New Phosphorus-containing Macrocyclic Sexidentate Ligands: Two Isomers of 4,7,13,16-Tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclo-octadecane and Crystal Structures of their Cobalt Bis-(tetraphenylborate) Complexes

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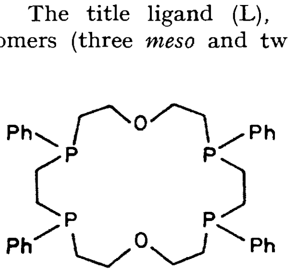
Summary Two geometrical isomers of the 18-membered macrocycle 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclo-octadecane (L) have been isolated and the crystal structures of their 1:1 complexes with cobalt bis(tetraphenylborate) are reported.

In recent years much interest has been devoted to macrocyclic compounds of the Pedersen's crown-ether type, with one or more oxygen atoms substituted by nitrogen and/or sulphur atoms.[1] Phosphine-containing macrocycles are few and only recently have tri- and quadri-dentate macrocyclic ligands containing up to four phosphine groups been synthesised.[2]

We now report the synthesis of the first 18-membered sexidentate macrocycle containing four phosphino and two ethereal groups. The title ligand (L), which has five possible stereoisomers (three *meso* and two ± pairs), has been prepared by adding 2,2′-dichlorodiethyl ether to a stoicheiometric mixture of 1,2-bis(phenylphosphino)ethane and phenyl-lithium in tetrahydrofuran (THF) at −20 °C. Standard work-up of the mixture gave two white crystalline isomers of (L) having m.p. 153—155 °C (L_α, 1·5% yield) and 191—193 °C (L_β, 2% yield).



(L)

These potentially sexidentate ligands readily react with cobalt(II) tetraphenylborate in EtOH giving low-spin complexes of formula $[Co(L_\alpha)][BPh_4]_2$ (A) and $[Co(L_\beta)][BPh_4]_3 \cdot 2DMF$ (B) (DMF = dimethylformamide) (after recrystallization from DMF). Complex (A) is a yellow crystalline solid having μ_{eff} (298 K) = 2·48 B.M. whereas complex (B) is a brick coloured solid with μ_{eff} (298 K) = 1·98 B.M. The crystal structures of both complexes have been determined by *X*-ray analyses.

Crystal data: (A) $C_{84}H_{84}B_2CoO_2P_4$. M = 1330·05, monoclinic, space group $P2_1/c$, a = 21·940(6), b = 14·242(5), c = 22·484(6) Å, β 90·22(8)°, U = 7025·5 Å^3, Z = 4, $F(000)$ = 2,812, μ(Mo-K_α) = 3·46 cm^{-1}, D_c = 1·26 g cm^{-3}. (B) $C_{90}H_{98}B_2CoN_2O_4P_4$, M = 1476·24, monoclinic, space group $P2_1/n$, a = 18·206(5), b = 12·572(4), c = 16·911(5) Å, β = 103·50(7)°, U = 3763·7 Å^3, Z = 2, F(000) = 1486, μ(Mo-K_α) = 3·23 cm^{-1}, D_c = 1·30 g cm^{-3}. Intensity data [2387 and 1479 unique observed reflections in the range $3° \leqslant \theta \leqslant 20°$ for compound (A) and (B), respectively] were collected on a Philips PW 1100 diffractometer with monochromatic Mo-K_α radiation. Absorption corrections were applied.

The structures were solved using the heavy atom technique and successive F_0 Fourier syntheses. Least squares refinements are still in progress, the R factors being 0·093 and 0·091, respectively in this first stage of calculation.†

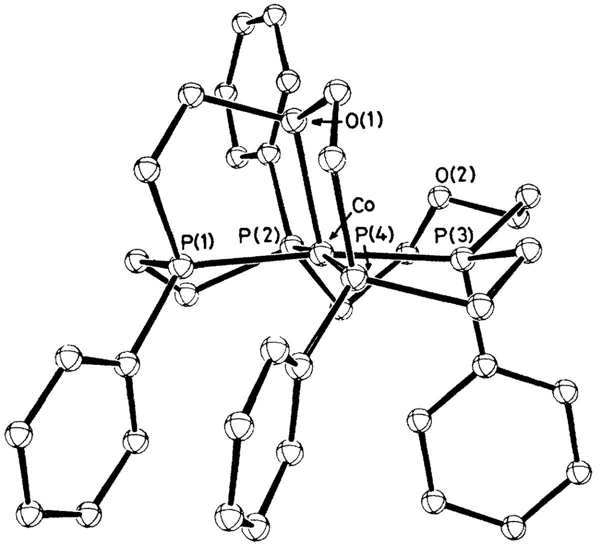


FIGURE 1. The structure of $[Co(L_{\alpha})]^{2+}$ cation of (A). Bond lengths: Co–P(1) = 2·221(6); Co–P(2) = 2·263(6); Co–P(3) = 2·305(6); Co–P(4) = 2·261(5); and Co–O(1) = 2·256(12) Å. Bond angles: P(1)–Co–P(2) = 85·9(2); P(3)–Co–P(4) = 82·8(2); P(1)–Co–O(1) = 80·5(4); and P(4)–Co–O(1) = 83·4(3)°.

The structure of (A) consists of $[Co(L_{\alpha})]^{2+}$ cations and $[BPh_4]^-$ anions; the structure of (B) consists of $[Co(L_{\beta})]^{2+}$ cations, $[BPh_4]^-$ anions, and interposed DMF solvent molecules. In complex (A), the cobalt atom is five-co-ordinated in a distorted square-pyramidal arrangement (Figure 1). An oxygen atom of the ligand is not co-ordinated, the Co–O(2) distance being 4·03 Å. The cobalt atom is *ca.* 0·15 Å above the basal plane of the four phosphorus atoms. In complex (B), however, the cobalt atom is six-co-ordinated according to a distorted octahedral geometry, where the metal atom is located at a crystallographic centre of symmetry (Figure 2). In both cations, the bound oxygen atoms do not reach the ideal apical positions, as shown by the P–Co–O angles within the chelate rings of 80·5—83·4°. This is probably due to strain in the ethylenic chains.

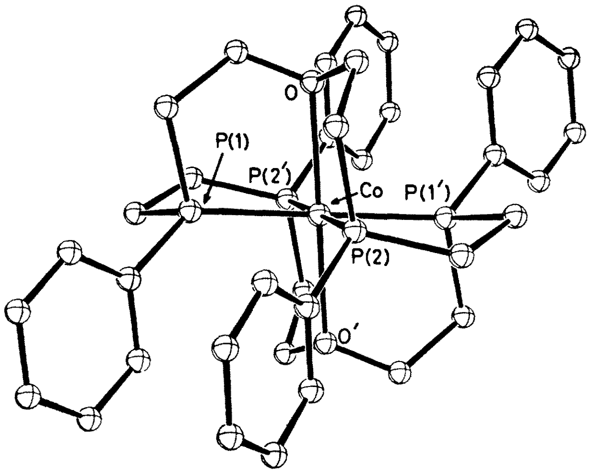


FIGURE 2. The structure of $[Co(L_{\beta})]^{2+}$ cation of (B). Bond lengths: Co–P(1) = 2·240(5); Co–P(2) = 2·245(6); and Co–O = 2·352(12) Å. Bond angles: P(1)–Co–O = 82·7(4); P(2)–Co–O = 82·3(4); and P(1)–Co–P(2′) = 85·3(2)°.

These structural results show that the L_{α} macrocycle is a ± pair (4*R**,7*R**,13*R**,16*S**) which has three phenyl groups on one side of the plane of the four phosphorus atoms. In contrast, the L_{β} macrocycle is a *meso* centrosymmetric isomer (4*R**,7*R**,13*S**,16*S**) which has the phenyl groups on two adjacent phosphorus atoms in the *trans*-position.

(*Received, 24th October* 1979; *Com.* 1135.)

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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