Synthesis and Characterisation of the Five Diastereoisomers of 4,7,13,16-Tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane: Crystal Structure of the Nickel Bromide Complex of the β-Isomer †

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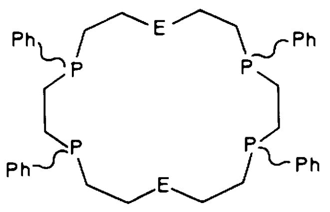
The novel dithiatetraphospha-macrocycle 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane (L^2) has been synthesised in 14% yield *via* a one-step procedure. All of the five possible diastereoisomers were isolated, and two of them (α and β) used to form cobalt(II) and nickel(II) complexes. The compound $[Ni(\beta\text{-}L^2)]Br_2{\cdot}2H_2O$ crystallises in a triclinic unit cell ($P\bar{1}$ space group) with lattice constants a = 9.645(3), b = 10.159(3), c = 10.869(3) Å, α = 68.07(4), β = 78.09(4), γ = 84.69(4)°, and Z = 1. Least-squares refinement gave R = 0.059 for 1 395 observed reflections. The *X*-ray diffraction study of this complex shows that the nickel atom is six-co-ordinated by two sulphur and four phosphorus atoms of the macrocycle forming an elongated *trans*-octahedral geometry. The stereochemistry of the β isomer is 4*RS*,7*RS*,13*SR*,16*SR*. The 4*RS*,7*RS*,13*RS*,16*SR* isomer (α isomer) has been identified by ^{31}P n.m.r. spectroscopy.

Macrocyclic phosphane ligands have been reported only in recent years [1] and interest concerning their synthesis and complex formation has grown very rapidly.[2-4] We have planned a systematic research on the synthesis and ligating behaviour of potential hexadentate macrocyclic ligands containing four phosphane groups and two different donor atoms. Our aim is to investigate the complex formation of such macrocycles as a function of: (*i*) the ring size, (*ii*) the nature of the two additional donors, and (*iii*) the nature of metal ions.

So far we have reported the preparation of macrocycles of the type I, namely 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclo-octadecane (L^1)[3,4] and 4,7,13,16-tetraphenyl-1,10-dipropyl-1,10-diaza-4,7,13,16-tetraphosphacyclo-octadecane.[5] These compounds can exist as five diastereoisomers due to the chirality of the phosphorus atoms (*e.g.* Figure 1). They are interconvertible at elevated temperature ($t_{\frac{1}{2}} \approx 7$ min at 140 °C) but are quite stable at room temperature.[3]

With L^1 we succeeded in separating its five diastereoisomers in a pure state.[3] The cobalt(II) and nickel(II) complexes showed a marked configurational and co-ordinative interdependence, the complexes having a substantially planar arrangement of the four phosphorus atoms and two, one, or no ethereal oxygens of the macrocycle co-ordinated to these metals as a consequence of the steric requisites of each isomer.[3,4]

We thought that the planar arrangement of phosphorus atoms could be due, at least in part, to the feeble donor ability of ethereal oxygens. Thioethereal sulphur, being a softer donor than ethereal oxygen, is expected to be more strongly binding and more competitive with phosphorus towards co-ordination of soft metal ions. A non-planar arrangement of the four phosphorus atoms might occur in metal complexes, thus also allowing a different denticity to each isomer.[3]



I

L^1: E = O
L^2: E = S

Accordingly, in this paper we report the synthesis of the ligand 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane (L^2) (structure I, E = S) and the separation of its five diastereoisomers. The stereochemistry of one of these isomers is definitely proved by determining the *X*-ray crystal structure of its nickel dibromide complex. A preliminary communication of this work has already appeared.[6] The configuration of a second isomer is unambiguously proved by ^{31}P n.m.r. spectroscopy. Some cobalt(II) and nickel(II) complexes of these two isomers are described.

Results and Discussion

Synthesis of the Macrocycle and Separation of Diastereoisomers.—The macrocycle L^2 has been synthesised according to the one-step reaction shown by equation (1). The isomeric

$$2\ Li_2[PhP{-}CH_2CH_2{-}PPh] + 2\ S(CH_2CH_2Cl)_2 \longrightarrow L^2 + 2\ LiCl \quad (1)$$

mixture of L^2 can be easily separated from the other products (predominantly polymers) of reaction (1) in an overall yield of *ca.* 14%. On the contrary, isolation of the single five diastereoisomers in a pure state is a lengthy process due to the very similar solubility and chromatographic properties of four of the five diastereoisomers. Progress in the separation can be effectively monitored by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

The β isomer of L^2 (Figure 1) can be readily separated owing to its low solubility in cold benzene. Fractional crystallisation

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† *Supplementary data available* (SUP No. 23801, 11 pp.): structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

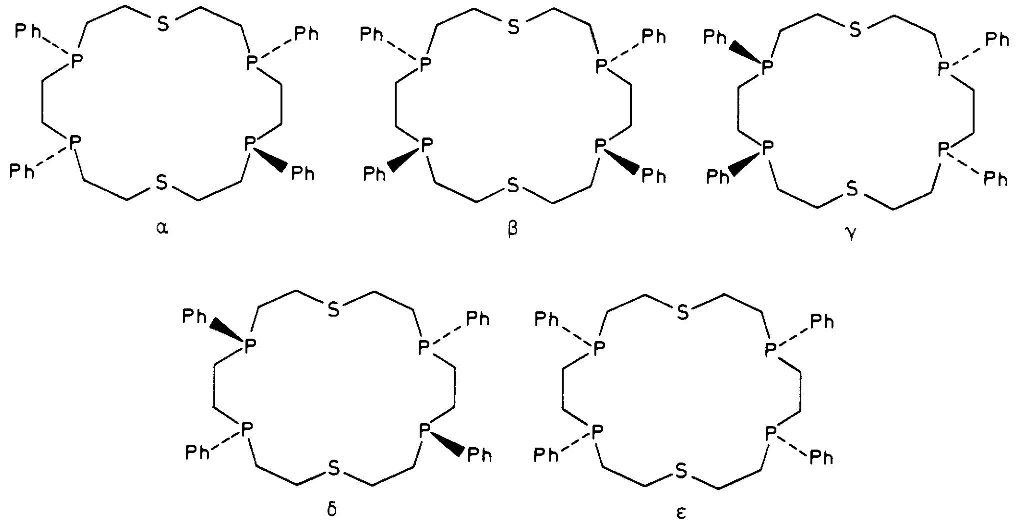

Figure 1. The five diastereoisomers of L^2

of the mixture of the remaining four isomers resulted only in enriched fractions. Ion-exchange chromatography on aqueous solutions of the nickel complexes, which proved to be successful for resolution of the isomeric mixture of L^1,[3] only led to a slight enrichment with L^2. Eventually, fractional crystallisation of the nickel complexes obtained from the enriched fractions allowed separation of the isomerically pure complexes. The pure diastereoisomers can be obtained from their respective nickel derivatives by cyanolysis (Table 1).

As found with L^1,[3] the present diastereoisomers of L^2 are thermally interconvertible, resulting in the same equilibrium mixture of the five diastereoisomers when boiled in *o*-xylene (144 °C) for 2 h. The equilibrium amounts of the diastereoisomers are, within experimental error, the statistically expected ones, *i.e.* α (50%), β, *c*, *d*, *e* (*ca.* each 12.5%).

The structural assignments of some of the five diastereoisomers are based on *X*-ray data and $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Our previous studies on the isomers of L^1 led us to substantiate an empiricism relating the mutual chiralities of the phosphane groups, as ascertained by *X*-ray analysis, to chemical shift values of the phosphorus resonances. We found that the resonances of *RR* and *SS* pairs of phosphane groups, linked by a CH_2CH_2 chain, fall at lower fields with respect to those of *RS* pairs.[3,5,7] Such an empiricism should reasonably hold true also in this case, due to the close similarity of the macrocycles. This was also found with the γ isomer of 4,7,13,16-tetraphenyl-1,10-dipropyl-1,10-diaza-4,7,13,16-tetraphosphacyclo-octadecane (L^3), the conformation of which was ascertained by *X*-ray crystallography.[5] Inspection of Figure 1 shows that the α isomer is unique in that it contains four non-equivalent phosphorus atoms: four resonances, therefore, are expected, two falling at lower fields (*RR* and *SS* pairs) and two at higher fields (*RS* pairs). Only one of the isolated isomers displays such a resonance pattern (−20.71, −20.83, −22.70, and −22.72 p.p.m.) to which the α structure is accordingly assigned. Each of the four remaining isomers presents equivalent phosphorus atoms, thus requiring a lone $^{31}P-\{^1H\}$ resonance. The two isolated isomers exhibiting lower-field $^{31}P-\{^1H\}$ lone signals at −20.87 and −21.06 p.p.m. should possess *RR*- or *SS*-$P-CH_2CH_2-P$ moieties. Accordingly, they should be assigned one of the two configurations β or δ of Figure 1. Indeed, a single-crystal *X*-ray structure determination on the nickel bromide complex of the isomer exhibiting the resonance at −20.87 p.p.m. confirms it to be the β isomer. Thus the *c* isomer exhibiting the resonance at −21.06 p.p.m. may tentatively be assigned the δ configuration. Finally, the two remaining *d* and *e* isomers, showing higher-field $^{31}P-\{^1H\}$ single resonances at −22.59 and −22.80 p.p.m., respectively, should be tentatively assigned one of the two configurations γ or ε of Figure 1.

Table 1. Analytical and physical data for the five diastereoisomers of L^2

Diastereoisomer	Found (%) * C	H	M.p. (°C)	$^{31}P-\{^1H\}$ N.m.r. (p.p.m.)
α-L^2	64.9	6.7	110—112	−20.71, −20.83, −22.70, −22.72
β-L^2	65.1	6.8	175—177	−20.87
c-L^2	65.0	6.6	144—145	−21.06
d-L^2	64.9	6.7	124—127	−22.59
e-L^2	65.1	6.6	166—167	−22.80

* Calc.: C, 65.05; H, 6.65%.

Cobalt(II) *and Nickel*(II) *Complexes with* α *and* β *Isomers*.—With the α and β isomers 1 : 1 complexes of cobalt(II) and nickel(II) are readily formed with bromide and tetraphenylborate anions (Table 2). All of these complexes are of the low-spin type. In order to ascertain both the configuration of the β diastereoisomer and the co-ordination geometry of its nickel complexes, the crystal structure of $[Ni(\beta-L^2)]Br_2\cdot 2H_2O$ has been determined by *X*-ray analysis (Tables 3 and 4). The compound consists of $[Ni(\beta-L^2)]^{2+}$ cations, Br^- anions, and lattice H_2O molecules. This diastereoisomer has the *meso* centrosymmetric configuration 4*RS*,7*RS*,13*SR*,16*SR*, thus justifying its β label according to Figure 1. The phenyl groups of two phosphorus atoms linked by CH_2CH_2 chains are in *trans* positions, confirming the ^{31}P n.m.r. criterion of configurational assignment for the present macrocycle.

The nickel atom lies in a centre of symmetry and is surrounded by the six donor atoms of the ligand (Figure 2). The four phosphorus atoms of the macrocycle lie in a plane with the two independent Ni−P distances having normal values [2.225(2) and 2.197(2) Å]. The two sulphur atoms lie approximately on the apical positions of a strongly elongated octahedron, the $P(CH_2)_2S(CH_2)_2P$ moieties adopting a facial arrangement. An essentially similar stereochemistry was found

Table 2. Analytical and physical data for some complexes of L^2

Compound	Colour	Analysis [a] (%)		$\tilde{\nu}$ [b]/cm^{-1}
		C	H	
$[Co(\alpha\text{-}L^2)][BPh_4]_2$	Yellow-green	73.6 (74.1)	6.7 (6.2)	Solid: 7 100 (sh), 9 400, 14 300, 21 000 (sh) MeCN: 9 200 (73), 14 700 (20), 21 500 (sh) (230), 26 600 (sh) (1 500), 33 500 (11 700)
$[Co(\alpha\text{-}L^2)]Br_2{\cdot}H_2O$	Yellow-green	47.6 (48.0)	5.2 (5.1)	Solid: 7 400 (sh), 9 100, 14 900, 21 700 (sh)
$[Ni(\alpha\text{-}L^2)][BPh_4]_2$	Brick red	74.2 (74.1)	6.4 (6.2)	Solid: 19 200, 25 600 MeCN: 19 200 (460), 26 200 (1 230), 33 400 (21 000)
$[Ni(\alpha\text{-}L^2)]Br_2{\cdot}3H_2O$	Pink	46.0 (46.1)	5.1 (5.4)	Solid: 19 600, 26 300 (sh)
$[Co(\beta\text{-}L^2)][BPh_4]_2$	Yellow-green	74.3 (74.1)	6.3 (6.2)	Solid: 14 800, 20 000 (sh)
$[Co(\beta\text{-}L^2)][BPh_4]_2{\cdot}2Me_2CO$	Yellow-green	73.5 (73.1)	6.5 (6.5)	Solid: 12 700
$[Co(\beta\text{-}L^2)]Br_2$	Light-green	48.3 (48.9)	5.1 (5.0)	Solid: 14 900, 20 400 (sh)
$[Ni(\beta\text{-}L^2)][BF_4]_2$	Violet	48.1 (48.2)	4.9 (4.9)	Solid: 18 100, 25 000 MeCN: 18 000 (215), 26 500 (sh) (1 160), 32 700 (23 800)
$[Ni(\beta\text{-}L^2)]Br_2{\cdot}2H_2O$	Violet	47.0 (47.0)	5.2 (5.3)	Solid: 18 200, 26 300

[a] Calculated values are given in parentheses. [b] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

Table 3. Positional ($\times 10^4$) non-hydrogen parameters with estimated standard deviations in parentheses for $[Ni(\beta\text{-}L^2)]Br_2{\cdot}2H_2O$

Atom	*x*	*y*	*z*
Ni	0	0	0
Br	3 358(1)	1 634(1)	3 426(1)
S	−737(3)	1 941(3)	1 489(3)
P(1)	−2 324(2)	−339(2)	660(2)
P(2)	−488(2)	1 420(2)	−1 958(2)
C(1)	−2 649(11)	1 711(11)	1 838(10)
C(2)	−3 056(10)	222(10)	2 076(9)
C(3)	−3 255(10)	852(10)	−672(10)
C(4)	−2 305(11)	2 076(11)	−1 658(10)
C(5)	−654(12)	478(12)	−3 055(11)
C(6)	304(12)	−690(12)	−3 136(11)
C(7)	−3 120(9)	−2 047(9)	1 111(8)
C(8)	−3 910(9)	−2 737(9)	2 387(9)
C(9)	−4 532(10)	−4 045(10)	2 659(9)
C(10)	−4 394(12)	−4 619(11)	1 717(11)
C(11)	−3 594(12)	−3 929(12)	419(11)
C(12)	−2 961(11)	−2 640(11)	136(10)
C(13)	479(8)	3 019(8)	−2 968(8)
C(14)	1 227(9)	3 257(9)	−4 269(8)
C(15)	1 944(10)	4 514(10)	−5 005(9)
C(16)	1 941(11)	5 493(11)	−4 469(10)
C(17)	1 220(11)	5 325(11)	−3 199(10)
C(18)	477(10)	4 053(10)	−2 419(9)
O	5 908(9)	1 777(9)	−4 915(8)

Table 4. Selected bond distances and bond angles with estimated standard deviations for $[Ni(\beta\text{-}L^2)]Br_2{\cdot}2H_2O$

Bond distances (Å)

Ni−S	2.942(2)	C(5)−C(6)	1.453(14)
Ni−P(1)	2.225(2)	C(7)−C(8)	1.390(11)
Ni−P(2)	2.197(2)	C(7)−C(12)	1.379(12)
S−C(1)	1.823(11)	C(8)−C(9)	1.412(12)
S−C(6)	1.872(11)	C(9)−C(10)	1.334(13)
P(1)−C(2)	1.823(10)	C(10)−C(11)	1.410(14)
P(1)−C(3)	1.842(10)	C(11)−C(12)	1.397(14)
P(1)−C(7)	1.816(9)	C(13)−C(14)	1.392(11)
P(2)−C(4)	1.826(10)	C(13)−C(18)	1.388(11)
P(2)−C(5)	1.823(11)	C(14)−C(15)	1.385(12)
P(2)−C(13)	1.800(8)	C(15)−C(16)	1.328(13)
C(1)−C(2)	1.511(13)	C(16)−C(17)	1.366(13)
C(3)−C(4)	1.531(13)	C(17)−C(18)	1.416(12)

Bond angles (°)

S−Ni−P(1)	79.8(1)	Ni−P(2)−C(5)	112.9(4)
S−Ni−P(2)	98.8(1)	Ni−P(2)−C(13)	122.2(3)
P(1)−Ni−P(2)	86.2(1)	C(4)−P(2)−C(5)	100.3(5)
Ni−S−C(1)	96.5(3)	C(4)−P(2)−C(13)	102.9(4)
Ni−P(1)−C(2)	112.2(3)	C(5)−P(2)−C(13)	108.3(4)
Ni−P(1)−C(3)	109.7(3)	S−C(1)−C(2)	113.0(7)
Ni−P(1)−C(7)	122.8(3)	P(1)−C(2)−C(1)	113.2(7)
C(2)−P(1)−C(3)	102.3(4)	P(1)−C(3)−C(4)	110.8(7)
C(2)−P(1)−C(7)	104.5(4)	P(2)−C(4)−C(3)	109.6(7)
C(3)−P(1)−C(7)	103.2(4)	P(2)−C(5)−C(6)	121.0(8)
Ni−P(2)−C(4)	107.6(3)		

with the cobalt ion $[Co(\beta\text{-}L^1)]^{2+}$ containing the ethereal analogue of the present macrocycle.[3] In $[Ni(\beta\text{-}L^2)]^{2+}$, however, the Ni−S distances [2.942(2) Å] appear to be very long when compared with normal Ni−S bond distances (2.3—2.4 Å). Such high values are usually considered non-bonding interactions. As is well known, regular octahedral low-spin complexes of nickel(II) have so far neither been ascertained by *X*-ray analysis, nor are expected to occur due to the energy requirements of a d^8 electron configuration.[8] These requirements are probably responsible for the weakness of the Ni−S interactions found in the present complex. Nonetheless, definite interactions between nickel and sulphur atoms do occur in this complex, affecting distinctly the electronic levels of a NiP_4 square-planar chromophore. Actually, the electronic spectrum of $[Ni(\beta\text{-}L^2)]^{2+}$ exhibits ligand-field bands at 18 000 (ε 215) and 26 500 cm^{-1} (1 160 dm^3 mol^{-1} cm^{-1}) (Table 2) and neatly differs from those of square-planar complexes with phosphane ligands. Such planar complexes usually show no absorption maximum below 25 000 cm^{-1}.[5,9,10] On the contrary, square pyramidal or supposed elongated octahedral complexes of the low-spin type are known to exhibit low-frequency transitions.[9,11] This has been attributed to the decrease in the energy differences among σ- and π-antibonding $d_{x^2-y^2}{}^*$, $d_{z^2}{}^*$, and $d_{xy}{}^*$ orbitals on going from square planar to five- or six-co-ordinate complexes.[12] Further indirect evidence of definite interactions between nickel and sulphur atoms in these complexes is also given by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. Indeed, $[Ni(\beta\text{-}L^2)]Br_2$ exhibits a single resonance at *ca.* 61 p.p.m. at room temperature in a variety of solvents including water, methanol and dimethyl sulphoxide (dmso) (63 p.p.m. in methanol at −85 °C). This chemical shift falls at a significantly lower-field value than that of the square-planar nickel complexes $[Ni(\gamma\text{-}L^3)]Br_2$, *i.e.* 45.1 p.p.m., where the amine groups are not co-ordinated.[5] Such a deshielding effect is indicative of phosphane groups sharing two five-membered chelate rings, which is the case for sulphur co-ordination, as opposed to phosphane groups involved in adjacent five- and eight-membered rings.[13]

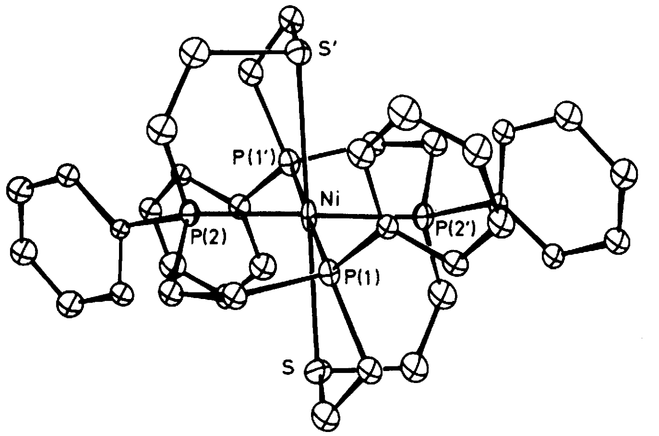

Figure 2. ORTEP drawing of the complex cation $[Ni(\beta\text{-}L^2)]^{2+}$

The solid cobalt(II) complexes of β-L^2 (Table 2) have reflectance spectra which are characteristic of octahedral low-spin configurations. They show no absorption below 12 000 cm^{-1} in contrast with square-planar and five-co-ordinate cobalt complexes which do exhibit electronic transitions in the range 5 000—10 000 cm^{-1}.[11–14] With the present complexes the frequencies of the peaks do not depend on the nature of the counter ions but depend on the presence of acetone molecules. Thus, the unsolvated complexes have $\nu_{max.}$ = 14 800 cm^{-1} whereas $[Co(\beta\text{-}L^2)][BPh_4]_2\cdot 2Me_2CO$ has $\nu_{max.}$ = 12 700 cm^{-1}. In order to account for these spectral data it is tentatively suggested that all the six donor atoms of the macrocycle are co-ordinated in the unsolvated complexes (CoP_4S_2 chromophores) but only the phosphorus atoms and acetone molecules in the solvate (CoP_4O_2 chromophore) are co-ordinated in the solvate complex. It may be recalled that the complexes $[Co(\beta\text{-}L^1)]^{2+}$ [3] and $[Co(\delta\text{-}L^1)]^{2+}$,[4] both containing CoP_4O_2 octahedral low-spin chromophores, exhibit the low-frequency band at 12 600 cm^{-1}.

All of these complexes are almost insoluble in non-co-ordinating solvents.

The ligand-field spectra of the cobalt compounds with the α-L^2 isomer are quite similar to each other (Table 2) and indicative of low-spin square-pyramidal configuration. Apart from a moderate blue shift, they closely resemble that of the ethereal analogue $[Co(\alpha\text{-}L^1)][BPh_4]_2\cdot 2Me_2CO$.[3] Actually, an *X*-ray structure analysis showed that the $[Co(\alpha\text{-}L^1)]^{2+}$ ion has a distorted square-pyramidal geometry with the four phosphorus atoms in a plane and one oxygen atom approximately in the apical position.[3] The oxygen atom spanning homochiral phosphane groups cannot co-ordinate to the metal atom due to the geometrical requisites of the α-macrocycle. According to the spectral results, a similar square-pyramidal geometry is thus attributed to the present thioethereal complexes.

With the nickel compounds of the α isomer, the ligand-field spectra are practically the same, both in the solid state and methyl cyanide solution, regardless of the nature of the counter ions. With respect to the spectrum of the elongated octahedral $[Ni(\beta\text{-}L^2)]^{2+}$ ion, these spectra show a considerable blue shift (1 200 cm^{-1}) and a moderate increase in intensity (ε 460 dm^3 mol^{-1} cm^{-1}) of the first band (Table 2). Both of these spectral features can be accounted for by assuming a square-pyramidal co-ordination for $[Ni(\alpha\text{-}L^2)]^{2+}$, as proposed for the cobalt analogue. Indeed, the blue shift of the first band is indicative of an overall weaker axial perturbation, and the increased band intensity is in agreement with the lack of the centre of symmetry in square-pyramidal compounds.

Experimental

Synthesis of Macrocycle.—Unless otherwise stated, all operations were performed under a dry nitrogen atmosphere. A 1.2 mol dm^{-3} benzene–diethyl ether 70% (v/v) solution of phenyl-lithium (125 cm^3, 150 mmol) was added dropwise to a stirred solution of 1,2-bis(phenylphosphino)ethane (18.6 g, 75 mmol) in absolute tetrahydrofuran (thf) (200 cm^3) at 20 °C. The yellow dilithium phosphide separated, and the suspension was refluxed for 15 min. After cooling to room temperature, a solution of 2,2'-dichlorodiethyl sulphide (12.0 g, 75 mmol) in thf was added dropwise over a 30 min period to the stirred suspension until a colourless solution resulted. This was allowed to warm at room temperature, refluxed for 30 min, and then evaporated to dryness. All subsequent operations were performed without protection against aerial oxidation.

The residue was suspended in benzene (400 cm^3) and centrifuged. The solution was chromatographed on silica gel and eluted with the same solvent (1 l). The combined benzene fractions were concentrated on a rotary evaporator, and the oily residue (23 g) was added with benzene (20 cm^3) and acetone (100 cm^3), separating a solid material (1.4 g). This material was recrystallised from benzene–acetone (40 cm^3, 1 : 1 v/v), giving white crystals of pure β-L^2 (yield 0.90 g, 3.5%) (Table 1). Since no further solid material could be obtained, the mother-liquors were again evaporated to dryness, the oily residue was dissolved in dichloromethane (50 cm^3) and added dropwise to an excess of $NiCl_2\cdot 6H_2O$ (8 g) in 95% ethanol (150 cm^3). The resulting deep brown solution was refluxed for 15 min, evaporated to dryness, and the residue extracted with 0.2 mol dm^{-3} NaCl aqueous solution (1 l). The filtered brown solution was poured on a column (8 × 20 cm) filled with SP-Sephadex C-25 Na^+ (Pharmacia). By elution with a 0.2 mol dm^{-3} NaCl aqueous solution, the central dark red fraction (*ca.* 8 l) was collected whereas the first and third fractions, orange in colour, were discarded. The central fraction was evaporated to dryness on a rotary evaporator, and reacted with an aqueous solution (50 cm^3) of KCN (8 g) at 80 °C under a nitrogen atmosphere (30 min). The warm reaction mixture was extracted with benzene three times, and the joint extracts were dried ($CaSO_4$) and evaporated to dryness. The oily residue was crystallised from acetone–ethanol, giving a solid material (m.p. 109—110 °C, yield 2.60 g). Analytical and $^{31}P\text{-}\{^1H\}$ n.m.r. data showed that this material was a mixture of L^2 isomers of approximate composition α (70), *c* (21), and *d* (9%). The overall yield in the separated isomers was 3.50 g, *i.e. ca.* 14%.

Either pure β-L^2 or the above isomeric mixture gave, when refluxed in *o*-xylene (144 °C) for 2 h, a material containing all of the five diastereoisomers in the following abundances: α, 50; β, 12; *c*, 12; *d*, 15; *e*, 11%, based on $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. Whilst the β isomer could be readily separated from the isomeric mixture, due to its very low solubility in cold benzene, we were unable to separate all the remaining four diastereoisomers by fractional crystallisation. Six recrystallisations of the isomeric mixtures from benzene–ethanol, collecting about one half of the starting material each time, afforded the pure α isomer (*ca.* 10% of the starting material) and two fractions (*ca.* 7% each) very rich in *c*, *d*, and *e* isomers, *i.e.*, α, 32; *c*, 24; *d*, 44%, and *c*, 70; *e*, 30%, respectively.

Isolation of α, *c*, and *d* isomers in the pure state was carried out by fractional crystallisation of their nickel complexes obtained from the isomerically enriched fractions. Firstly, the complexes with nickel chloride were prepared. The mixture of the solid complexes was then extracted with 0.2 mol dm^{-3} NaCl aqueous solution, leaving the nickel chloride complex of the *e* isomer as an insoluble material. On addition of KCN in slight excess to the filtered solution, the cyanide complexes of the remaining α, *c*, and *d* isomers precipitated. From this material the complex cyanide of the *c* isomer was isolated due to its solubility in chloroform. Pure $[Ni(\alpha\text{-}L^2)]Cl_2$ could also be recovered in high yield as the intermediate crops of a fractional crystallisation of α-rich nickel complexes in chloroform. Finally, the *d* isomer was obtained in low yield from the mixtures of $[Ni(L^2)]Cl_2$ complexes, rich in *d* isomer, by extracting the more soluble α and *c* complexes with chloroform. Cyanolysis of the isomerically pure nickel complexes gave pure α, *c*, *d*, and *e* isomers in *ca.* 50% yield.

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%.

$[Ni(\beta\text{-}L^2)][BF_4]_2$. A solution of $Ni(BF_4)_2\cdot6H_2O$ (0.2 mmol) in ethanol (3 cm^3) was added to a solution of the ligand (0.2 mmol) in dichloromethane (8 cm^3). Crystals separated which were filtered off, washed with dichloromethane, and dried *in vacuo*.

$[M(L^2)][BPh_4]_2$. A solution of $M(BF_4)_2\cdot6H_2O$ (0.2 mmol) and $Na(BPh_4)$ (0.5 mmol) in 15 cm^3 of 1 : 1 (v/v) ethanol–acetone 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 (b.p. 40—60 °C), and dried under vacuum.

$[M(L^2)]Br_2$. 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 20 cm^3 of 1 : 1 (v/v) acetone–dichloromethane. The resulting solution was evaporated to *ca.* 5 cm^3. On standing overnight, crystals separated which were filtered off, washed with ethanol–diethyl ether, and dried *in vacuo*.

Crystal Data.—$C_{36}H_{48}Br_2NiO_2P_4S_2$, $M = 919.3$, triclinic, space group $P\bar{1}$, $a = 9.645(3)$, $b = 10.159(3)$, $c = 10.869(3)$ Å, $\alpha = 68.07(4)$, $\beta = 78.09(4)$, $\gamma = 84.69(4)°$, $U = 966.5$ Å^3, $Z = 1$, $D_c = 1.588$ g cm^{-3}, $F(000) = 470$, $\lambda(\text{Mo-}K_\alpha) = 0.709\ 26$ Å, $\mu(\text{Mo-}K_\alpha) = 27.93$ cm^{-1}.

Data Collection.—The deep violet crystals are triclinic and belong to the space group $P\bar{1}$ with one $[Ni(\beta\text{-}L^2)]Br_2\cdot2H_2O$ formula per unit cell. Intensity data were collected on a Philips PW 1100 automatic computer-controlled diffractometer, 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 0.08° s^{-1} in a variable range of $(0.74 + 0.3 \tan \omega)°$ 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 [15] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $< 3\sigma(I)$. From the total 1 807 reflections, 1 395 had intensity $\geqslant 3\sigma(I)$. An absorption correction was applied by a numerical method. Atomic scattering factors for neutral non-hydrogen atoms were taken from ref. 16, those for hydrogen atoms from ref. 17. Correction for anomalous dispersion effects were also applied.[18]

Structure Determination and Refinement.—The positions of the nickel and bromine atoms were obtained from a Patterson synthesis. The other non-hydrogen atoms were obtained from successive F_o Fourier maps. The structure was refined by a full-matrix least-squares program.[19] The minimized 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 were introduced in calculated positions (C–H = 1.08 Å) with an overall isotropic thermal parameter of 0.05. Anisotropic thermal parameters were used for nickel, bromine, sulphur, and phosphorus atoms; isotropic thermal parameters were used for the other atoms. The final refinement gave an R value of 0.059, whereas R', defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, was 0.060. A final difference-Fourier map did not show remarkable features. The positional parameters are reported in Table 3.

N.M.R. Spectra.—$^{31}P\text{-}\{^1H\}$ N.m.r. spectra were recorded at 20 °C on a Varian CFT 20 spectrometer operating at 31.19 MHz with proton-noise decoupling and a deuterium lock. The solvent was $CDCl_3$ (Merck, 99.8%) unless otherwise stated. The deuterium frequency of the solvent was used for internal heteronuclear stabilization of the magnetic field. Shifts were referenced against external H_3PO_4 (85%), upfield shifts being negative.

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