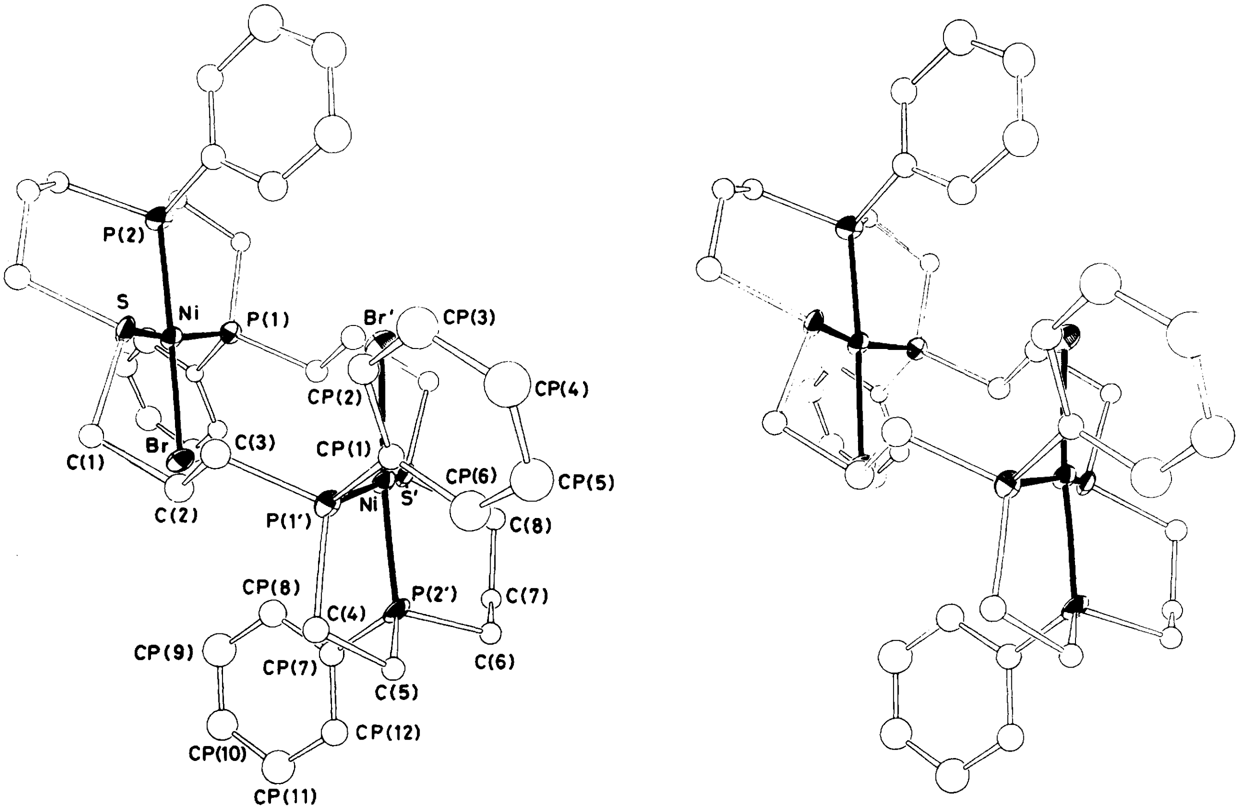

Figure 2. Stereoscopic view of the complex cation $[Ni_2Br_2(\beta\text{-}L^3)]^{2+}$ with the atom labelling scheme

Table 2. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot MeOH$

Ni–Br	2.314(7)	P(1)–C(3)	1.84(4)	P(2)–CP(7)	1.75(3)	C(7)–C(8)	1.53(5)
Ni–S	2.243(13)	P(1)–C(4)	1.92(4)	C(1)–C(2)	1.66(6)	B–CB(1)	1.79(4)
Ni–P(1)	2.190(15)	P(1)–CP(1)	1.86(3)	C(2)–C(3)	1.66(6)	B–CB(7)	1.76(5)
Ni–P(2)	2.202(12)	P(2)–C(5)	1.84(4)	C(4)–C(5)	1.55(5)	B–CB(13)	1.68(5)
S–C(1)	1.92(4)	P(2)–C(6)	1.86(4)	C(6)–C(7)	1.46(6)	B–CB(19)	1.63(5)
S–C(8)	1.91(4)						

S–Ni–Br	100.0(4)	C(3)–P(1)–Ni	111.2(1.3)	C(6)–P(2)–C(5)	107.6(1.7)	C(8)–C(7)–C(6)	121.7(3.2)
P(1)–Ni–Br	86.4(4)	C(4)–P(1)–Ni	109.8(1.3)	CP(7)–P(2)–Ni	117.5(1.1)	C(7)–C(8)–S	108.9(2.6)
P(2)–Ni–S	88.6(5)	C(4)–P(1)–C(3)	108.4(1.8)	CP(7)–P(2)–C(5)	108.2(1.7)	CB(1)–B–CB(7)	103.3(2.4)
P(2)–Ni–P(1)	86.6(5)	CP(1)–P(1)–Ni	116.8(1.1)	CP(7)–P(2)–C(6)	101.6(1.6)	CB(1)–B–CB(13)	109.0(2.6)
P(1)–Ni–S	166.0(5)	CP(1)–P(1)–C(3)	104.1(1.7)	C(2)–C(3)–P(1)	102.9(2.5)	CB(7)–B–CB(13)	108.0(2.6)
P(2)–Ni–Br	169.5(4)	CP(1)–P(1)–C(4)	106.1(1.5)	C(5)–C(4)–P(1)	107.3(2.6)	CB(1)–B–CB(19)	105.8(2.6)
C(1)–S–Ni	111.6(1.3)	C(5)–P(2)–Ni	109.6(1.4)	C(4)–C(5)–P(2)	107.5(2.5)	CB(7)–B–CB(19)	113.1(2.8)
C(8)–S–Ni	100.3(1.3)	C(6)–P(2)–Ni	111.7(1.4)	C(7)–C(6)–P(2)	112.1(2.7)	CB(13)–B–CB(19)	116.8(2.8)
C(8)–S–C(1)	97.9(1.7)						

co-ordination planes are related by a crystallographic centre of symmetry. The Ni ··· Ni separation is 5.13 Å which rules out any direct interaction between the metal ions. Interaction *via* the bromine atoms within the dinuclear species must also be precluded by the large Ni ··· Br non-bonded distances (4.64 Å).

The co-ordination plane is slightly distorted towards a tetrahedron, the deviations of the atoms from the least-squares plane being +0.05 (Ni), +0.18 (Br), −0.18 (S), −0.21 P(1), +0.21 Å P(2). Bond lengths and angles in the complex cation and around the boron atom in $[BPh_4]^-$, with estimated standard deviations, are reported in Table 2. The nickel–ligand bond distances are typical of low-spin square-planar nickel(II) complexes, as reported in the literature.[6,9]

The macrocycle has the *meso* centrosymmetric configuration (5*RS*, 8*RS*, 16*SR*, 19*SR*) thus justifying its β label according to Figure 1.

The ligand-field spectrum of solid $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot$MeOH exhibits a broad absorption band with the peak at 23 500 cm^{-1} in accordance with the NiP_2SBr square-planar chromophores. No significant spectral change is found in methanol solution (Table 1), suggesting that the same stereochemistry holds in solution also. This conclusion is also supported by the electrical conductivity measurements, which indicate a 2 : 1 electrolyte behaviour and by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy which shows an AB resonance pattern.

The other 2 : 1 metal–ligand complexes $[Ni_2Br_2(\beta\text{-}L^3)]Br_2$ and $[Ni_2Cl_2(\beta\text{-}L^3)][BPh_4]_2$ should be attributed the same kind of dinuclear structure on the basis of (*i*) the close similarity of the ligand-field spectra, (*ii*) electrical conductivity values of 2 : 1 electrolytes, and (*iii*) the AB pattern of their ^{31}P n.m.r. spectra (Table 1).

With the non-co-ordinating tetrafluoroborate anion the yellow 1 : 1 metal–ligand complex $[Ni(\beta\text{-}L^3)][BF_4]_2$ is formed; its reflectance spectrum is typical of a square-planar NiP_4 chromophore [ν = 26 700(sh) cm^{-1}].[3,7] On grinding, the complex turns dark red and shows a reflectance spectrum with peaks at 18 500 and 25 600 cm^{-1}. This spectrum is very similar to that shown by $[Ni(\beta\text{-}L^2)]Br_2\cdot2H_2O$ (peaks at 18 200 and 26 300 cm^{-1}), which was found by *X*-ray crystallography to have a strongly elongated *trans*-octahedral co-ordination (Ni–S 2.9 Å).[5] The spectroscopic evidence, however, cannot clearly rule out a square-pyramidal co-ordination (NiP_4S chromophore), like that found in $[Ni(\alpha\text{-}L^2)][BPh_4]_2$, since the latter complex exhibits a similar reflectance spectrum (peaks at 19 200 and 25 600 cm^{-1}).[5] Nevertheless, it is apparent that two forms are present in the solid state, one with a square-planar NiP_4 chromophore and one with additional axially co-ordinated sulphur atom(s).

In methanol solution both forms show the same absorption spectrum which is quite similar to that of the solid dark red form (Table 1). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[Ni(\beta\text{-}L^3)][BF_4]_2$ in MeCN at 30 °C shows a broad singlet at 56.4 p.p.m. On cooling down to −40 °C the singlet splits steadily into a AA′BB′ resonance pattern, a fact which does not agree with a symmetrical *trans*-octahedral structure of the complex. On the basis of the electronic and n.m.r. spectroscopic data, for $[Ni(\beta\text{-}L^3)]^{2+}$ in solution is proposed a square-pyramidal co-ordination (NiP_4S chromophore) or an elongated *trans*-octahedral co-ordination (NiP_4S_2 chromophore) with an unsymmetrical folding of the ligand.

As far as the cobalt(II) complexes are concerned the mononuclear $[Co(\beta\text{-}L^3)][BF_4]_2$ derivative is low-spin ($\mu_{eff.}$ = 2.01 B.M.) and exhibits a reflectance spectrum typical of square-pyramidal cobalt(II) complexes (Table 1). It closely resembles that of $[Co(\alpha\text{-}L^1)][BPh_4]_2$ for which such a co-ordination geometry was ascertained by an *X*-ray analysis.[2] No significant spectral change is apparent on dissolving the complex in methanol, so that the same square-pyramidal co-ordination should be kept in solution also. This co-ordinative behaviour toward cobalt(II) must be contrasted with that of the chirally analogous isomer β-L^2, which acts as a sexidentate ligand in its cobalt(II) complexes.[5]

The compound $(CoBr_2)_2(\beta\text{-}L^3)$ has a room-temperature magnetic moment *per* cobalt atom of 3.46 B.M. This value closely corresponds to that expected ($\mu_{eff.}$ = 3.5 B.M.) for an equimolar assembly of low-spin ($\mu_{eff.}$ = 2.0 B.M.) and high-spin ($\mu_{eff.}$ = 4.5 B.M.) cobalt atoms.[10] Its reflectance spectrum can be rationalised in terms of superimposed transitions of the low-spin square-pyramidal $[Co(\beta\text{-}L^3)]^{2+}$ cation and of the high-spin tetrahedral $[CoBr_4]^-$ anion. Accordingly, the complex is tentatively formulated as $[Co(\beta\text{-}L^3)][CoBr_4]$.

Conclusions

A comparison between the co-ordinative behaviour of β-L^2 (*n* = 2, E = S) and β-L^3 (*n* = 3, E = S) towards cobalt(II) and nickel(II) allows some comments on the effect of the ring size of these macrocycles. In its mononuclear complexes the larger macrocycle shows a lower ligating tendency of its sulphur atoms than the smaller one. Indeed, square-planar and square-pyramidal co-ordinations are achieved instead of octahedral. Thus, at least for the d^7 and d^8 electron configurations with soft ligands, it appears that the more favourable bite angle of the chelate rings involving the propylene chains (*ca.* 90°) is outweighed by the lower stability of six-membered chelate rings with respect to five-membered ones.[11]

The larger macrocycle β-L^3 gives dinuclear nickel(II) complexes as contrasted to the smaller β-L^2 ligand. The presence of co-ordinating anions (Cl^-, Br^-) is crucial in order to obtain dinuclear complexes probably because they provide an additional donor per metal atom. Furthermore, they reduce the coulombic repulsion between the metal ions. Under the same conditions, cobalt(II) does not yield dinuclear complexes, a fact which might be tentatively attributed to the higher stability of $[CoX_4]^{2-}$ ions with respect to $[NiX_4]^{2-}$ ions. Furthermore, whilst square-planar nickel(II) complexes are known to be very stable, those of cobalt(II) are less so.[10]

Experimental

Synthesis of the Macrocycle L^3.—The reaction between the dilithium salt of 1,2-bis(phenylphosphino)ethane (0.10 mol) and bis(3-chloropropyl) sulphide (0.10 mol) in tetrahydrofuran (thf) at −20 °C has been carried out according to the procedure already described for the preparation of L^2.[5] The reaction mixture was evaporated under vacuum, the residue extracted into benzene (500 cm^3), the solution filtered through silica gel and eluted with the same solvent (1 l). The combined benzene fractions were evaporated to dryness on a rotary evaporator, and the oily residue (31 g) was dissolved in acetone (40 cm^3) and left overnight. The precipitated material (4.3 g) was recrystallised from dichloromethane–acetone (40 cm^3, 1 : 1 v/v) yielding white crystals (3.9 g, 10.8%; m.p. 120—155 °C) of an isomeric mixture of L^3. According to the ^{31}P n.m.r. spectrum, this contained mainly the α and β isomers and smaller amounts of the γ and ε isomers. The above material was extracted with hot acetone (4 × 25 cm^3) and the solid residue was recrystallised from dichloromethane–acetone yielding white crystals of the pure β isomer (0.60 g, 1.7%; m.p. 163—165 °C; $^{31}P\text{-}\{^1H\}$, δ −20.83 p.p.m.). The combined acetone extracts were concentrated to 50 cm^3 and left overnight. The precipitate product [2.5 g, 6.9%; m.p. 122—125 °C; $^{31}P\text{-}\{^1H\}$ n.m.r., δ −20.83(s), −20.88(s), −22.20 p.p.m.] consisted of the pure α isomer. Evaporation of the mother-liquor gave a mixture of the α, γ, and ε isomers.

Finally, the δ isomer was obtained from the acetone solution of the chromatographic eluates after separation of the solid mixture of the α, β, γ, and ε isomers. This solution was diluted with chloroform (50 cm^3) before adding dropwise a hot solution of hexa-aquanickel(II) chloride (12.5 g, an excess) in methanol (50 cm^3). The red-brown solution was evaporated to dryness and the residue extracted with boiling water (1 l). Solid sodium chloride (0.5 mol) was added to the well stirred solution which was then filtered and chromatographed through a cation-exchange column (SP-Sephadex C25; 7 × 15 cm). Elution with 0.5 mol dm^{-3} sodium chloride gave three fractions and the dark red central fraction was collected. By addition of sodium cyanide solution a red solid separated, which was collected by filtration and reacted with further sodium cyanide solution (1 g in 20 cm^3) at 60 °C. After cooling to room temperature the yellow solution was extracted with benzene (3 × 25 cm^3) and the combined benzene extracts were evaporated to dryness. The solid residue was recrystallised from hot acetone yielding white hair-like needles of the δ isomer (0.70 g, 1%; m.p. 128—130 °C; $^{31}P\text{-}\{^1H\}$, δ −20.96 p.p.m.).

Synthesis of the Cobalt(II) *and Nickel*(II) *Complexes*.—All cobalt(II) complexes were prepared under a nitrogen atmosphere. The yields of the recrystallised complexes were in the range 70—80%.

$[M(\beta\text{-}L^3)][BF_4]_2$ (M = Co *or* Ni). A solution of $M(BF_4)_2\cdot$-

Table 3. Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot MeOH$

Atom *	*x*	*y*	*z*	Atom *	*x*	*y*	*z*
Ni	1 405(3)	147(3)	215(2)	CB(1)	3 542(9)	1 562(15)	1 157(10)
Br	626(2)	167(3)	1 029(2)	CB(2)	3 130(9)	2 126(15)	1 201(10)
S	1 008(5)	1 029(5)	−247(6)	CB(3)	2 355(9)	2 103(15)	1 291(10)
P(1)	1 687(6)	−828(7)	475(6)	CB(4)	1 991(9)	1 517(15)	1 337(10)
P(2)	2 302(5)	59(8)	−446(5)	CB(5)	2 403(9)	953(15)	1 293(10)
C(1)	348(20)	1 524(17)	239(17)	CB(6)	3 178(9)	976(15)	1 203(10)
C(2)	495(22)	−1 185(19)	−211(19)	CB(7)	4 880(14)	877(11)	1 244(14)
C(3)	855(21)	−1 349(19)	443(17)	CB(8)	5 180(14)	744(11)	1 796(14)
C(4)	2 436(22)	−1 165(19)	−44(16)	CB(9)	5 425(14)	129(11)	1 929(14)
C(5)	2 934(20)	−601(18)	−245(19)	CB(10)	5 369(14)	−352(11)	1 509(14)
C(6)	2 879(22)	796(20)	−492(17)	CB(11)	5 069(14)	−219(11)	956(14)
C(7)	2 438(22)	1 346(19)	−680(16)	CB(12)	4 825(14)	396(11)	823(14)
C(8)	1 816(21)	1 626(18)	−294(18)	CB(13)	4 749(16)	1 810(12)	382(8)
CP(1)	2 056(18)	−943(14)	1 231(9)	CB(14)	4 213(16)	1 979(12)	−37(8)
CP(2)	1 617(18)	−1 176(14)	1 691(9)	CB(15)	4 428(16)	2 074(12)	−620(8)
CP(3)	1 951(18)	−1 290(14)	2 239(9)	CB(16)	5 179(16)	2 001(12)	−784(8)
CP(4)	2 704(18)	−1 171(14)	2 327(9)	CB(17)	5 715(16)	1 832(12)	−364(8)
CP(5)	3 143(18)	−938(14)	1 867(9)	CB(18)	5 500(16)	1 736(12)	219(8)
CP(6)	2 819(18)	−824(14)	1 319(9)	CB(19)	4 789(16)	2 176(12)	1 573(13)
CP(7)	2 030(16)	−44(13)	−1 181(10)	CB(20)	4 523(16)	2 146(12)	2 149(13)
CP(8)	1 277(16)	−138(13)	−1 330(10)	CB(21)	4 715(16)	2 621(12)	2 551(13)
CP(9)	1 987(16)	−349(13)	−1 892(10)	CB(22)	5 172(16)	3 126(12)	2 376(13)
CP(10)	1 650(16)	−466(13)	−2 305(10)	CB(23)	5 438(16)	3 156(12)	1 800(13)
CP(11)	2 402(16)	−371(13)	−2 156(10)	CB(24)	5 247(16)	2 681(12)	1 399(13)
CP(12)	2 592(16)	−160(13)	−1 594(10)	O_{MeOH}	2 524(0)	2 077(0)	3 557(0)
B	4 542(21)	1 646(20)	1 085(19)	C_{MeOH}	2 082(0)	2 006(0)	3 013(0)

* CP = carbons of phenyl groups attached to the macrocyclic ring; CB = phenyl carbons of $[BPh_4]^-$ anion.

$6H_2O$(0.10 mmol) in 10 cm^3 of methanol was added dropwise to a solution of the ligand (0.10 mmol) in dichloromethane (10 cm^3). The resulting solution was warmed and evaporated to *ca.* 8 cm^3. On standing overnight, crystals separated which were filtered off, washed with ethanol–light petroleum (b.p. 40–60 °C) and dried *in vacuo.*

$(MBr_2)_2(\beta\text{-}L^3)$ (M = Co *or* Ni). A solution of MBr_2 (0.22 mmol) in methanol (30 cm^3 of 90%) was added dropwise to a solution of the ligand (0.10 mmol) in dichloromethane (25 cm^3). The mixture was refluxed for 10 min, filtered from solid materials, and the resulting solution was evaporated to *ca.* 8 cm^3. On standing, crystals separated which were filtered off, washed with ethanol–light petroleum and dried *in vacuo.*

$[Ni_2X_2(\beta\text{-}L^3)][BPh_4]_2$ (X = Cl *or* Br). The combined solutions of NiX_2 (0.22 mmol) in methanol (30 cm^3) and of the ligand in dichloromethane (25 cm^3) were refluxed for 10 min, filtered, and evaporated near to dryness. The residue was dissolved in hot methanol (30 cm^3) and a solution of $NaBPh_4$ (0.22 mmol) in acetone (10 cm^3) was added. The crystalline complexes which separated were washed with methanol–light petroleum and dried *in vacuo.*

Crystal Data for $[Ni_2Br_2(\beta\text{-}L^3)][BPh_4]_2\cdot MeOH$.—$C_{89}H_{96}B_2Br_2Ni_2OP_4S_2$, *M* = 1 668.63, orthorhombic, space group *Pbca*, $a = 17.791(4)$, $b = 20.993(4)$, $c = 22.758(5)$ Å, $U = 8\,499.8$ Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, $F(000) = 3\,464$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 14.87$ cm^{-1}.

Data Collection.—Well shaped crystals were obtained by slow evaporation of a methanol solution of the complex. The crystals rapidly lost solvent in air with consequent decomposition; for this reason the small needle-shaped crystal chosen for data collection (approximate dimensions: 0.3 × 0.05 × 0.10 mm) was sealed in a glass capillary bathed in a drop of mother-liquor, and mounted on a Philips automatic diffractometer. A least-squares fit of 25 carefully centred reflections was used to determine the cell constants. Intensity data were collected with the θ—2θ scan technique, with a variable scan width at a scan speed of 0.06° s^{-1} within the range $2 < \theta < 20°$. Background counts were performed on each side of the peak for half of the total scan time. 917 Independent reflections had $I \geqslant 2.5\sigma(I)$ and were used for the structure solution and refinement. The standard deviation of intensity, $\sigma(I)$, was computed as: $\sigma(I) = [P + B_1 + B_2 + (0.02I)^2]^{\frac{1}{2}}$ where *P* is the total integrated count, B_1 and B_2 are the background counts, *I* is the peak intensity after subtraction of the background, and 0.02*I* is a correction for unrealistically small standard deviations in strong reflections. Three reflections, monitored periodically, did not show any systematic variation in intensity during data collection. Intensities were corrected for Lorentz-polarisation effects but not for absorption. The space group *Pbca* was completely determined by systematic absences and its symmetry constrained the four molecules in the cell to be located on the four centres of symmetry at (0 0 0), ($\frac{1}{2}$ $\frac{1}{2}$ 0), (0 $\frac{1}{2}$ $\frac{1}{2}$), and ($\frac{1}{2}$ 0 $\frac{1}{2}$), so the asymmetric unit consisted only of half the macrocycle and of one tetraphenylborate counter ion.

Structure Determination and Refinement.—The structure was solved by means of Patterson and electron-density syntheses which readily showed the positions of all the non-hydrogen atoms. Refinement of the atom parameters was performed by blocked-matrix least-squares cycles with isotropic thermal parameters for all the atoms, except those of the co-ordination polyhedron which were refined anisotropically. The two blocks consisted respectively of the independent half of the macrocycle and the tetraphenylborate counter ion. In order to reduce the number of parameters, rigid-group refinement was used for the six independent benzene rings and this gave a total of 153 parameters to be refined. The minimised function was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/\sigma^2(F_o)$ where *k* is a variable parameter refined to 1.2088.

A final difference synthesis showed the presence of two unresolved peaks which were attributed to disordered solvent molecules. Therefore in the last least-squares cycle a methanol molecule was refined with a fixed C–O distance (1.47 Å) and an occupation factor of 0.5 for both atoms. The final agreement indexes R and R' were respectively 0.092 and 0.085; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w/|F_o|^2]^{\frac{1}{2}}$.

The program used for all the calculations was SHELX 76,[11] with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from International Tables.[12] Final atomic co-ordinates with estimated standard deviations are reported in Table 3. Molecular plots were obtained using ORTEP.[13]

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