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Novel Phosphorus-containing Macrocyclic Sexidentate Ligands: Synthesis of (4*R**, 7*R**13*S**, 16*S**)-4,7,13,16-Tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclo-octadecane and Crystal Structure of its Nickel Dibromide Dihydrate Complex

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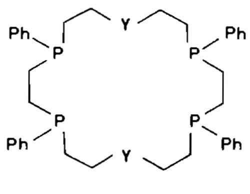
Phosphine-containing macrocycles are few and only recently have macrocyclic ligands containing four phosphino groups been synthesized [1]. Lately we reported synthesis and coordination behaviour of a 18-membered potentially sexidentate macrocycle, which contains four phosphino and two ethereal groups ([18]ane P_4O_2; L, Y = O). Five diastereoisomers are expected to occur due to the high racemisation energy of tertiary phosphines. In fact, two diastereoisomers were isolated displaying different coordination behaviour according to the absolute stereochemistry at the phosphorus atoms [2].

As a part of a systematic research on macrocyclic phosphine ligands we now report the synthesis of the title ligand containing four phosphino and two thioethereal groups ([18]ane P_4S_2; L, Y = S).



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Since thioethers are softer ligands than ethers, the present thioethereal macrocycle is expected to exhibit a stronger ligating ability towards soft transition metal ions than the ethereal analogue.

This ligand has been prepared by adding 2,2'-dichlorodiethylsulphide to a stoichiometric mixture of 1,2 (phenyl = phosphino) ethane and phenyllithium in tetrahydrofuran at –20 °C. Standard work up of the mixture gives one of the five possible diastereoisomers of [18]ane P_4S_2 as white crystals having m.p. 175–177 °C, 1% yield, (A). The formulation of the product is confirmed by analytical, molecular weight, and ^{31}P NMR spectral data. Its ^{31}P NMR spectrum (in $CDCl_3$) consists of a single peak in the region upfield from 85% H_3PO_4 (δ = 20.87).

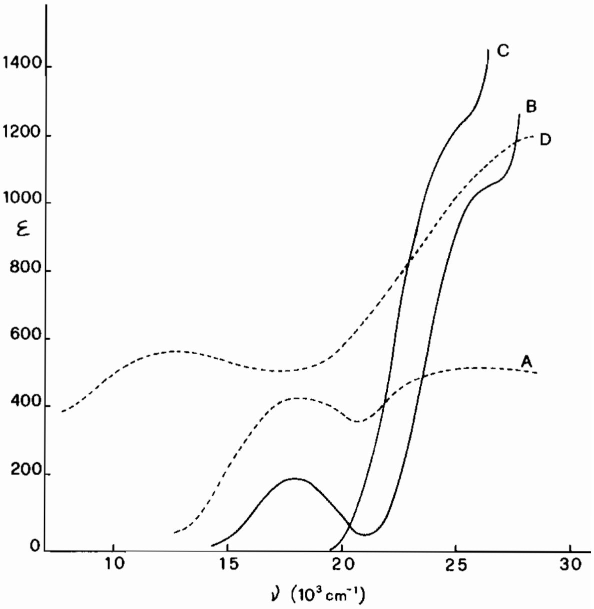

Fig. 1. Diffuse reflectance spectra: (A), $[Ni(A)](BF_4)_2$; (D), $[Co(A)][BPh_4]_2$ (absorbance arbitrary units). Absorption spectra in MeCN: (B), $[Ni(A)](BF_4)_2$; (C), $[Ni(Ph_2PCH_2CH_2PPh_2)_2](BF_4)_2$.

This diastereoisomer readily gives complexes with cobalt(II) and nickel(II).The deep violet $[Ni(A)]^{2+}$ ion is diamagnetic and exhibits a ligand field spectrum with bands at 18,000 and 26,000 cm^{-1} (Fig. 1). Such a spectrum differs significantly from those of square-planar NiP_4 chromophores, *e.g.* $[Ni(Ph_2PCH_2CH_2PPh_2)_2][BF_4]_2$. On the contrary, it closely resembles those of low-spin square-pyramidal nickel(II) complexes, [3], thus indicating a strong axial component of the ligand field.

In order to ascertain both configuration and ligating behaviour of ligand (A), the crystal structure of $[Ni(A)]Br_2\cdot 2H_2O$ has been determined by X-ray analysis. Crystals are triclinic, space group $P\bar{1}$, with 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)°, U = 966.5 Å^3, Z = 1, $F(000)$ 470, μ(Mo-Kα) = 27.9 cm^{-1}, D_c = 1.588 g cm^{-3}. Intensity data [1395 unique observed reflections in the range 2.5° $\leqslant \theta \leqslant$ 20°] were collected on a Philips PW 1100 diffractometer with monochromatic Mo-Kα radiation. Absorption corrections were applied. The structure was solved using the heavy atom technique and successive F_o Fourier syntheses. Least-squares refinement was performed to a conventional R factor of 0.059.

The structure of $[Ni(A)]Br_2\cdot 2H_2O$ consists of $[Ni(A)]^{2+}$ cations, Br^- anions and lattice H_2O mole-

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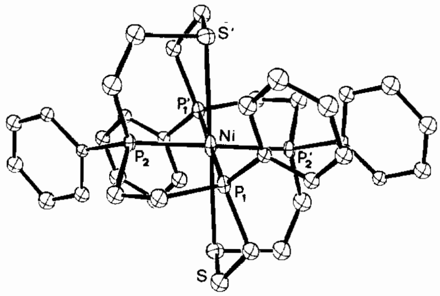

Fig. 2. The structure of [Ni(A)]$^{2+}$ cation. Bond lengths: Ni–S = 2.942(2); Ni–P(1) = 2.225(2); Ni–P(2) = 2.197(2) A. Bond angles: P(1)–Ni–S = 79.8(1); P(2)–Ni–S = 98.8(1); P(1)–Ni–P(2) = 86.2(1)°.

cules. Stereoisomer (A) has a *meso* centrosymmetric configuration (4*R**, 7*R**, 13*S**, 16*S**), the phenyl groups on two adjacent phosphorus atoms being in the *trans* positions. It has the same stereoisomeric configuration of β-[18]ane P_4O_2 [2].

The nickel atom lies in a centre of symmetry and is surrounded by the six donor atoms of the ligand (Fig. 2). The four phosphorus atoms lie in a plane at normal bond distances from the nickel atom, the mean bond distance being of 2.21 Å. The sulphur atoms lie approximately on the apical positions of a strongly elongated octahedron. The very long nickel–sulphur distances of 2.94 Å indicate rather weak interactions which, nonetheless, significantly affect the electronic spectral features of the complex. No spectral evidence of axial interaction, on the contrary, is found with the nickel complexes of β-[18]ane P_4O_2.

The low-spin green complex [Co(A)] $[BPh_4]_2$ is octahedral as shown by its electronic spectrum (Fig. 1). In this cobalt complex, therefore, macrocycle A actually behaves as a sexidentate ligand like its ethereal analogue β-[18]ane P_4O_2 does [2].

Acknowledgments

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