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Synthesis and Characterization of the Five Diastereoisomers of the First Crown Ether Type Phosphorus-Containing Macrocycle: Configurational and Coordinative Interdependence

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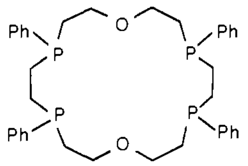
The first crown ether type phosphorus-containing macrocyle 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane ([18]aneP_4O_2) was synthesized in good yield via a one-step procedure. All of the five possible diastereoisomers were isolated and characterized. It was found that any given diastereosisomer racemizes at 140 °C through inversion at the phosphorus atoms, thus giving an isomeric mixture whose composition is close to the statistically expected one. The two most easily available isomers were used to form nickel(II) and cobalt(II) complexes of general formula $[M([18]aneP_4O_2)]X_2$ ($X = BF_4^-, BPh_4^-$), which were characterized via the usual physical techniques. The previously reported X-ray diffractometric results of the two cobalt(II) derivatives are discussed. It appears that the hexa- and pentacoordinate geometries of the two low-spin $Co^{II}([18]aneP_4O_2)$ chromophores are essentially due to the configurational properties of the two ligands. The expected coordination properties of the other three isomers are also discussed.

Introduction

Polyphosphanes are largely used as ligands toward transition-metal ions because of their property of stabilizing particular stereochemistries and often unusual oxidation states of metal ions, thus giving rise to systems of great interest in the area of coordination chemistry and homogeneous catalysis.[2-6] However, the difficulties involved in phosphane chemistry itself often interfere with further development of the research. For example, it is well-known that macrocyclic ligands form metal complexes characterized by enhanced thermodynamic stability and by peculiar patterns of reactivity.[7-9] However, although the chemistry of cyclic ligands containing nitrogen, oxygen, and sulfur as donor atoms has been successfully developed for two decades,[10] phosphorus-containing macrocycles are still rather rare and only recently have these compounds received considerable attention.[11-16]

We now report the synthesis of the first crown ether type phosphorus-containing macrocyle, i.e., the 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane ([18]aneP_4O_2) (I). This potentially hexadentate ligand can exist in five basic structural forms, which are interconvertible diastereoisomers. This is due to the high-inversion barriers of the phosphane groups.[17] All of these five isomers have been isolated and characterized; the two most easily available isomers in the pure state, L_α and L_β, have been used to form cobalt(II) and nickel(II) complexes of general formula $M([18]aneP_4O_2)X_2$ ($M = Co, Ni$; $X = BF_4^-, BPh_4^-$) which have been characterized via the usual physical techniques. The X-ray crystal structures of two cobalt(II) tetraphenylborate derivatives are also discussed.[18]



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Results and Discussion

The [18]aneP_4O_2 ligand has been synthesized via the one step macrocyclization process according to reaction 1 involving

$$2Li_2[(CH_2PPh)_2] + 2O(CH_2CH_2Cl)_2 \rightarrow [18]aneP_4O_2 \quad (1)$$

the electrophilic attack of two molecules of the bis(electrophile) bis(2-chloroethyl) ether on two bis(nucleophile) 1,2-bis(phenylphosphino)ethane moieties. Although the [18]aneP_4O_2 is a secondary product of this procedure, it can be easily separated from higher and lower molecular weight products and can be obtained in reasonable yield (12%).

Due to the difficulties involved in the isolation and manipulation of reactants and intermediates, attempts to perform multistep procedures were believed to be disadvantageous and not convenient at a practical level, although higher yields might be expected.

Since the structure of the molecule involves presence of four asymmetric phosphorus centers, the [18]aneP_4O_2 can exist in five basic structural forms (Figure 1). They differ from one another in the relative configurations of the four phosphorus atoms. Forms a, b, and c are nonenantiomeric, whereas forms d and e exist together with their respective enantiomers. The five forms are interconvertible diastereosisomers; however, since phosphorus racemization in these compounds occurs at relatively high temperatures, they may be separated and isolated at room temperature.

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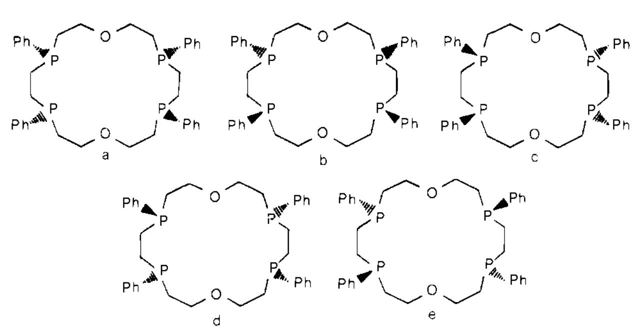

Figure 1. The five possible diastereoisomers of the [18]aneP_4O_2 ligand.

Table I. Analytical and Physical Data for the Five [18]aneP_4O_2 Diastereoisomers

diastereoisomer	anal. found,[a] % C	H	mol wt (osm)[b]	mp, °C	^{31}P NMR, δ
α-[18]aneP_4O_2	68.6	7.1	648	165-166[d]	21.67, 21.68 23.19, 23.23
β-[18]aneP_4O_2[c]	68.6	7.4	653	202-203[d]	21.54
γ-[18]aneP_4O_2	68.1	7.0	643	172-174	23.18
δ-[18]aneP_4O_2	68.4	7.2	612	112-114	21.87
ε-[18]aneP_4O_2	68.2	7.2	618	112-113	23.58

[a] Calcd: C, 68.34; H, 7.01. [b] Calculated molecular weight, for $C_{36}H_{44}P_4O_2$, is 632.65. [c] Calcd: P, 19.58. Found: P, 19.8. [d] These values are higher than those reported in ref 18.

In fact, the ^{31}P NMR spectra of chloroform solutions of crude [18]aneP_4O_2 samples show a pattern of eight resonances, which, as it will be discussed below, indicates simultaneous existence of all five diastereoisomers as products of the synthesis. However, attempts to achieve a complete resolution of the isomeric mixture into the five individual constituents were only partially successful. One isomer, labeled as β-[18]aneP_4O_2, can be separated and obtained in a pure crystalline form as a result of its significantly lower solubility in cold benzene. The four remaining isomers are characterized by very similar solubility and adsorption properties; thus their separation by means of fractional crystallization or chromatographic methods is very difficult. We succeeded in our task by using the ion-exchange chromatography technique on aqueous solutions of the nickel(II) derivatives. A 0.2 M NaCl solvent was found to be an efficient eluent, with SP-Sephadex C-25 as support (Table I).

In the above hypothesis, the diastereomeric nature of the constituents present in the crude [18]aneP_4O_2 is supported by the following experimental evidence. The proton-decoupled ^{31}P NMR spectrum of the β isomer consists of a single resonance; however, if a sample of this isomer is refluxed in *o*-xylene at 142 °C, the solid material recovered exhibits a ^{31}P NMR spectrum consisting of eight resonances lines, the line of the starting β isomer being still present. The half-life for the racemization of the β isomer is approximately 7 min at this temperature. The relative intensities of the eight signals do not vary if reflux times longer than 1 h are employed (Figure 2). A superimposable spectrum is also obtained when a similar procedure is performed with the α isomer: once again the spectrum consists in the same eight resonances, among which are the four lines of the starting pure α isomer. Therefore, it can be suggested that in both cases inversion processes at the phosphorus atoms take place leading to the same final mixture.

Similar results are obtained by melting [18]aneP_4O_2 samples under nitrogen. However, this procedure is less desirable than the one shown above since mass spectroscopy at various temperatures indicates that partial decomposition of the macrocycle is taking place above 200 °C.

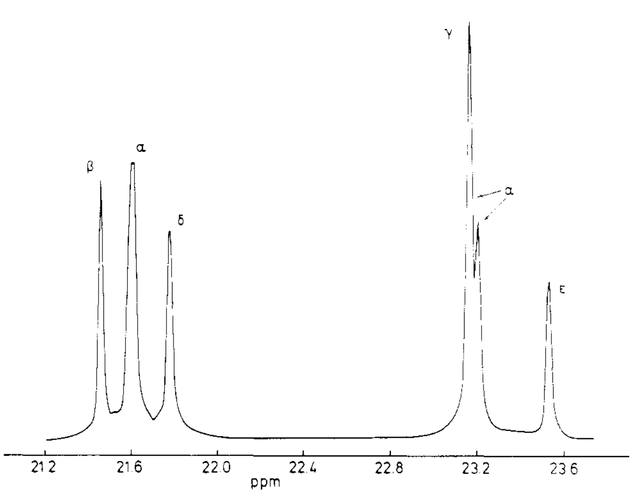

Figure 2. Proton-decoupled ^{31}P NMR spectrum at 20 °C of a $CDCl_3$ solution of a β-[18]aneP_4O_2 sample after refluxing in *o*-xylene.

The assignment of the resonances as reported in Figure 2 has been performed on the assumption that the [18]aneP_4O_2 molecule contains two 1,2-ethylenediphospha fragments, which in turn may exist as meso or *dl* moieties, depending on the chirality of the phosphane groups. We may tentatively suppose that the two fragments do not significantly interact with each other since they are separated by the two long aliphatic chains containing the ethereal groups. If these considerations hold true, then it seems reasonable to expect that the resonances of the *RR* and *SS* pairs of phosphane groups would fall in a given spectral range, whereas those of the *RS* pairs would fall in a different spectral range. Since, as it will be shown below, the configuration of the β and α isomers are those labeled in Figure 1 as b and d, respectively, we suggest that signals falling in the 21.54–21.87-ppm range are to be attributed to *RR* or *SS* pairs and those falling in the 23.18–23.58-ppm range belong to *RS* pairs. As a matter of fact, the b diastereoisomer is characterized by the coexistence of *RR* and *SS* pairs in the molecule, whereas the d enantiomers contain *RR* or *SS* pair together with an *RS* pair. As expected, the b diastereoisomer exhibits only one resonance signal at 21.54 ppm, whereas four resonances at 21.67, 21.68, 23.19, and 23.23 ppm appear in the spectrum of the d diastereoisomer which has four nonequivalent phosphorus atoms. On this basis, the δ isomer, which exhibits a single signal at 21.87 ppm, is tentatively assigned to the e isomer. In fact, its enantiomers contain two *RR* or two *SS* pairs. On the contrary, uncertainties arise in assigning the signals at 23.18 and 23.58 ppm to the a and c diastereoisomers since both of them contain couples of *RS* pairs.

The resonance overlap inhibits an accurate estimation of the relative amount of each diastereoisomer at equilibrium. A rough estimation of the integrated intensities gave the following values: α, 49; β, 16; γ, 12; δ, 14; ε, 9%. On the basis of statistical considerations, the expected proportions are 50% for the α isomer and 12.5% for the other four isomers. The close agreement between observed and expected patterns of intensities suggests that in the [18]aneP_4O_2 molecule the racemization process at the phosphorus atom does not significantly depend on chirality of neighboring atoms and, in conclusion, on the overall stereochemistry of a given diastereoisomer. In fact the present data show that the free energy change for the interconversion reaction

$$[18]\text{ane}P_4O_{2(i)} \rightleftarrows [18]\text{ane}P_4O_{2(j)}$$

$$i, j = a\text{–}e$$

is, when corrected for statistical effects, near zero. This indicates that both internal and solvation energy terms must be very similar for each diastereoisomer.

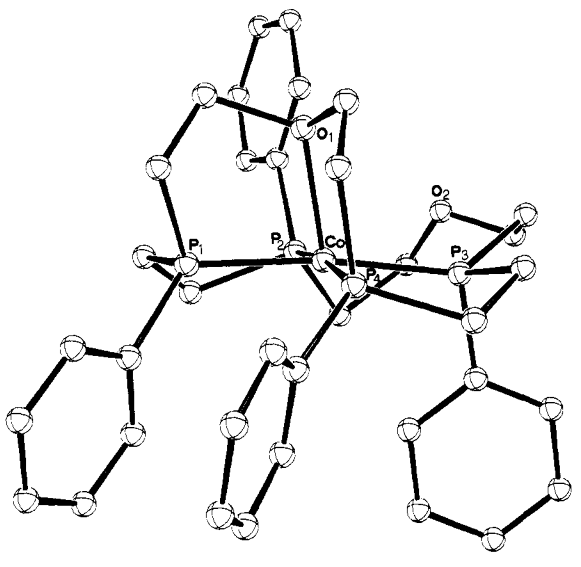

Figure 3. ORTEP drawing of the Co(α-[18]aneP$_4$O$_2$)$^{2+}$ cation.

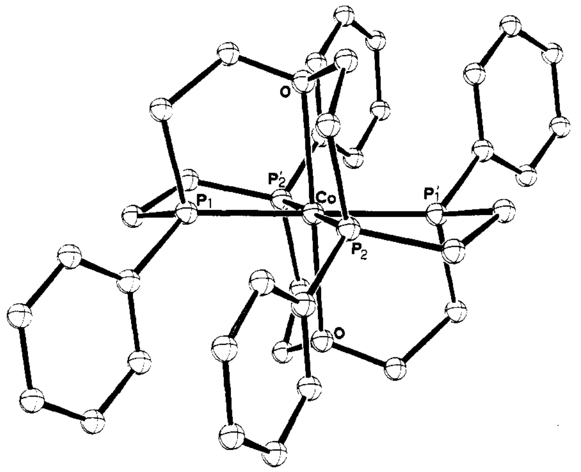

Figure 4. ORTEP drawing of the Co(β-[18]aneP$_4$O$_2$)$^{2+}$ cation.

Compounds of general formula M([18]aneP$_4$O$_2$)X$_2$ (M = Co, Ni; X = BPh$_4^-$, BF$_4^-$) have been synthesized with both α and β diastereoisomers. All of the complexes are low-spin, the nickel(II) derivatives being diamagnetic and the cobalt(II) analogues exhibiting effective magnetic moments in the 2.0–2.5-μ_B range at room temperature.[18] The results of X-ray diffractometric analysis of bis(tetraphenylborate)cobalt(II) derivatives with both α and β diastereoisomers have already been reported and only briefly discussed.[18] It has been shown that both compounds consist of Co([18]aneP$_4$O$_2$)$^{2+}$ cations and BPh$_4^-$ anions. The structures of the two cations are schematically reported in Figures 3 and 4.

The Co(α-[18]aneP$_4$O$_2$)$^{2+}$ cation exists in two enantiomeric forms as a result of the racemic nature of the ligand. The configurations of the phosphane groups are 4*RS*, 7*RS*, 13*RS*, and 16*SR*. Thus this diastereoisomer can be described in terms of the structure d shown in Figure 1. The cobalt(II) ion is pentacoordinated in a distorted square-pyramidal arrangement (Figure 3). This geometry is achieved through the coordination of the four phosphorus atoms of the ligand and one of the two ethereal oxygen atoms. The phosphorus atoms lie approximately on the basal plane of the coordination polyhedron, the deviations from the mean plane being small (0.0050–0.0054 Å). The five-membered chelate rings adopt gauche $\delta\lambda$ conformations. As a consequence of the different configurational character of the phosphane groups, the phenyl substituents have pseudoequatorial character as far as the (*RR*)- or (*SS*)-ethylenediphospha units are considered and occupy pseudoequatorial and pseudoaxial positions in the (*RS*)-ethylenediphospha unit. This difference is reflected in the conformations of the five-membered chelate rings, the *RS* unit adopting an asymmetric gauche conformation, whereas the *RR* and *SS* ones are quite symmetric. Therefore, three phenyl groups are oriented on the same side of the basal plane, and one on the opposite side.

Although the [18]aneP$_4$O$_2$ may be considered a potentially hexadentate ligand, it is apparent that the actual pentadentate ligand behavior is a direct consequence of the peculiar configurational propertis of the α-[18]aneP$_4$O$_2$ diastereoisomer. As a matter of fact, if the four phosphorus atoms adopt a planar coordinating arrangement, the ethereal group may act as a donor only if the ethylenic chains spanning the oxygen and the phosphorus atoms occupy pseudoaxial positions with respect to the five-membered chelate rings containing the phosphorus atoms themselves. When this occurs, the facial coordination of the phosphorus–oxygen–phosphorus moiety is possible. This condition can be satisified only if the phenyl groups behave as pseudoequatorial substituents and if the two phosphane groups have opposite chirality. Therefore, the bis(ethylenic) ethereal moiety joining the phosphorus atoms 4 and 16 can adopt a favorable conformation for oxygen coordination since the above phosphorus atoms have opposite configurations. On the contrary, the other ethereal group cannot act as a donor since the phosphorus atoms have the same configuration.

The coordination polyhedron observed in this compound is not an unusual one for low-spin five-coordinate cobalt(II) complexes.[19] When the electronic properties of the cobalt(II) ion are considered and the steric requirements of the actual [18]aneP$_4$O$_2$ ligand neglected, it is obvious that a square-pyramidal geometry is favored with respect to the trigonal-bypyramidal one.[20] Examples are the chromophores [Co(CN)$_5$]$^{3-}$,[21] [Co(NP$_3$)I]$^+$,[22] [Co(PNNP)Br]$^{2+}$,[23] and [Co(dpe)$_2$X]$^+$.[24] On the other hand, if one considers the geometrical features of the [18]aneP$_4$O$_2$ ligand, the acute angle bite of the ethylenediphospha unit is apparently unfavorable for a trigonal-bipyramidal geometry. Molecular models strongly support this suggestion. The cobalt(II) ion lies slightly above the mean basal plane (0.12 Å). The metal–phosphorus distances are in the 2.2–2.3-Å range, as is usually found in low-spin five-coordinate cobalt(II) complexes with polyphosphane ligands.[19] Again the P–Co–P angles exhibit the values of 80–85°, a common condition for these five-membered chelate rings. On the other hand, the cobalt(II)–oxygen distance (2.26 Å) is rather long. It is noteworthy that the oxygen atom does not reach the ideal apical position of the coordination polyhedron, the deviation being about 9° with respect to the perpendicular to the mean basal plane. These results are believed to be essentially due to the steric constraints of the ligand. A regular facial coordination of the phosphorus–oxygen–phosphorus donor system would require more flexible aliphatic chains.

The structure of the Co(β-[18]aneP$_4$O$_2$)$^{2+}$ cation is shown in Figure 4. In this compound the metal ion is hexacoordinate,

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a rather rare stereochemistry for low-spin cobalt(II) complexes. The four phosphorus atoms occupy the four equatorial positions while the two oxygens fill in the apical ones. The coordination polyhedron is an elongated octahedron. The complex cation is centrosymmetric as it is allowed by the stereochemical properties of the ligand, the configurations of the phosphane groups being 4*R*, 7*R*, 13*S*, and 16*S*. The hexadentate behavior of this diastereoisomer is a result of its peculiar configurational properties. The two ethylenediphospha units adopt highly symmetrical gauche conformation ($\delta\lambda$), the phenyl substituents occupying pseudoequatorial positions, as far as the five-membered chelate rings are considered. Therefore, since couples 4,16 and 7,13 of phosphorus atoms have opposite configurations, coordination of both ethereal groups is possible.

The metal ion lies in the plane of the four phosphorus donors. Both distances and angles between the acceptor and the donors are similar to those observed for the α-diastereoisomer derivative. Again the oxygen atoms do not achieve their ideal apical positions, the deviation from the perpendicular to the equatorial plane being 7°. The cobalt(II)–oxygen distances are rather long: the observed value of 2.35 Å is still higher than the one observed in the α-isomer derivative. This result may be attributed to the occurrence of large in-plane distance due to the Co–P bonds and to the constraints imposed by the ethylenic chains. In the pentacoordinate derivative, the observed shorter Co–O distance may be favored by removal of the metal ion from the equatorial plane.

The low-spin configuration of these cobalt(II) complexes is not an unexpected result. The in-plane field strength produced by the four phosphorus atoms is sufficiently strong to induce spin-pairing in the d^7 electronic configuration, a condition found common to cobalt(II) complexes of other polyphosphane ligands.[25] The observed effective magnetic moments are consistent with those usually found in low-spin penta- and hexacoordinate cobalt(II) complexes.[19]

The different nature and coordination geometry of the cobalt(II) chromophores with the α and β diastereoisomers is reflected in their EPR and electronic spectra. The EPR spectra of polycrystalline samples of both bis(tetraphenylborate) derivatives were recorded at liquid-nitrogen temperature with both X-band and Q-band frequencies. The spectrum of the α-isomer complex shows a rhombic symmetry with g_1, g_2, and g_3 values of 2.48, 2.30, and 2.00, respectively. Hyperfine splitting is observed in the g_3 region, the hyperfine A_3 coupling constant being equal to 89×10^{-4} cm^{-1}. On the other hand, the spectrum of the β-isomer derivative shows a pseudoaxial symmetry, the observed g_1, g_2, and g_3 values being 2.20, 2.18, and 2.00, respectively. Hyperfine splitting was also observed in this case in the g_3 region, the H_3 coupling constant being 75×10^{-4} cm^{-1}.

The observed pattern of g values can be interpreted by assuming an electronic $(d_{xy})^2(d_{z^2})^1$ ground state, which is the expected one for both elongated octahedral and square-pyramidal chromophores.[26-28] A pattern $g_x \geq g_y > g_z \approx 2.0$ is theoretically predicted and experimentally supported for low-spin square-pyramidal cobalt(II) complexes. Again, for hexacoordinate axially elongated chromophores theory predicts a $g_\perp > g_\parallel$ spectral behavior, as in fact it occurs in the β-diastereoisomer derivative spectrum.

The electronic spectra of the two cobalt(II) complexes are shown in Figure 5. The α derivative exhibits a pattern of bands at 7.7, 14.8, and 22.8×10^3 cm^{-1} that are typical of pentacoordinate low-spin cobalt(II) in square-pyramidal geometry.[19] Again the spectrum of the β derivative, which shows bands at 11.5 and 21.3×10^3 cm^{-1}, is fully consistent with an elongated octahedral geometry of a low-spin d^7 chromophore.[29]

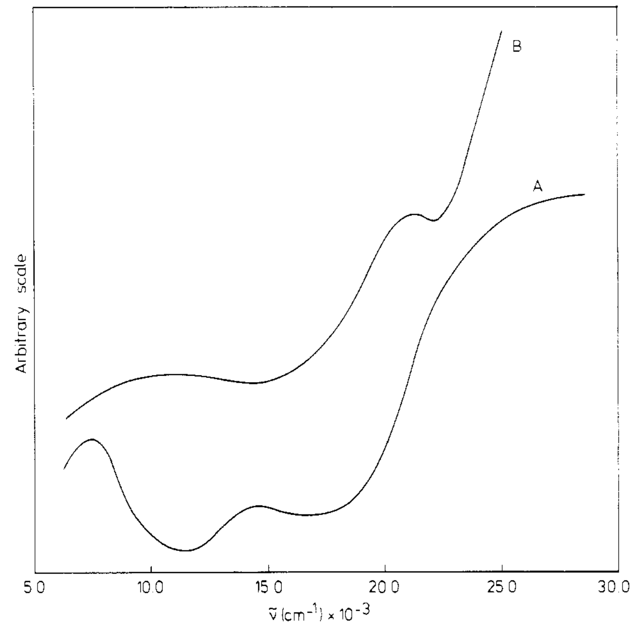

Figure 5. Electronic spectra of Co(α-[18]aneP_4O_2)[BPh_4] (A) and of Co(β-[18]aneP_4O_2)[BPh_4]·2DMF (B).

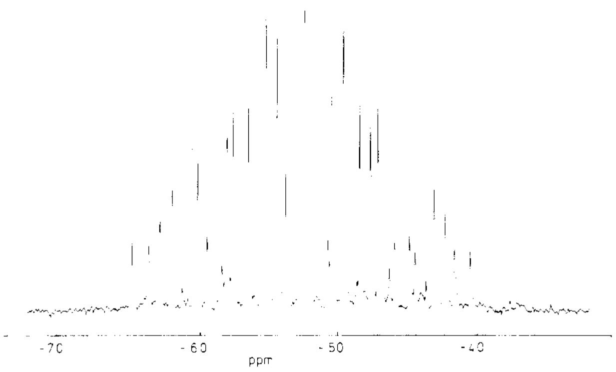

Figure 6. Proton-decoupled ^{31}P NMR spectrum at 20 °C of Ni(α-[18]aneP_4O_2)[BF_4]$_2$ in dimethyl-d_6 sulfoxide.

The electronic spectra of the nickel(II) tetraphenylborate complexes exhibit a single band in the high energy region at ca. 26×10^3 cm^{-1}. These spectra show striking similarity with those of well-known square-planar NiP_4 chromophores, thus suggesting that this transition has to be assigned as $^1A_{1g} \rightarrow {}^1E_g$ of d^8 square-planar complexes.[30] It is well-known, however, for these chromophores that this electronic transition is rather insensitive to weak axial perturbations. It should be recalled that controversies have arisen concerning the coordination numbers of claimed hexacoordinate nickel(II) complexes having a singlet ground state. Examples are $Ni(das)_2I_2$[31] or $Ni(dpe)X_2$ (X = Cl, Br).[32] In particular, as far as ethereal donors are considered, it was shown that the pentacoordinate $[Ni(NOP_2)I]^+$ chromophore exhibits an electronic spectrum

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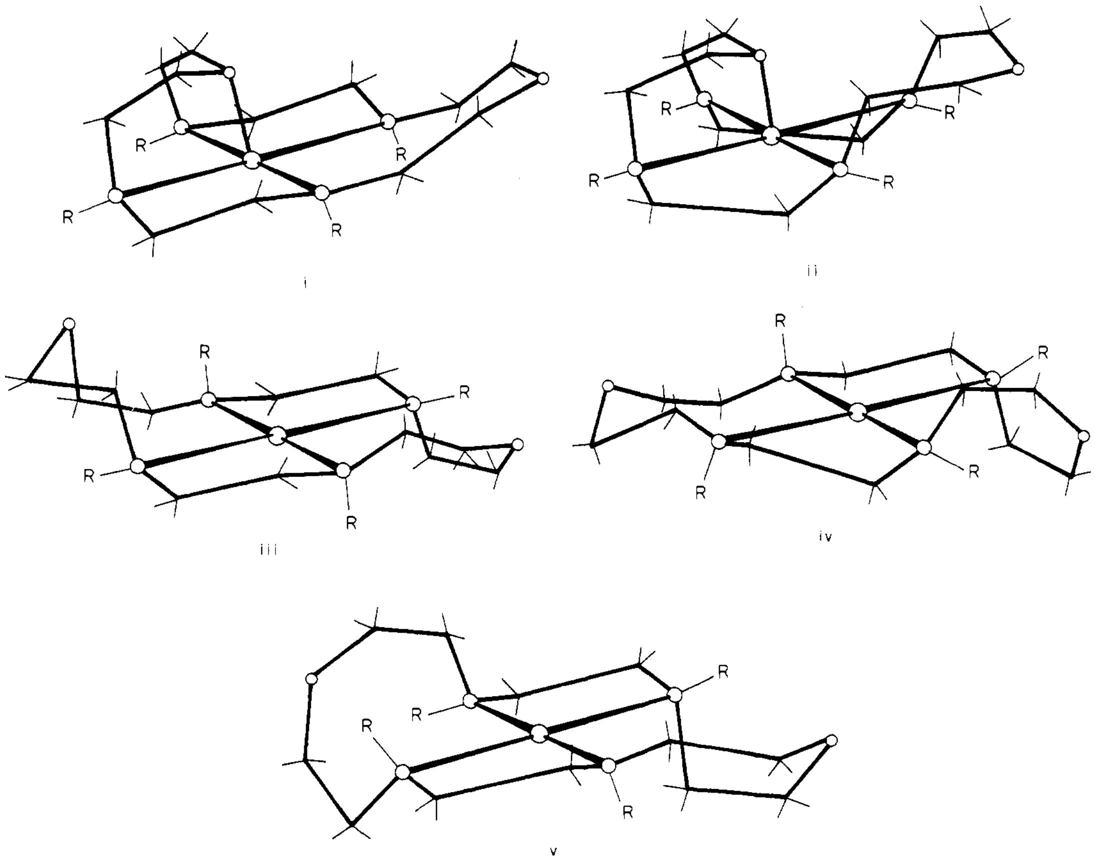

Figure 7. Proposed conformational structures for metal complexes of (i) 4*R*,7*S*,13*R*,16*S*-[18]aneP_4O_2 ($\delta\lambda$), (ii) 4*R*,7*S*,13*R*,16*S*-[18]aneP_4O_2 (eclipsed), (iii) 4*R*,7*S*,13*S*,16*R*-[18]aneP_4O_2 ($\delta\lambda$), (iv) 4*R*,7*S*,13*S*,16*R*-[18]aneP_4O_2 ($\lambda\lambda$), and (v) 4*R*,7*R*,13*R*,16*R*-[18]aneP_4O_2 ($\delta\lambda$).

superimposable on that of square-planar chromophores such as $[Ni(PNP)I]^+$, although the pentacoordinate square-pyramidal nature of the former chromophore has been supported by an X-ray diffractometric analysis.[33] No definite conclusions therefore can be drawn about the coordination number of these complexes, the electronic spectra failing to give unambiguous information.

The different configurational properties of the two chromophores clearly show up from proton-decoupled ^{31}P NMR spectra of dimethyl-d_6 sulfoxide solutions of the two α- and β-isomer derivatives.

The spectrum of the β derivative consists of a single resonance line at −53.03 ppm, in agreement with the postulated centrosymmetric nature of this cation. On the other hand, a very complicated spectrum is obtained for the α derivative (Figure 6). A total of 31 resonance lines are detected in the −64 to −40 ppm range as a result of four mutually interacting nonequivalent phosphorus atoms in the chromophore. A 32-line pattern is in fact expected for an ABCD (AA′A″B) type spectrum. This result is therefore consistent with the expected asymmetry of the cation.

The downfield shifts experienced by the phosphorus resonances upon coordination to the nickel(II) ion are not unexpected, and it has previously been observed for other five-membered chelate rings formed by diphosphane donors.[34] Although ^{31}P NMR data on nickel(II) complexes with polyphosphane ligands are very infrequent, it is apparent that the shift of −74.5 ppm observed for the β diastereoisomer derivative is in the expected range for aryl- and alkyl-substituted diphosphanes. As outlined in the above discussion, despite its potential hexadentate character, the ligating behavior of the [18]aneP_4O_2 molecule is strictly related to the configurational properties of each given diastereoisomer. The coordination geometry of the two cobalt(II) derivatives with the two isolated α and β diastereoisomers can be interpreted as determined by the peculiar stereochemistry of the ligand alone. From this point of view, the observed diffractometric results must be considered quite regular ones. Of course the electronic properties of the acceptor metal ion play a significant role in determining the coordination number, as it is suggested by the presumably square-planar stereochemistry of the nickel(II) chromophores. However, it should be stressed that the steric requirements of the present [18]aneP_4O_2 diastereoisomers are rather exclusive in determining the stereochemical properties of their complexes.

In all of the investigated cobalt(II) and nickel(II) complexes, both X-ray and spectroscopic results show existence of a planar or pseudoplanar arrangement of the four phosphorus atoms. Although the possibility of a folded conformations of the P_4 moiety cannot in principle be ruled out as far as other derivatives are considered, it appears highly unlikely because of the steric crowding of aliphatic chains and phenyl substituents. Molecular models strongly support this suggestion. Therefore, if a planar arrangement of the four phosphorus atoms has to be postulated as a result of the balance of intramolecular nonbonding repulsion interactions, the ligating behavior of the five diastereoisomers can be predicted on the basis of qualitative configurational considerations as well as of coordination geometry of their metal complexes. Indeed, the present data show that the possibility of coordination of ethereal oxygens is not always allowed, it being strictly dependent on the configurational character of the phosphorus donors. Therefore, the three diastereoisomers (labeled as a, c, and e in Figure 1), whose complexes have not yet been investigated, may be expected to exhibit preferential coordinative behaviors, according

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[33] Dapporto, P.; Morassi, R.; Sacconi, L. *J. Chem. Soc. A* **1970** 1298 (NOP_2 = *N*,*N*-bis(2-(diphenylphosphino)ethyl)-2-methoxyethylamine; PNP = *N*,*N*-bis(2-(diphenylphosphino)ethyl)-*n*-propylamine).

[34] King, R. B.; Cloyd, J. C. *Inorg. Chem.* **1975**, *14*, 1550.

to the following considerations.

The diastereoisomer a is a meso form with phosphane configuration 4*R*, 7*S*, 13*R*, and 16*S*. As far as its metal complexes are concerned, it should be expected, by looking at the five-membered chelate rings formed by the ethylenediphospha units, that the phenyl groups would occupy in turn pseudoaxial and pseudoequatorial positions, the ethylenic chains adopting unsymmetrical gauche conformations. If this is the case, only one of the two ethereal groups can act as a donor (Figure 7i), and therefore this diastereoisomer would behave as a pentadentate ligand giving metal complexes of C_s symmetry. On the other hand, eclipsed conformations (or more probably strongly distorted gauche ones) would also allow the coordination of the second ethereal group. However, this latter hypothesis should prove less likely to occur, since both oxygens would concur to occupy the same apical position; therefore, a pentacoordinate polyhedron would again be obtained (Figure 7ii). Of course, a hexacoordinate geometry would require removal of the metal ion from the phosphorus plane and achievement of a pseudo-trigonal-prismatic coordination polyhedron, which again is highly unfavorable.

The c diastereoisomer is also a meso form with configuration 4*R*, 7*S*, 13*S*, 16*R*. As an inherent property of the stereochemistry of the ligand, two conformational isomers are possible upon coordination because of the different chirality of opposite phosphorus atoms. In both cases the ethylenic chains spanning the phosphorus atoms are expected to adopt unsymmetrical gauche conformations; however, when a $\delta\lambda$ conformation is considered (Figure 7iii), the phenyl substituents attached to the opposite donors occupy in turn pseudoaxial and pseudoequatorial positions; on the other hand, when $\lambda\lambda$ or $\delta\delta$ conformations are taken into account, the opposite phenyl substituents have different conformational characters (with respect to the five-membered chelate rings) (Figure 7iv). In both cases, however, the configuration of the phosphane groups does not allow the coordination of the ethereal groups and therefore this diastereoisomer is expected to behave as a tetradentate ligand.

The e diastereoisomer is a racemate, the configuration of the phosphorus atoms being 4*RS*, 7*RS*, 13*RS*, and 16*RS*. As a consequence the complexes of this diastereoisomer should be expected to exhibit twofold symmetry. Three possible conformational isomers may be expected depending on the conformational character of the gauche ethylenic chains, which span the phosphorus atoms, and the conformational character of the phenyl substituents. Again, however, the coordination of the oxygens is precluded because of the configurational properties of the phosphorus donors. Therefore a tetradentate behavior is expected for this diastereoisomer (Figure 7v), unless meridional coordination of the phosphorus–oxygen–phosphorus moieties occurs.

These expectations are quite reasonable on the basis of the results reported here for the b (β) and d (α) diastereoisomers. The characterization of these compounds is currently under investigation. The main obvious conclusion, is the fact that, due to their peculiar configurational properties, the use of appropriate diastereoisomers of this type of ligands may be quite effective in forcing a metal ion to adopt a given coordination geometry. In this sense, the synthesis of other macrocyclic polyphosphane ligands of different size and donor set would bring further knowledge and perspectives in coordination chemistry.

Experimental Section

Synthesis of Macrocycles. Unless otherwise noted, all operations were performed under a dry-nitrogen atmosphere. A 1.8 M benzene–diethyl ether 70% (v/v) solution of phenyllithium (94 mL, 170 mmol) was added dropwise to a stirred solution of 1,2-bis(phenylphosphino)ethane[35] (20.9 g, 85 mmol) in absolute tetrahydrofuran (200 mL) at 20 °C. The yellow dilithium phosphide separated, and the suspension was stirred for 0.5 h at −20 °C. A solution of 2,2′-dichloroethyl ether (12.1 g, 85 mmol) in tetrahydrofuran (50 mL) was added dropwise over a 0.5-h period to the stirred suspension at −20 °C until a colorless solution resulted. This was allowed to warm to room temperature, refluxed for 0.5 h, and then evaporated to dryness. All subsequent operations were performed without protection against aerial oxidation.

The residue was suspended in benzene (400 mL) 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 was extracted with ethanol (50 mL), leaving a solid material (3.8 g). This material was dissolved in refluxing benzene (30 mL), and ethanol (30 mL) was added to the solution. On overnight standing, white crystals separated (1.0 g); they were filtered off and recrystallized in the same way from benzene–ethanol (20 mL, 1:1 v/v), giving pure β-[18]aneP_4O_2 (0.75 g, 2.8% yield) (Table I). The ^{31}P NMR spectra of the mother liquors showed the occurrence of all the expected α–ϵ five diastereoisomers together with small amounts of phosphine impurities. Concentration of the combined mother liquors on a rotary evaporator (20 mL) allowed separation of a crop of crystals (1.80 g). Aerial evaporation of the mother liquor (10 mL) gave a further crop (0.70 g). Analytical and osmometric molecular weight data as well as ^{31}P NMR spectra indicated that both materials were mixtures of pure [18]aneP_4O_2 isomers, the overall yield of the five [18]aneP_4O_2 being 3.25 g (12%). All attempts to achieve a complete resolution of the isomeric mixture by fractional crystallization from benzene–ethanol or 1,2-dichlorobenzene were unsuccessful. However, a careful crystallization from the above solvents gave crops of crystals containing the α-[18]aneP_4O_2 isomer with an impurity of about 10% of the γ isomer.

Chromatographic Separation of the Nickel Chloride Complexes. Either pure β-[18]aneP_4O_2 or the isomeric reaction mixture were refluxed for 2 h in *o*-xylene. After the evaporation of the solvent, white materials resulted which contained all the five diastereoisomers in the equilibrium proportions. A solution of this isomeric mixture (1.6 g) in chloroform (30 mL) was added to a stoichiometric amount of nickel(II) chloride in ethanol (15 mL) and then gently warmed for 0.5 h and taken to dryness on a rotary evaporator under reduced pressure. A 0.2 M NaCl aqueous solution (250 mL) was added to the orange residue, and the resulting suspension was filtered to remove a solid material (0.15 g). This product proved to be the crude nickel dichloride complex of γ-[18]aneP_4O_2. The filtered solution was poured on a column (ϕ 8 × 80 cm) filled with SP-Sephadex C-25 Na^+ form (Pharmacia). By elution with a 0.2 M NaCl aqueous solution (150 mL/h), three colored bands were obtained in succession: B_1, dark yellow (from 137 to 159 h); B_2, pale yellow (from 170 to 185 h); B_3, red (from 199 to 219 h). The eluates were collected separately and evaporated to dryness on a rotary evaporator, and the residues were extracted with $CHCl_3$. Evaporation of the solvent gave the crude nickel(II) dichloride complexes of the macrocyclic ligands in 65–80% yield, which were used without further purification.

The pure diastereoisomers were obtained by cyanolysis of the concentrated aqueous solutions of the appropriate nickel(II) complexes by using a tenfold excess of KCN at 80 °C under a nitrogen atmosphere (20 min). The warm reaction mixture was extracted with benzene three times, and the joint extracts were dried ($CaSO_4$) and evaporated to dryness (yield 50–60%).

The residue from such a workup of fraction B_1 was recrystallized from benzene–ethanol mixtures, giving the pure L_α diastereoisomer. Workup of fraction B_2 gave a mixture of β and ϵ isomers which was easily separated due to the low solubility of the β isomer in cold benzene. Evaporation of the benzene solution gave a residue which was recrystallized from hot ethanol. The pure ϵ isomer was thus obtained as thin needles. Workup of fraction B_3 gave the pure δ isomer after recrystallization from benzene–ethanol. Finally, the γ isomer was obtained with use of a similar procedure to the one described above for the crude nickel(II) dichloride complex of γ-[18]aneP_4O_2 (Table I).

All these macrocycles are quite stable toward atmospheric oxygen both as solids and in solution. They are soluble in benzene, $CHCl_3$, and CH_2Cl_2 and slightly soluble in alcohols and acetone.

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[35] Issleib, K.; Weichmann, H. *Chem. Ber.* **1968**, *101*, 2197.

Synthesis of the Metal Complexes. All cobalt complexes were prepared under a nitrogen atmosphere. The yields of the complexes were in the 70–90% range.

M[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$ (M = Co, Ni). A solution of the β ligand (0.2 mmol) in 20 mL of THF was added to a hot solution of M(BF$_4$)$_2$·6H$_2$O in 10 mL of EtOH. With the cobalt complex, a pink solid soon separated which was filtered off, washed with THF, and dried. With the nickel complex the solution was evaporated to about 8 mL. Crystals separated which were recrystallized from Me$_2$CO–EtOH. Anal. Calcd for $C_{36}H_{44}P_4O_2B_2F_8Co$: C, 49.97; H, 5.12. Found: C, 49.8; H, 5.4. Calcd for $C_{36}H_{44}P_4O_2B_2F_8Ni$: C, 49.99; H, 5.12. Found: C, 50.0; H, 5.3.

Co[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$·2DMF and Ni[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$. A solution of CoBr$_2$ (0.2 mmol) in 20 mL of Me$_2$CO was added to a solution of the β ligand (0.2 mmol) in 30 mL of THF. A solution of Na(BPh$_4$) (0.2 mmol) in 10 mL of Me$_2$CO was then added. The resulting suspension was evaporated to about 20 mL, and a 20 mL sample of EtOH was added in order to complete the precipitation. The crystals were filtered off and recrystallized from hot DMF. The nickel complex was prepared in a similar way, but it was recrystallized from Me$_2$CO. Anal. Calcd for $C_{90}H_{98}P_4N_2O_4B_2Co$: C, 73.22; H, 6.69; N, 1.90. Found: C, 72.9; H, 6.8; N, 1.8. Calcd for $C_{84}H_{84}P_4O_2B_2Ni$: C, 75.80; H, 6.37. Found: C, 75.7; H, 6.4.

M[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$ (M = Co, Ni). A solution of M(BF$_4$)$_2$·6H$_2$O (0.2 mmol) in 5 mL of EtOH was added to a hot solution of the α ligand (0.2 mmol) in 100 mL of Me$_2$CO. A solution of Na(BPh$_4$) (0.4 mmol) in 10 mL of Me$_2$CO was added dropwise. The resulting solution was evaporated to about 30 mL, and a 20-mL sample of EtOH was slowly added. Crystals of the complex separated, which were filtered, washed with EtOH, and recrystallized from Me$_2$CO–EtOH. Anal. Calcd for $C_{84}H_{84}P_4O_2B_2Co$: C, 75.80; H, 6.37. Found: C, 75.6; H, 6.3. Calcd for $C_{84}H_{84}P_4O_2B_2Ni$: C, 75.82; H, 6.36. Found: C, 75.6; H, 6.5.

Technique. IR spectra, electronic spectra, and magnetic susceptibilities were measured with standard methods. ^{31}P NMR 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$_3$PO$_4$ (85%), upfield shifts being positive. Q-Band powder EPR spectra were recorded with a VARIAN E-9 spectrometer equipped with a VARIAN E-66 cavity.

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Registry No. α-[18]aneP$_4$O$_2$, 74783-07-6; β-[18]aneP$_4$O$_2$, 74807-53-7; γ-[18]aneP$_4$O$_2$, 79731-36-5; δ-[18]aneP$_4$O$_2$, 79731-37-6; ϵ-[18]aneP$_4$O$_2$, 79732-81-3; Co[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$, 79733-78-1; Ni[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$, 79682-22-7; Co[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 74776-04-8; Ni[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 79732-94-8; Co[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 74776-02-6; Ni[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 79682-24-9.

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Preparation and Oxygen-Transfer Properties of Novel Palladium(II) and Platinum(II) Hydroperoxo and Alkylperoxo Complexes

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A series of mononuclear hydroperoxo and *tert*-butylperoxo complexes L$_2$M(Rx)(OOR) (L = $^1/_2$ diphosphine or monophosphine; M = Pd or Pt; Rx = activated alkyl; R = H or *t*-Bu) have been prepared by condensation reactions of L$_2$M(Rx)(OH) with ROOH (R = H or *t*-Bu). While *t*-BuOOH reacts in all the cases tested, with H$_2$O$_2$ the preparation reaction is sensitive to the nature of the alkyl ligand Rx. These compounds behave as typical oxygen-transfer agents, reacting with PPh$_3$, CO, NO, and benzaldehyde. In one case it is possible to oxidize terminal olefins to the corresponding methyl ketones.

Introduction

The current interest in the synthesis of group 8 transition-metal complexes containing "activated" oxygen is still high, in particular with the aim of achieving cleaner, more convenient routes to oxygenated organic compounds.[2]

A useful concept elucidated recently by Sheldon and Kochi[2a] in reactions of oxygen transfer to olefins is that the principal role of a catalyst is to withdraw electrons from peroxidic oxygens in order to make them more susceptible to attack by nucleophiles such as olefins. Consequently by adding an electrophile such as benzoyl chloride to (PPh$_3$)$_2$PtO$_2$, Chen and Kochi[3] prepared a compound, (PPh$_3$)$_2$Pt(OOCOPh)Cl, stable only at very low temperatures, capable of successfully epoxidizing olefins. On the other hand the presence of an ancillary electron-withdrawing ligand has been found[4] to stabilize the platinum–oxygen σ bond and allowed us the synthesis of stable hydroxo and methoxo complexes of platinum(II).

However, not very much is known about stable hydroperoxo and alkylperoxo species of platinum metals. Except for compounds containing "bio" type ligands like porphyrins or Schiff bases, which have been extensively studied in the last decade, reports on these kinds of compounds include only a few Rh(III) and Co(III) hydroperoxo species[5-7] and Ir(III) alkylperoxo species.[8]

In a preliminary account of this paper,[9] we have reported the synthesis and reactivity of novel hydroperoxoplatinum(II) complexes starting from the corresponding hydroxo species via a route that appears to be of fairly general applicability. More recently Mimoun et al. have prepared[10] tetranuclear

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(1) (a) Istituto di Chimica Generale. (b) Centro del CNR.

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