Inorganica Chimica Acta, 76 (1983) L153–L154

Crystal and Molecular Structure of the (4RS, 7SR, 13RS, 16SR)-4,7,13,16-Tetraphenyl-1,10-Dioxa-4,7,13,16-Tetraphospha-cyclooctadecane

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Received November 10, 1982

The phosphorus-containing macrocycle 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphospha-cyclooctadecane ([18]aneP$_4$O$_2$) is a potentially hexadentate ligand which occurs at room temperature in five interconvertible diastereoisomers due to the high-inversion barriers of the phosphane groups [1] (Fig. 1). These five diastereoisomers, which have all been isolated and characterized, have also been studied with respect to their ligational abilities toward cobalt(II) and nickel(II) [2, 3]. The crystal structures of cobalt(II) complexes with L$_\alpha$ [2], L$_\beta$ [2], and L$_\delta$ [3] isomers, which have been recently reported, allowed us to attribute phosphane configurations to the corresponding diastereoisomers. They also showed the different ligational capacity of these isomers in the formation of metal complexes: the L$_\alpha$ forms a five coordinated complex with an oxygen atom out of the coordination polyhedron, whereas the L$_\beta$ and L$_\delta$ reach the hexacoordination in two different ways [2, 3]. Structural assignments of the remaining γ and ϵ isomers were tentatively performed on the basis of a comparison of their coordinative behaviour toward cobalt(II) and nickel(II) as deduced from electronic spectra and electric conductivity data [3]. In order to prove definitely the proposed configuration of the ϵ diastereoisomer and to study its ligational capability, the crystal structure of the nickel(II) complex with this ligand was undertaken.

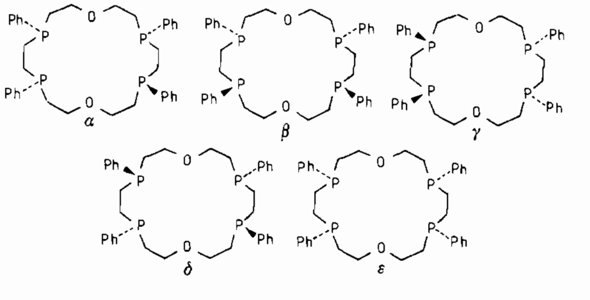

Fig. 1. The five diastereoisomers of [18]aneP$_4$O$_2$, L$_{\alpha-\epsilon}$.

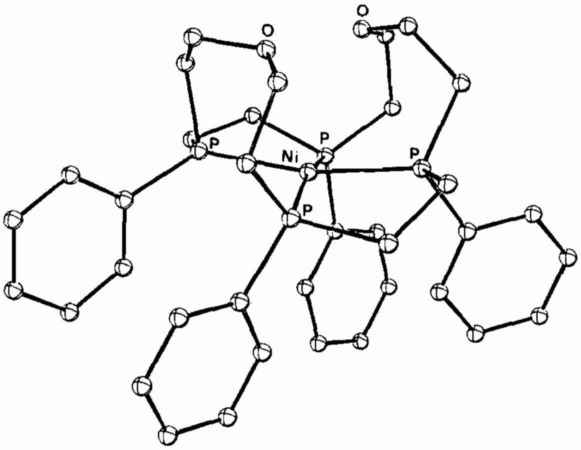

Fig. 2. The structure of one Ni(L$_\epsilon$)$^{2+}$ cation. The mean Ni–P bond length for both independent cations is 2.23 Å (range 2.20–2.26 Å). The P–Ni–P angles are 87.4(9), 96.7(9), 86.1(9), 93.0(9), 167.3(9), and 165.5(9)° around Ni(1), and 83.8(9), 95.5(9), 87.6(9), 97.6(9), 165.5(10), and 160.5(10)° around Ni (2).

[Ni(L$_\epsilon$)] [BPh$_4$]$_2$·2Me$_2$CO crystals are monoclinic, space group $P2_1/a$, with a = 38.137(9), b = 13.364(3), c = 29.610(7) Å, β = 94.31(4)°, V = 15068.2 Å^3, Z = 8, M = 1446.0, F(000) = 6128, D_c = 1.27 g cm^{-3}. The intensity data (2328 unique observed reflections in the range 5° $\leqslant 2\theta \leqslant$ 40°) were collected on a Philips PW 1100 diffractometer with monochromatic Mo-K$_\alpha$ radiation. The structure was solved using the heavy atom technique and successive F_o Fourier syntheses. The asymmetric unit is constituted by two independent [Ni(L$_\epsilon$)] [BPh$_4$]$_2$·2Me$_2$CO formulae. The least-squares refinement was performed to a final conventional R factor of 0.115. Despite this rather high value of the R factor, due to the scarce quality of the intensity data, to the high number of the independent non-hydrogen atoms (202), and to the disorder of the acetone solvent molecules, the results are satisfactory enough for the chemical purposes of the structural analysis.

The structure consists of [Ni(ϵ-[18]aneP$_4$O$_2$)]$^{2+}$, of tetraphenylborate anions, and of interposed acetone molecules. The two independent cations do not show substantial differences. The macrocycle has phosphorus configurations 4RS, 7SR, 13RS, 16SR thus confirming our previous tentative assignment [3]. Each nickel atom is linked to four phosphorus atoms of the ligand molecule (Fig. 2). The nickel

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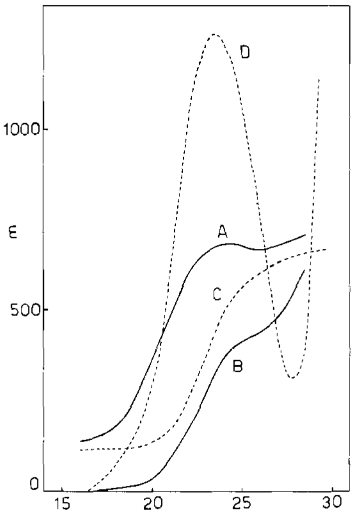

Fig. 3. Electronic spectra of [NiL][BPh$_4$]$_2$. L = ε-[18]aneP$_4$O$_2$: (A) solid state, arbitrary scale; (B) MeCN solution. L = γ-[18]aneP$_4$O$_2$: (C) solid state, arbitrary scale; (D) MeCN solution.

atoms lie approximately in the mean plane of the four phosphorus atoms (0.02 and 0.06 Å for the two independent molecules), which alternatively deviate by 0.26 (average) and 0.031 Å (average), respectively. The two oxygen atoms of the ligand lie on the same side of this plane, as is requested by the configuration of the ε macrocycle, which has all the phenyl rings in *cis*-positions. The nickel to oxygen distances of the two independent cations are 2.97(3) and 3.18(3) Å, and 3.11(3) and 3.22(3) Å. These distances are much longer than those expected for Ni–O covalent bonds, but may account for the weak interaction between oxygen and nickel atoms, as the electronic spectrum shows (Fig. 3). Indeed, this complex exhibits an absorption peak at a lower frequency than square-planar NiP$_4$ chromophores with similar donor sets, *e.g.* [Ni(γ-[18]aneP$_4$O$_2$)][BPh$_4$]$_2$ [3]. Such a spectral feature is characteristic of an axial contribution to the ligand field [4]. As is shown by the close similarity between the solid state and solution spectra, such a structure is kept substantially unchanged in MeCN solution and coordination of solvent molecules is prevented because of shielding operated by the phenyl groups and ethereal oxygens of the macrocycle. On the contrary, the less shielded planar [Ni(γ-[18]aneP$_4$O$_2$)]-[BPh$_4$]$_2$ complex, where the ethereal oxygens are forced to be away from nickel [5], shows very different absorption spectra in MeCN solution due to coordination of the solvent (Fig. 3).

References

1 R. D. Baechler and K. Mislow, *J. Am. Chem.Soc., 92,* 3090 (1970).
2 M. Ciampolini, P. Dapporto, A. Dei, N. Nardi and F. Zanobini, *Inorg. Chem., 21,* 489 (1982).
3 M. Ciampolini, P. Dapporto, N. Nardi and F. Zanobini, *Inorg. Chem.*, in the press.
4 C. Furlani, *Coord. Chem. Rev., 3,* 141 (1968).
5 This conformational requisite is clearly shown by the X-ray structure of the nickel tetraphenylborate complex with the diamine analogue of γ-[18]aneP$_4$O$_2$, *i.e.* 1,10-dipropyl-4RS,7SR,13SR,16RS-4,7,13,16-tetraphenyl-1,10-diaza-4,7,13,16-tetraphospha-cyclooctadecane;
M. Ciampolini, N. Nardi, F. Zanobini, R. Cini and P. L. Orioli, *Inorg. Chim. Acta Letrs.*, L452, in the press.