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Macrocyclic Polyphosphane Ligands. Cobalt(II) and Nickel(II) Complexes of 5*RS*,8*RS*,16*RS*,19*RS*-Tetraphenyl-5,8,16,19-tetraphospha-1,12-dithiacyclodocosane (δ-L^1) and the Crystal Structure of $[Co(\delta\text{-}L^1)][BF_4]_2\cdot0.5H_2O$†

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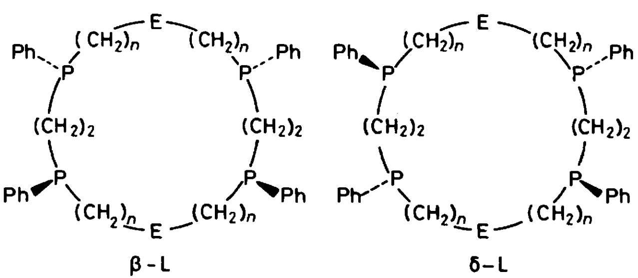
The chiral configuration of the title ligand, δ-L^1, has been established by the *X*-ray crystal structure determination of its cobalt complex $[Co(\delta\text{-}L^1)][BF_4]_2\cdot0.5H_2O$. The compound crystallises in the orthorhombic space group *Fddd*, with a = 31.424(6), b = 24.633(5), c = 22.223(5) Å, and Z = 16. Least-squares refinement gave R = 0.080 for 1 695 observed reflections. The cobalt atom is low-spin and octahedrally co-ordinated by the macrocycle which adopts meridional configurations for the $P(CH_2)_3S(CH_2)_3P$ moieties. The stereochemistry of some cobalt(II) and nickel(II) complexes of δ-L^1 with 1:1, 2:1, and 3:2 metal-to-ligand ratios is discussed.

Much interest is presently being devoted to macrocyclic polyphosphane ligands.[1] As part of our programme concerning the co-ordinative abilities of tetraphosphane macrocycles containing two additional donors, we have reported the syntheses and complex formation of a number of macrocycles of the type L, where n = 2 and E = O,[2,3] S,[4,5] or N-Pr.[6,7] The co-ordinative behaviour of these ligands toward iron(II), cobalt(II), and nickel(II) appears to be related markedly to (*i*) the mutual chiralities of the phosphane groups, which give rise to five diastereoisomers of each macrocycle, (*ii*) the nature of the E donor atoms, and (*iii*) the nature of the metal atom. In order to study the effect of the ring size we have recently reported the synthesis of the macrocycle L^1 (n = 3, E = S) and the isolation of three diastereoisomers in the pure form.[8] For one of these macrocycles, *i.e.* β-L^1, binuclear compounds of nickel have been obtained and their structure has been elucidated by *X*-ray analysis as well as by electronic and ^{31}P n.m.r. spectroscopy.[8] This paper describes the preparation and properties of some complexes of cobalt(II) and nickel(II) with another diastereoisomer, δ-L^1, of metal-to-ligand ratios 1:1, 2:1, and 3:2. The *X*-ray structure determination of $[Co(\delta\text{-}L^1)][BF_4]_2\cdot0.5H_2O$ is reported.



L^1; n = 3, E = S
L^2; n = 2, E = O
L^3; n = 2, E = S

Results and Discussion

The present diastereoisomer δ-L^1 readily forms complexes with cobalt(II) and nickel(II) (Table 1). The crystal structure of the low-spin complex $[Co(\delta\text{-}L^1)][BF_4]_2\cdot0.5H_2O$ has been determined by an *X*-ray analysis in order to ascertain the precise stereochemistry of the cation and to confirm the chiral configuration of the ligand, which had been tentatively proposed from ^{31}P n.m.r. data.[8] The structure consists of $[Co(\delta\text{-}L^1)]^{2+}$ cations, BF_4^- anions, and lattice water molecules. The Figure shows an ORTEP drawing of the cation. Bond distances and angles are reported in Table 2.

The macrocycle has the chiral configuration 5*RS*,8*RS*,16*RS*,19*RS* for the four phosphorus atoms. Due to the enantiomeric nature of the δ-L^1 ligand, the complex cations occur in two antipodic forms. The cobalt atom is octahedrally co-ordinated by the four phosphorus and the two sulphur atoms of the ligand. The phosphorus atoms are approximately coplanar with the cobalt atom, the largest deviation from the least-squares plane being 0.08 Å. The cations possess C_2 crystallographic symmetry, the two-fold axis passing through the cobalt atom and bisecting the P(1)–Co–P(1′) angle. The BF_4^- anions and the water molecules are also situated on the two-fold axes.

It is noteworthy that the P–E–P moieties adopt *mer* configurations as found with the $[Co(\delta\text{-}L^2)]^{2+}$ ion.[3] Such an arrangement, which contrasts with the *fac* configuration occurring with the complexes of the β-isomers, is a consequence of the mutual chiralities of the phosphorus atoms in the P $\cdots$ S $\cdots$ P moieties. This point was discussed previously in some detail.[2,3]

The Co–P bond distances of 2.295(3) Å (mean) are normal but slightly longer than values [2.25 Å (mean)] found with other polyphospha-macrocycles.[2,3,7] The two Co–S distances of 2.513(3) Å (mean) are significantly longer than the Co–P bonds (in spite of the similar covalent radii of sulphur and phosphorus), making the co-ordination octahedron an elongated one. These Co–S distances compare well with axial ones,

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† *Supplementary data available* (No. SUP 56202, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

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

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

Compound	Colour	Analysis (%)[a] C	H	Electronic spectra,[b] ν/cm^{-1}
$[Co(\delta\text{-}L^1)][BF_4]_2\cdot 0.5H_2O$[c]	Yellow-green	50.0 (50.40)	5.5 (5.50)	Solid: 12 900, 25 000 (sh) MeOH: 13 300 (30), 24 100 (1 800)
$[Co(\delta\text{-}L^1)][CoBr_4]$	Green	41.0 (41.45)	4.8 (4.50)	Solid: 5 500, 12 900, 13 800, 14 300, 14 900, 15 600, 25 000 (sh)
$[Ni(\delta\text{-}L^1)][BF_4]_2$	Red	50.1 (50.40)	5.4 (5.50)	Solid: 20 800, 25 000 MeOH: 20 800 (1 600), 25 000 (1 050)
$[Ni(\delta\text{-}L^1)][BPh_4]_2\cdot H_2O$	Red-brown	73.8 (73.60)	7.0 (6.60)	Solid: 21 000
$[Ni(\delta\text{-}L^1)]I_2\cdot 2H_2O$	Violet-brown	44.8 (44.90)	5.0 (5.30)	Solid: 20 400, 26 700
$[Ni(\delta\text{-}L^1)][CF_3CO_2]_2\cdot H_2O$	Violet	51.5 (51.60)	5.5 (5.30)	Solid: 20 800
$[\{NiBr_2\}_3(\delta\text{-}L^1)_2]\cdot 6H_2O$[d]	Brown	43.8 (43.55)	5.0 (5.25)	Solid: 23 300
$[\{Ni(NCS)_2\}_3(\delta\text{-}L^1)_2]\cdot H_2O$[e]	Orange	51.6 (52.05)	5.2 (5.40)	Solid: 23 300

[a] Calculated values are given in parentheses. [b] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] $\mu_{eff.}$ = 2.11 B.M. at 20 °C. [d] P, 11.0 (11.25); S, 5.6 (5.80); Br, 22.3 (21.75); Ni, 7.8 (8.00%). [e] N, 4.5 (4.25%).

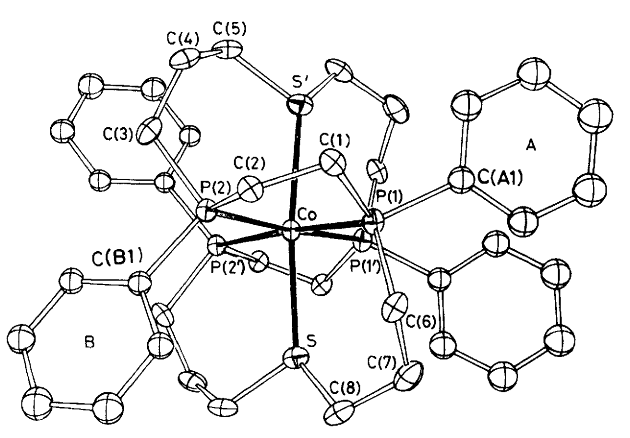

Figure. ORTEP drawing of the complex cation $[Co(\delta\text{-}L^1)]^{2+}$

Table 2. Bond lengths (Å) and angles (°)[a] with estimated standard deviations in parentheses, for $[Co(\delta\text{-}L^1)][BF_4]_2\cdot 0.5H_2O$[b]

Co–P(1)	2.291(3)	P(2)–C(3)	1.82(1)
Co–P(2)	2.298(3)	C(3)–C(4)	1.53(2)
Co–S	2.519(3)	C(4)–C(5)	1.52(2)
P(1)–C(1)	1.85(1)	C(5)–S′	1.81(1)
P(1)–C(A1)	1.83(1)	C(6)–C(7)	1.51(1)
P(1)–C(6)	1.84(1)	C(7)–C(8)	1.52(2)
C(1)–C(2)	1.50(1)	C(8)–S′	1.79(1)
P(2)–C(2)	1.85(1)	B(1)–F(1)	1.34(1)
P(2)–C(B1)	1.82(1)	B(1)–F(11)	1.37(1)

P(1)–Co–P(2)	83.8(1)	C(B1)–P(2)–Co	124.3(3)
P(1)–Co–P(1′)	94.9(2)	C(B1)–P(2)–C(2)	101.8(4)
S–Co–P(1)	85.0(1)	C(B2)–P(2)–C(3)	103.7(5)
P(2)–Co–P(2′)	97.9(2)	C(8)–S–Co	121.7(4)
S–Co–P(2)	84.9(1)	P(1)–C(1)–C(2)	111.8(7)
S′–Co–P(1)	99.4(1)	C(1)–C(2)–P(2)	109.0(2)
S′–Co–P(2)	90.7(1)	P(2)–C(3)–C(4)	120.1(9)
S′–Co–S	173.5(1)	C(3)–C(4)–C(5)	113.3(11)
C(1)–P(1)–Co	110.1(4)	C(4)–C(5)–S′	111.1(9)
C(6)–P(1)–Co	117.6(4)	C(5)–S′–Co	122.4(4)
C(6)–P(1)–C(1)	101.4(5)	P(1)–C(6)–C(7)	118.0(8)
C(A1)–P(1)–Co	119.5(3)	C(6)–C(7)–C(8)	115.2(10)
C(A1)–P(1)–C(1)	102.5(4)	F(11)–B(1)–F(11′)	107.0(18)
C(A1)–P(1)–C(6)	103.2(4)	C(7)–C(8)–S	111.7(8)
C(2)–P(1)–Co	106.9(4)	F(1)–B(1)–F(11)	108.0(5)
C(3)–P(2)–Co	116.7(4)	F(1)–B(1)–F(1′)	114.5(20)
C(3)–P(2)–C(2)	99.8(5)		

[a] For the benzene rings, bonds and angles were fixed at 1.395 Å and 120°, respectively; C–H distances were fixed at 1.08 Å. For the second BF_4^- anion B–F and F–B–F were fixed at 1.371 Å and 109.4°, respectively. [b] Primed atoms are related by the two-fold axis through the cobalt atom.

i.e. 2.479(1) Å, in the cobalt(II) complex ion of 1,4,7,10,13,16-hexathiacyclo-octadecane.[9]

Octahedral low-spin cobalt(II) complexes which have been characterised by *X*-ray structure determination are rare.[10] The paucity of such complexes can be attributed to the strong antibonding character of the e_g^* orbitals in regular octahedral co-ordination with such strong donors as those required to induce low-spin behaviour. Assuming only σ-donor capabilities, such octahedral complexes are 19-electron species which thus can gain some energy stabilisation by a moderate increase of the axial and/or equatorial bond distances. Furthermore, such species should distort due to the operation of a Jahn–Teller effect and, in fact, elongated[7,9,11] or compressed[12] octahedral geometries have always been found. Otherwise, the more usual five-co-ordinate 17-electron species occur.

It is interesting to compare the present structure with those adopted by the cobalt complexes of the 18-membered ligands L^2 and L^3 having analogous chirality. The $[Co(\delta\text{-}L^3)]^{2+}$ ion has been shown by spectral evidences to contain a trigonal-bipyramidal CoP_4S chromophore, a sulphur atom of the macrocycle being unco-ordinated.[5] We think that, in this case, the meridional arrangement of the P ··· S ··· P chains does not allow Co–P and Co–S distances long enough for the energy requirements of a d^7 low-spin octahedral configuration. On the contrary, the $[Co(\delta\text{-}L^2)]^{2+}$ ion adopts an octahedral stereochemistry as shown by an *X*-ray structural determination.[3] This is not surprising since the weak donor nature of the ethereal oxygen atoms should not make the d_{z^2} orbitals too antibonding in character.

The reflectance spectrum of $[Co(\delta\text{-}L^1)][BF_4]_2\cdot 0.5H_2O$ is typical of low-spin octahedral cobalt(II) complexes, exhibiting a band at 12 900 cm^{-1} and a shoulder at 25 000 cm^{-1}. No significant spectral change is found when the compound is dissolved in methanol (Table 1); thus octahedral stereochemistry is retained for this complex in solution.

The compound $2CoBr_2 \cdot \delta\text{-}L^1$ must be formulated as $[Co(\delta\text{-}L^1)][CoBr_4]$ according to its reflectance spectrum which shows the superimposed transitions of the low-spin octahedral $[Co(\delta\text{-}L^1)]^{2+}$ cation and the high-spin tetrahedral $[CoBr_4]^{2-}$ anions. Its room temperature magnetic moment, $\mu_{eff.} = 3.55$ B.M., is just that expected for an equimolar assembly of low-spin ($\mu_{eff.} = 2.1$ B.M.) and high-spin ($\mu_{eff.} = 4.5$ B.M.) cobalt(II) ions.

Different stoicheiometries are found with the nickel(II) complexes of δ-L^1 according to the nature of the anions. With anions of low co-ordinating ability (BF_4^-, BPh_4^-) or large volume (CF_3COO^-, I^-) complexes of a 1:1 nickel-to-ligand ratio are formed. They all exhibit reflectance and solution spectra typical of a low-spin trigonal-bipyramidal configuration such as that exhibited by $[Ni(\delta\text{-}L^3)]^{2+}$.[5] For the latter complex an *X*-ray investigation showed the presence of a trigonal-bipyramidal NiP_4S chromophore, one sulphur atom of the macrocycle being unco-ordinated.[5] This is in accordance with the well known reluctance of a d^8 electron configuration to form six-co-ordinate complexes with soft donors, whereas square planar or five-co-ordinate low-spin complexes readily occur. In this connection, however, it should be pointed out that $[Ni(\beta\text{-}L^3)]^{2+}$ has a very elongated octahedral geometry [Ni–S distances of 2.942(2) Å] which is also retained in solution.[4] This is made possible with the β-isomer, since the P···S···P moieties can adopt facial arrangements, thus allowing very long Ni–S distances. With the δ-isomers, as seen above for the cobalt derivative, only meridional arrangements of the P···S···P moieties can occur for an octahedral or a trigonal-bipyramidal geometry. Apparently, such weak Ni–S interactions result in an energetically more favourable arrangement than that of a square planar (NiP_4) or a five-co-ordinate (NiP_4S) structure. It appears that even the long propylenic chains of δ-L^1 do not allow the Ni–S distances to become long enough for the energy demands of the d^8 electron configuration in an elongated octahedral geometry.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the above nickel complexes, in methanol solution at room temperature, show only a singlet at 51.39 p.p.m. which is indicative of a fast co-ordinative rearrangement, on the n.m.r. time-scale, in the trigonal-bipyramidal ion.

With nickel(II) bromide and thiocyanate, 3:2 metal-to-ligand complexes are isolated. They are stable only in the solid state whereas in solution they dissociate almost completely to the trigonal-bipyramidal $[Ni(\delta\text{-}L^1)]^{2+}$ species. This contrasts with the behaviour of the 2:1 nickel complexes of β-L^1, which have been found to be quite stable towards dissociation.[8] *X*-Ray crystal structure determinations on these complexes could not be performed since we were unable to obtain crystals of diffraction quality. They are diamagnetic solids and exhibit reflectance spectra typical of square-planar nickel(II) complexes (Table 1).

Experimental

Synthesis of the Metal Complexes.—The ligand was prepared as previously described.[7] The cobalt(II) complexes were prepared under a nitrogen atmosphere. All the complexes were synthesised with minor modifications of the following general procedure. A solution of the ligand in acetone (*ca.* 4 mmol dm^{-3}) and a solution of the appropriate metal salt in 90% ethanol (20 mmol dm^{-3}) were mixed in stoicheiometric amounts. The resulting solution was refluxed for *ca.* 10 min and the same volume of boiling ethanol added. The solution was then reduced to *ca.* one fifth of its volume by boiling and then cooled to room temperature. On standing, crystals of the desired product separated, which were filtered off and washed with ethanol–light petroleum (b.p. 40—60 °C). The yields of the recrystallised complexes were in the range 70—80%.

Table 3. Positional parameters ($\times 10^4$), with estimated standard deviations in parentheses, for $[Co(\delta\text{-}L^1)][BF_4]_2 \cdot 0.5H_2O$

Atom	*x*	*y*	*z*
Co	1 584(1)	3 750(1)	3 750(0)
P(1)	2 077(1)	3 176(1)	4 164(1)
P(2)	1 103(1)	3 203(1)	4 241(1)
S	1 538(1)	3 055(1)	2 921(1)
C(1)	1 807(3)	2 614(4)	4 562(5)
C(2)	1 361(3)	2 532(4)	4 338(5)
C(3)	992(4)	3 367(5)	5 024(5)
C(4)	887(4)	3 951(6)	5 204(6)
C(5)	1 280(4)	4 303(5)	5 292(5)
C(6)	2 428(4)	2 800(5)	3 645(5)
C(7)	2 224(4)	2 412(5)	3 205(6)
C(8)	1 996(4)	2 679(5)	2 678(5)
C(A1)	2 298(2)	3 516(3)	5 321(3)
C(A2)	2 569(2)	3 731(3)	5 765(3)
C(A3)	2 988(2)	3 864(3)	5 607(3)
C(A4)	3 135(2)	3 782(3)	5 022(3)
C(A5)	2 864(2)	3 566(3)	4 587(3)
C(A6)	2 446(2)	3 433(3)	4 736(3)
C(B1)	216(3)	3 249(3)	4 167(3)
C(B2)	−181(3)	3 094(3)	3 945(3)
C(B3)	−209(3)	2 702(3)	3 493(3)
C(B4)	161(3)	2 446(3)	3 264(3)
C(B5)	558(3)	2 621(3)	3 486(3)
C(B6)	585(3)	3 013(3)	3 938(3)
B(1)	3 750(0)	2 543(10)	3 750(0)
F(1)	3 658(3)	2 837(4)	3 261(4)
F(11)	4 087(3)	2 212(3)	3 614(4)
B(2)	1 250(0)	1 250(0)	2 276(10)
F(21)	1 361(0)	1 499(0)	3 304(10)
F(22)	1 161(0)	1 636(0)	3 349(10)
F(23)	1 427(0)	1 751(0)	2 678(10)
F(24)	853(0)	1 232(0)	2 521(10)
O_w	1 250(0)	2 006(10)	1 250(0)

The tetraphenylborate derivatives were prepared by adding a strong solution of $NaBPh_4$ (50% excess) in ethanol to the acetone solution of the tetrafluoroborate derivatives. Attempts to prepare the nickel chloride complex gave irreproducible results.

Physical Measurements.—Visible and u.v. spectra were recorded on solutions with a Cary 17 and on solids with a Beckman DK-2 spectrophotometer. Magnetic susceptibility measurements were carried out with a Faraday balance. $^{31}P\text{-}\{^1H\}$ 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 CD_3OD (Merck, 99.8%). Shifts were referenced against external H_3PO_4 (85%).

Crystal Data for $[Co(\delta\text{-}L^1)][BF_4]_2 \cdot 0.5H_2O$.—$C_{40}H_{52}B_2CoF_8P_4S_2 \cdot 0.5H_2O$, $M = 962.43$, orthorhombic, space group *Fddd*, $a = 31.424(6)$, $b = 24.633(5)$, $c = 22.223(5)$ Å, $U = 17\,202.0$ Å^3, $Z = 16$, $D_c = 1.49$ g cm^{-3}, $F(000) = 7\,968$, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 6.57$ cm^{-1}.

Data Collection.—A crystal of approximate dimensions 0.05 × 0.05 × 0.10 mm was mounted on a Philips PW 1 100 automatic diffractometer. The unit-cell parameters were obtained by least-squares refinement of the setting angles for 22 reflections.

With graphite monochromatised Mo-K_α ($\lambda = 0.7107$ Å) radiation, 2 786 independent reflections were measured in the range $2.5 < \theta < 22.5°$ using the ω—2θ scan technique. A total of 1 695 reflections with intensity greater than $3\sigma(I)$[6,8] were considered observed and used in the structure analysis. Three reflections, monitored periodically, did not show any appreciable variation in intensity during data collection. Intensities were corrected for Lorentz polarisation effects but not for absorption.

Structure Determination and Refinement.—The structure was solved by means of Patterson and electron-density syntheses which gave readily the positions of all the non-hydrogen atoms.

Refinement was continued by the least-squares technique with anisotropic thermal parameters for non-hydrogen atoms, except for phenyl carbon atoms which were refined as rigid groups with isotropic thermal parameters.

The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/\sigma^2(F)$, where k is a variable factor. Hydrogen atoms were included in calculated positions with an overall thermal parameter of $U = 0.059$ Å^2 and their parameters were not refined.

Some difficulties arose in the refinement of one of the two independent BF_4^- anions, which was heavily affected by rotational disorder. The best results for this ion were obtained by refining two slightly rotated tetrahedral models, with a unique B–F distance and F–B–F angle, with a site occupation factor of 0.5.

The final difference Fourier synthesis showed only an isolated low-intensity peak, which was attributed to a water molecule with site occupation factor of 0.5.

Final R and R' agreement factors were respectively 0.080 and 0.079; R' is defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. All calculations were carried out with the SHELX 76[13] set of programs, which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms taken from the International Tables.[14]

Table 3 shows the final atomic co-ordinates for the non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plot of the Figure was produced by the program ORTEP.[15]

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