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Synthesis and Characterization of Some Cobalt(II) and Nickel(II) Complexes of Three Diastereoisomers of the Phosphorus-Containing Macrocycle 4,7,13,16-Tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane

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Some cobalt(II) and nickel(II) complexes have been synthesized with three diastereoisomers of the phosphorus-containing crown ether 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane ([18]aneP_4O_2). The compound [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO ($C_{90}H_{96}O_4P_4B_2Co$) crystallizes in a monoclinic unit cell ($P2_1/n$ space group) with lattice constants of a = 17.988 (3) Å, b = 13.117 (2) Å, c = 16.785 (3) Å, and β = 103.82 (4)°, with D_c = 1.25 g/cm^3 for Z = 2 and V = 3845.7 Å^3. Least-squares refinement gave R = 0.098 for the 2036 observed reflections. The X-ray diffraction study of the complex [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO shows that the cobalt atom is hexacoordinated by two oxygen and four phosphorus atoms of the macrocycle forming a distorted trans-octahedral geometry with a meridional arrangement of the two $P(CH_2)_2O(CH_2)_2P$ moieties. The phosphorus configurations of the δ-[18]aneP_4O_2 diastereoisomer are 4*RS*,7*RS*,13*RS*,16*RS*. Electronic spectra and electric conductivity data show that the remaining two diastereoisomers γ- and ϵ-[18]aneP_4O_2 behave toward cobalt(II) as tetradentate and pentadentate ligands, respectively. Such coordination behaviors lead us to tentatively assign the 4*RS*,7*SR*,13*RS*,16*SR* phosphorus configurations to ϵ-[18]aneP_4O_2 and the 4*RS*,7*SR*,13*SR*,16*RS* ones to γ-[18]aneP_4O_2. The electronic spectra of the nickel(II) compounds are discussed.

Introduction

We have recently described the synthesis of the macrocycle 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane, [18]aneP_4O_2.[2,3] All five possible diastereoisomers were isolated by a combination of ion-exchange chromatography and fractional crystallization of their nickel(II) complexes (Figure 1). Some cobalt(II) and nickel(II) complexes were synthesized and structurally characterized with the two most easily available diastereoisomers, α- and β-[18]aneP_4O_2. The X-ray diffraction studies of two cobalt(II) derivatives allowed us to attribute the 4*RS*,7*RS*,13*RS*,16*SR* and 4*RS*,7*RS*,13*SR*,16*SR* phosphorus configurations to the α- and β-[18]aneP_4O_2 diastereoisomers, respectively.[2] The assignment of the ^{31}P NMR spectra of the [18]aneP_4O_2 diastereoisomers led us to tentatively attribute the 4*RS*,7*RS*,13*RS*,16*RS* phosphorus configuration to a third isomer, namely, δ-[18]aneP_4O_2, whereas no definite assignment could be made between the 4*RS*,7*SR*,13*RS*,16*SR* and 4*RS*,7*SR*,13*SR*,16*RS* configurations for the remaining two γ- and ϵ-[18]aneP_4O_2 isomers.[3]

This paper reports the synthesis and characterization of some cobalt(II) and nickel(II) complexes of the γ-, δ-, and ϵ-[18]aneP_4O_2 macrocycles. These isomers as well as the α and β ones display different coordination behavior according to the absolute stereochemistry of the phosphorus atoms. The X-ray crystal structure of [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO confirms the previously assigned phosphorus configurations of the δ isomer. Analytical and electronic spectral data of the cobalt(II) complexes are discussed in order to ascertain the phosphorus configurations of the γ and ϵ isomers.

Experimental Section

Preparation of the Compounds. All cobalt complexes were prepared under a nitrogen atmosphere.

[MCl(γ-[18]aneP_4O_2)][BPh_4] (M = Co, Ni). A solution of $MCl_2·6H_2O$ (0.012 g, 0.05 mmol) in 2 mL of H_2O was added to a hot solution of the γ ligand (0.032 g, 0.05 mmol) in 50 mL of acetone. The solution was evaporated to about 8 mL, and a solution of $NaBPh_4$ (0.025 g, 0.07 mmol) in 3 mL of ethanol was added. When the solution stood, crystals separated, which were filtered off and recrystallized from ethanol/acetone. The yield was 52% (0.027 g) and 61% (0.032 g) for the cobalt and nickel complexes, respectively.

[Ni(γ-[18]aneP_4O_2)][BPh_4]$_2$. A solution of $Ni(BF_4)_2·6H_2O$ (0.033 g, 0.10 mmol) in 5 mL of ethanol was added to a hot solution of the γ ligand (0.063 g, 0.10 mmol) in 50 mL of acetone. A solution of $NaBPh_4$ (0.102 g, 0.30 mmol) in 10 mL of acetone was added dropwise. The resulting solution was evaporated to about 20 mL, and a 20-mL sample of ethanol was slowly added. Crystals of the complex separated, which were filtered and recrystallized from acetone/ethanol. The yield was 77% (0.103 g).

[Ni(δ-[18]aneP_4O_2)]$Cl_2·2H_2O$. A solution of $NiCl_2·6H_2O$ (0.048 g, 0.20 mmol) in 5 mL of 80% ethanol was added to a solution of the δ ligand (0.126 g, 0.20 mmol) in 70 mL of acetone. The solution was evaporated to about 8 mL and left standing overnight. Crystals of the complex separated, which were recrystallized from chloroform/petroleum ether. The yield was 68% (0.108 g).

[M(δ-[18]aneP_4O_2)][BPh_4]$_2$ (M = Co, Ni). To a solution of [M(δ-[18]aneP_4O_2]Cl_2, prepared as described above, was added $NaBPh_4$ (0.204 g, 0.60 mmol) dissolved in 5 mL of acetone. Upon evaporation of the solution to about 15 mL and addition of 15 mL of ethanol, crystals of the complex separated, which were recrystallized from acetone/ethanol. The yields were about 75% for both complexes.

[M(ϵ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO (M = Co, Ni). The procedure employed for the δ analogues was followed. The yields were about 25%.

The analytical and physical data of the compounds are summarized in Table I.

Crystallographic Data. Crystal data for $C_{90}H_{96}O_4P_4B_2Co$: M = 1446.2; monoclinic, space group $P2_1/n$; a = 17.988 (3), b = 13.117 (2), c = 16.785 (3) Å; β = 103.82 (4)°; V = 3845.7 Å^3; Z = 2; D_c = 1.25 g/cm^3; $F(000)$ = 1530; λ(Mo Kα) = 0.70926 Å; μ(Mo Kα) = 3.17 cm^{-1}.

Data Collection. The red crystals of [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO are parallelepipeds. The crystal used for data collection, delimited by 010, 101, $10\bar{1}$ and their centrosymmetric faces, had dimensions 0.15 × 0.25 × 0.60 mm^3. Cell parameters were determined by carefully measuring the setting angles of 25 reflections at room temperature (about 22 °C) on a Philips PW 1100 diffractometer. The intensity data were collected, on the same diffractometer, in the $6° \leq 2\theta \leq 40°$ range with use of graphite-monochromatized Mo Kα radiation and the θ–ω scan technique: scans of 0.8° in ω were recorded across the peaks in 10-s intervals (background counted for 5 s on each side of the peak). Three standard reflections were measured every 120 min, but no significant variation was noticed during the data collection. The intensity data were corrected for Lorentz and polarization effects; the standard deviations $\sigma(I)$ were estimated as described elsewhere[4] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $<3\sigma(I)$. From the 2810 total reflections 2036 had intensity $\geq 3\sigma(I)$. An absorption correction was applied by a numerical method: transmission

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Table I. Analytical and Physical Data for Some Complexes of [18]aneP_4O_2

compd	color	% C calcd	% C found	% H calcd	% H found	Λ_M[a]
[CoCl(γ-[18]aneP_4O_2)][BPh_4]	orange	68.88	68.8	6.16	6.8	86
[NiCl(γ-[18]aneP_4O_2)][BPh_4]	red	68.88	68.9	6.16	6.4	86
[Ni(γ-[18]aneP_4O_2)][BPh_4]$_2$	yellow	75.85	75.7	6.36	6.4	
[Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO	red	74.75	74.6	6.69	6.4	
[Ni(δ-[18]aneP_4O_2)]Cl_2·2H_2O	red	54.16	54.0	6.06	5.9	
[Ni(δ-[18]aneP_4O_2)][BPh_4]$_2$	brick	75.86	76.1	6.37	6.5	
[Co(ϵ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO	brown	74.75	74.8	6.69	6.6	
[Ni(ϵ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO	yellow	74.75	74.5	6.69	6.7	

[a] In units of $cm^2\ \Omega^{-1}\ M^{-1}$. Solutions were 1×10^{-3} M in MeCN at 25 °C.

Table II. Positional Parameters (×10^4), Anisotropic Temperature Factors[a] (×10^3), and Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0	0	0	46 (2)	40 (2)	40 (2)	2 (2)	13 (1)	4 (2)
O(1)	775 (5)	−1138 (7)	884 (5)	61 (7)	75 (7)	41 (6)	15 (6)	5 (5)	9 (6)
P(1)[b]	1125 (5)	626 (7)	2 (5)	55 (6)	62 (6)	74 (6)	5 (5)	18 (5)	7 (5)
P(2)	−101 (5)	1251 (6)	863 (5)	63 (6)	59 (6)	62 (6)	2 (5)	24 (5)	−6 (5)
P(3)	−943 (4)	−1010 (6)	285 (5)	57 (5)	44 (5)	60 (5)	−13 (4)	32 (4)	−9 (4)
P(4)	−261 (4)	−948 (6)	−1169 (5)	58 (5)	52 (5)	55 (5)	−15 (4)	26 (4)	−6 (5)

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + ...)]$. [b] The phosphorus atoms have population parmaeters of 0.5.

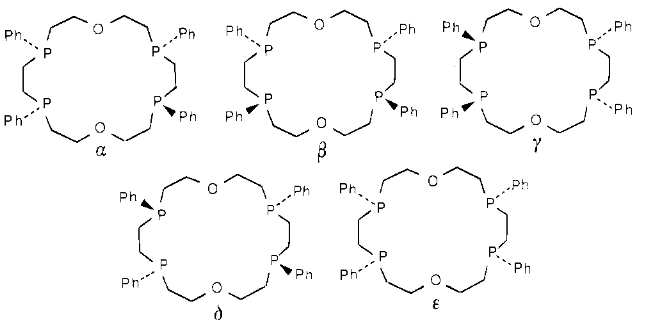

Figure 1. The five diastereoisomers of the [18]aneP_4O_2 ligand: α (4*RS*,7*RS*,13*RS*,16*SR*), β (4*RS*,7*RS*,13*SR*,16*SR*), γ (4*RS*,7*SR*,13*SR*,16*RS*), δ (4*RS*,7*RS*,13*RS*,16*RS*), ϵ (4*RS*,7*SR*,13*RS*,16*SR*).

factors varied between 0.92 and 0.96. Scattering factors for neutral atoms were taken from ref 5 and were modified for both the real and the imaginary components of anomalous dispersion.

Structure Determination and Refinement. The positions of the cobalt and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. Successive F_o Fourier syntheses, performed in the $P2_1/n$ space group, showed the positions of the other non-hydrogen atoms. The $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation is in a disordered array, as is clearly evidenced by the position of the cobalt atom, which occupies a center of symmetry of the cell ($Z = 2$), whereas the δ-[18]aneP_4O_2 ligand is not centrosymmetric. This disorder can be markedly noticed on the carbon atoms of the $P(CH_2)_2O(CH_2)_2P$ chains, on the phenyl groups belonging to the phosphorus atoms, and also on the four phosphorus atoms, which have been found to occupy two different positions, which are however rather close to each other. Also, if the center of symmetry is taken away, i.e., working in the acentric $P2_1$ and Pn space groups, this disorder remains. For this reason we continued to work in the $P2_1/n$ centrosymmetric space group. The $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation is therefore disordered since the unit cells are statistically occupied by two different individuals, which are acentric but mutually centrosymmetric. The solution of this disorder has been obtained on the basis of chemical knowledge of the ligand and on an account of some short contacts which let us rule out the coexistence of some atoms in one type of molecule. The only atoms that are not disordered in the cation are the cobalt atom, the oxygen atoms, and the C(1) and C(2) atoms of the chains that directly join the phosphorus atoms. Some models showed that the occupancy of the space for the two individuals is rather close, thus accounting for this disorder in the crystal lattice. Obviously this disorder is responsible for rather high discrepancy factors and standard deviation values, although it has been successfully rationalized as shown by the successful refinement.

The refinement was performed by use of the full-matrix least squares of the SHELX program.[6] The minimized function was $\sum w(|F_o| - |F_c|)^2$, $|F_c|)^2$, in which w is the weight assigned to the F_o values according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms were not introduced since the disorder of the structure induces population parameters of 0.5 also for these atoms, which therefore have very small single contributions. The carbon atoms of the phenyl groups were refined like a rigid body, with assumption of a D_{6h} geometry for the rings. Anisotropic temperature factors were used for the cobalt, phosphorus, and oxygen atoms of the complex cation. A population parameter of 0.5 was assigned to the disordered atoms. The final conventional R is 0.098. The R_w factor, defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, is 0.097. A final ΔF Fourier did not show remarkable features. The final values of the atomic parameters and their standard deviations are reported in Tables II and III. The observed and calculated structure factors are available as supplementary material.

Results and Discussion

Cobalt(II) and Nickel(II) Complexes of δ-[18]aneP_4O_2. The δ-[18]aneP_4O_2 macrocycle forms the cobalt(II) complex of the formula [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO. Its electronic spectra both in MeCN solution and in the solid state show bands at 12 600 and 20 800 cm^{-1}, being diagnostic of an octahedral low-spin configuration (Figure 2).[7] An X-ray crystal analysis shows that the structure of this compound consists of the $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation, $[BPh_4]^-$ anions, and interposed Me_2CO solvent molecules. The $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation is present in two enantiometric forms due to the racemic nature of the ligand. The absolute configurations of the four chiral centers in the δ diastereoisomer are 4*RS*, 7*RS*, 13*RS*, and 16*RS*, thus confirming the assignment based on a ^{31}P NMR spectrum.[3] The cobalt atom is hexacoordinated by the six atoms of the macrocycle, yielding a distorted-octahedral arrangement (Figure 3). Table IV lists selected bond lengths and angles. The four phosphorus atoms lie significantly off of the mean equatorial plane of the coordination polyhedron (0.37–0.39 Å). The cobalt atom lies

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Table III. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors ($\times 10^3$), and Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
C(1)	1353 (8)	1889 (11)	531 (9)	64 (5)
C(2)	835 (8)	2040 (11)	1147 (9)	66 (5)
C(3)[a]	1782 (15)	−169 (22)	767 (16)	61 (8)
C(4)	1512 (18)	−1227 (24)	787 (19)	73 (10)
C(5)	351 (17)	−2164 (24)	996 (19)	69 (10)
C(6)	−472 (17)	−1933 (22)	1098 (18)	66 (9)
C(7)	1504 (10)	766 (15)	−905 (9)	47 (4)
C(8)	2039 (10)	50 (15)	−1029 (9)	77 (9)
C(9)	2358 (10)	136 (15)	−1706 (9)	103 (12)
C(10)	2142 (10)	938 (15)	−2259 (9)	94 (11)
C(11)	1608 (10)	1654 (15)	−2135 (9)	77 (10)
C(12)	1288 (10)	1568 (10)	−1458 (9)	49 (8)
C(13)	−413 (11)	1134 (14)	1808 (9)	57 (7)
C(14)	−30 (11)	430 (14)	2385 (9)	59 (9)
C(15)	−276 (11)	255 (14)	3100 (9)	80 (10)
C(16)	−905 (11)	785 (14)	3240 (9)	78 (10)
C(17)	−1289 (11)	1489 (14)	2663 (9)	56 (14)
C(18)	−1042 (11)	1663 (14)	1947 (9)	70 (10)
C(19)	−749 (15)	2207 (21)	239 (17)	64 (9)
C(20)	−679 (14)	2240 (20)	−640 (16)	50 (8)
C(21)	−865 (15)	964 (20)	−1716 (16)	53 (8)
C(22)	−1002 (14)	−175 (21)	−1868 (16)	57 (8)
C(23)	−1714 (9)	−537 (14)	675 (14)	44 (7)
C(24)	−2195 (9)	167 (14)	182 (12)	75 (9)
C(25)	−2824 (9)	560 (14)	431 (12)	92 (11)
C(26)	−2971 (9)	248 (14)	1173 (12)	90 (11)
C(27)	−2490 (9)	−456 (14)	1666 (12)	71 (9)
C(28)	−1861 (9)	−849 (14)	1417 (12)	73 (9)
C(29)	403 (9)	−1334 (14)	−1784 (11)	45 (8)
C(30)	803 (9)	−2247 (14)	−1588 (11)	56 (8)
C(31)	1254 (9)	−2620 (14)	−2093 (11)	80 (10)
C(32)	1305 (9)	−2081 (14)	−2794 (11)	67 (8)
C(33)	905 (9)	−1168 (14)	−2990 (11)	74 (9)
C(34)	454 (9)	−795 (14)	−2485 (11)	76 (9)
B	2425 (9)	−96 (14)	−5169 (10)	60 (5)
C(35)	2619 (6)	365 (10)	−6044 (6)	84 (5)
C(36)	2965 (6)	−314 (10)	−6484 (6)	116 (7)
C(37)	3159 (6)	5 (10)	−7201 (6)	146 (8)
C(38)	3006 (6)	1003 (10)	−7479 (6)	104 (6)
C(39)	2661 (6)	1683 (10)	−7039 (6)	105 (6)
C(40)	2467 (6)	1364 (10)	−6322 (6)	95 (6)
C(41)	1895 (6)	736 (8)	−4793 (7)	67 (5)
C(42)	1102 (6)	638 (8)	−4939 (7)	73 (5)
C(43)	677 (6)	1366 (8)	−4634 (7)	78 (5)
C(44)	1045 (6)	2191 (8)	−4182 (7)	124 (7)
C(45)	1839 (6)	2289 (8)	−4035 (7)	186 (10)
C(46)	2264 (6)	1561 (8)	−4341 (7)	136 (8)
C(47)	1934 (5)	−1181 (6)	−5433 (7)	62 (4)
C(48)	1384 (5)	−1185 (6)	−6176 (7)	111 (6)
C(49)	932 (5)	−2048 (6)	−6415 (7)	106 (6)
C(50)	1032 (5)	−2907 (6)	−5911 (7)	81 (5)
C(51)	1582 (5)	−2903 (6)	−5168 (7)	82 (5)
C(52)	2033 (5)	−2040 (6)	−4929 (7)	63 (4)
C(53)	3255 (5)	−296 (7)	−4439 (5)	63 (4)
C(54)	3197 (5)	−571 (7)	−3653 (5)	66 (4)
C(55)	3857 (5)	−710 (7)	−3030 (5)	88 (5)
C(56)	4576 (5)	−575 (7)	−3193 (5)	83 (5)
C(57)	4634 (5)	−301 (7)	−3979 (5)	94 (6)
C(58)	3973 (5)	−161 (7)	−4602 (5)	78 (5)
C(59)[b]	4468 (19)	−873 (23)	1215 (18)	181 (11)
C(60)	4295 (14)	−1972 (20)	1594 (15)	168 (10)
C(61)	5134 (17)	−922 (21)	980 (17)	186 (11)
C(62)	3784 (17)	−625 (21)	855 (17)	193 (11)

[a] The C(3)–C(34) atoms have population parameters of 0.5.
[b] The C(59)–C(62) atoms belong to the acetone solvent molecule. All these atoms were treated as carbon since it was not possible to distinguish the oxygen atom.

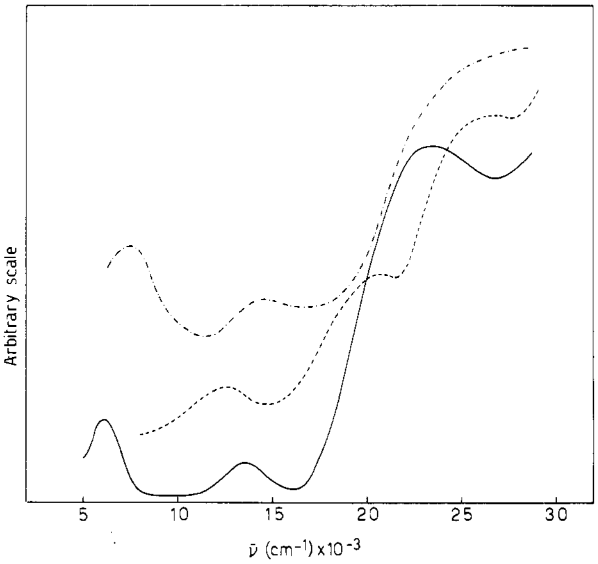

Figure 2. Absorption spectra of [CoCl(γ-[18]aneP_4O_2)][BPh_4] (—), [Co(δ-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO (- - -), and [Co(ε-[18]aneP_4O_2)][BPh_4]$_2$·2Me_2CO (–·–).

Table IV. Interatomic Distances (Å), Angles (Deg), and Their Respective Standard Deviations

(A) Selected Bond Lengths			
Co–O(1)	2.320 (9)	P(3)–C(23)	1.78 (2)
Co–P(1)	2.183 (9)	P(4)–C(2′)	1.77 (2)
Co–P(2)	2.225 (9)	P(4)–C(22)	1.85 (2)
Co–P(3)	2.292 (8)	P(4)–C(29)	1.83 (2)
Co–P(4)	2.275 (8)	C(1)–C(2)	1.56 (2)
P(1)–C(1)	1.88 (2)	C(3)–C(4)	1.47 (4)
P(1)–C(3)	1.85 (3)	C(4)–O(1)	1.38 (4)
P(1)–C(7)	1.82 (2)	O(1)–C(5)	1.58 (3)
P(2)–C(2)	1.94 (2)	C(5)–C(6)	1.56 (4)
P(2)–C(19)	1.86 (3)	C(19)–C(20)	1.51 (4)
P(2)–C(13)	1.81 (2)	C(20)–O(1′)	1.50 (3)
P(3)–C(1′)	1.81 (2)	O(1′)–C(21)	1.38 (3)
P(3)–C(6)	1.87 (3)	C(21)–C(22)	1.53 (4)
(B) Selected Bond Angles			
P(1)–Co–P(2)	86.6 (3)	C(1′)–P(3)–C(23)	106.8 (8)
P(1)–Co–P(3)	161.7 (3)	C(6)–P(3)–C(23)	102.4 (12)
P(1)–Co–P(4)	102.0 (3)	Co–P(4)–C(2′)	102.5 (9)
P(1)–Co–O(1)	80.0 (3)	Co–P(4)–C(22)	102.5 (9)
P(2)–Co–P(3)	96.4 (3)	Co–P(4)–C(29)	127.7 (6)
P(2)–Co–P(4)	158.8 (3)	C(2′)–P(4)–C(22)	96.9 (10)
P(2)–Co–O(1)	100.8 (3)	C(2′)–P(4)–C(29)	104.5 (9)
P(3)–Co–P(4)	81.6 (3)	C(22)–P(4)–C(29)	105.2 (11)
P(3)–Co–O(1)	81.7 (3)	Co–O(1)–C(4)	115.2 (14)
P(4)–Co–O(1)	99.7 (3)	Co–O(1)–C(5)	113.0 (11)
Co–P(1)–C(1)	115.5 (6)	C(4)–O(1)–C(5)	116.5 (19)
Co–P(1)–C(3)	103.2 (10)	Co–O(1′)–C(20)	115.6 (10)
Co–P(1)–C(7)	124.7 (7)	Co–O(1′)–C(21)	116.5 (12)
C(1)–P(1)–C(3)	98.0 (10)	C(20)–O(1′)–C(21)	114.3 (16)
C(1)–P(1)–C(7)	102.9 (9)	P(1)–C(1)–C(2)	109.1 (10)
C(3)–P(1)–C(7)	109.4 (12)	P(2)–C(2)–C(1)	113.0 (10)
Co–P(2)–C(2)	110.7 (6)	P(3)–C(1′)–C(2′)	112.5 (10)
Co–P(2)–C(13)	126.7 (7)	P(4)–C(2′)–C(1′)	110.8 (10)
Co–P(2)–C(19)	105.6 (10)	P(1)–C(3)–C(4)	112.8 (18)
C(2)–P(2)–C(13)	105.3 (8)	O(1)–C(4)–C(3)	104.8 (24)
C(2)–P(2)–C(19)	99.8 (10)	O(1)–C(5)–C(6)	110.2 (22)
C(13)–P(2)–C(19)	105.5 (12)	P(3)–C(6)–C(5)	108.8 (21)
Co–P(3)–C(1′)	113.5 (7)	P(2)–C(19)–C(20)	112.5 (20)
Co–P(3)–C(6)	107.3 (10)	O(1′)–C(20)–C(19)	102.0 (19)
Co–P(3)–C(23)	123.8 (7)	O(1′)–C(21)–C(22)	107.8 (20)
C(1′)–P(3)–C(6)	99.9 (10)	P(4)–C(22)–C(21)	111.5 (16)

only 0.02 Å out of the equatorial mean plane. The two ethereal oxygens are displaced slightly from the ideal axial positions, the deviations being 1.02° with respect to a perpendicular to the mean basal plane. These deviations from strict octahedral geometry are essentially due to the steric constraints of the ligand which allow small "bite" angles of about 80–86°. The cobalt–phosphorus distances are in the 2.2–2.3-Å range as is found in the α- and β-[18]aneP_4O_2 cobalt(II) complexes.[2] These values are normal for low-spin cobalt(II) phosphorus complexes. The cobalt–oxygen distances (2.32 Å) are very close to those found in the octahedral [Co(β-[18]aneP_4O_2)]$^{2+}$ cation (2.35 Å) and slightly longer than the one found in the

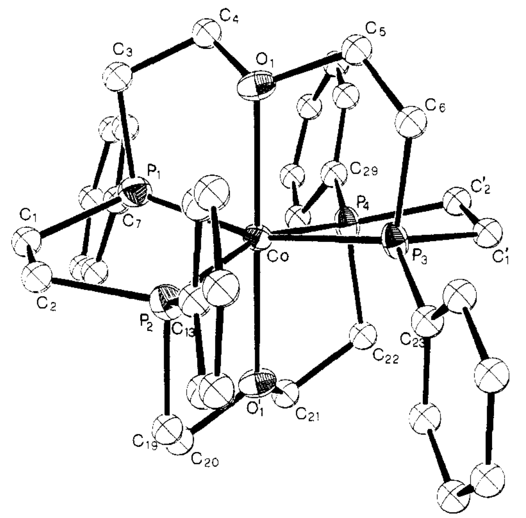

Figure 3. ORTEP drawing of the complex cation $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$.

square-pyramidal $[Co(\alpha\text{-}[18]aneP_4O_2)]^{2+}$ cation (2.256 Å).[2] All these cobalt–oxygen distances are rather long, thus indicating rather weak cobalt–oxygen bonds. Some marked differences in the C–O distances (see Table IV) are probably due to the assumed model in which the possible disorder of the oxygen atoms could not be considered.

It is interesting to compare the coordinating abilities and the steric arrangements assumed by the α, β, and δ diastereoisomers in their cobalt(II) complexes. In all three cases a planar or pseudoplanar arrangement of the four phosphorus atoms occurs, probaby in order to minimize steric crowding of aliphatic chains and phenyl substituents as well as to create a strong in-plane field. Both β and δ diastereoisomers behave as hexadentate ligands toward cobalt(II), giving distorted-octahedral complexes. The most significant structural difference between these cations is in the arrangement of the $P(CH_2)_2O(CH_2)_2P$ moieties, which adopt facial coordination with the $[Co(\beta\text{-}[18]aneP_4O_2)]^{2+}$ cation[2] but meridional coordination with the $[Co(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation. It appears that coordination of the oxygen atom strongly depends on the chiralities of its adjacent phosphorus atoms. In order for facial coordination to occur with a P_4 pseudoplanar arrangement, the two phenyl groups on the phosphorus atoms linked by the $(CH_2)_2O(CH_2)_2$ chains must be on the same side of the macrocycle plane, giving couples 4*RS*,16*SR* or 7*RS*,13*SR* of phosphorus atoms. On the contrary, meridional coordination is allowed when the two phenyl groups are on opposite sides on the macrocycle plane, the couples 4*RS*,16*RS* or 7*RS*,13*RS* being present. With the β and δ isomers all-facial or all-meridional coordination, respectively, of the two $P(CH_2)_2O(CH_2)_2P$ moieties can occur without mutual interference, so that hexacoordination results. With the α isomer, however, one $(CH_2)_2O(CH_2)_2$ chain links phosphorus atoms of opposite chirality whereas the other chain links phosphorus atoms of the same chirality. This isomer behaves as a pentadentate ligand toward cobalt(II), only facial coordination of the P(*RS*)OP(*SR*) moiety taking place.[2] In fact, molecular models show existence of mutual interferences between the two $P(CH_2)_2O(CH_2)_2P$ moieties, so that neither facial and meridional octahedral coordination nor meridional square-pyramidal coordination can occur with a planar arrangement of phosphorus atoms.

Nickel(II) chloride and tetraphenylborate react with δ-$[18]aneP_4O_2$ to give dark red low-spin complexes. The electronic absorption spectra of both solid compounds show a broad low-frequency absorption band with a maximum at about 23 000 cm^{-1}, irrespective of the nature of the counterions (Figure 4). When these complexes are dissolved in MeCN, Me_2CO, or water, the absorption maximum occurs at 22 700 cm^{-1}. These maxima occur at significantly lower frequencies than those shown by square-planar NiP_4 chromophores. For example, the square-planar $[Ni(benzo\text{-}15\text{-}P_4)]^{2+}$ cation exhibits its lowest energy d–d transition at 29 400 cm^{-1}.[8] Low-frequency transitions usually occur with five-coordinate and elongated-octahedral low-spin nickel(II) complexes.[9-11] The electronic spectra of the present complexes, therefore, suggest a rather strong axial component of the ligand field, the oxygen atoms of the δ-$[18]aneP_4O_2$ isomer interacting effectively with the nickel atom. Screening of the nickel atom by coordinated macrocycle oxygens is also consistent with ion-exchange chromatographic behavior of the $[Ni\text{-}(\delta\text{-}[18]aneP_4O_2)]^{2+}$ cation.[3] Actually, this is the most slowly eluted by 0.2 M NaCl among the soluble isomers, thus suggesting the weakest interactions between the nickel atom and the coordinating Cl^- anions of the eluent.

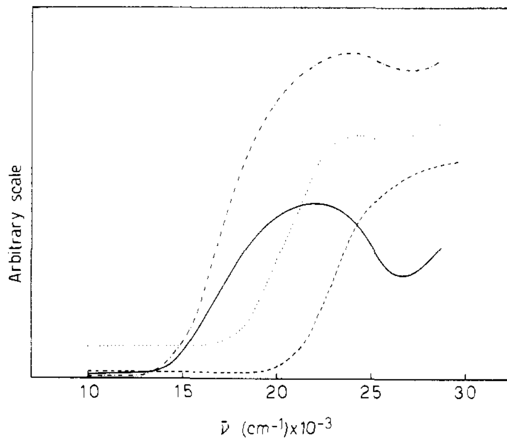

Figure 4. Absorption spectra of $[NiCl(\gamma\text{-}[18]aneP_4O_2)][BPh_4]$ (—), $[Ni(\gamma\text{-}[18]aneP_4O_2)][BPh_4]_2$ (- - -), $[Ni(\delta\text{-}[18]aneP_4O_2)][BPh_4]_2$ (–•–•), and $[Ni(\epsilon\text{-}[18]aneP_4O_2)][BPh_4]_2\cdot 2Me_2CO$ (···).

Cobalt(II) and Nickel(II) Complexes of γ- and ϵ-$[18]aneP_4O_2$. So far no X-ray crystal structure is available for the γ- and ϵ-$[18]aneP_4O_2$ macrocycles or for their metal complexes. A tentative configurational assignment, however, can be made on the basis of their coordinative behavior.

With cobalt(II) the ϵ-$[18]aneP_4O_2$ isomer gives the compound $[Co(\epsilon\text{-}[18]aneP_4O_2)][BPh_4]_2\cdot 2Me_2CO$. Its electronic spectra, both in MeCN solution and in the solid state, show bands at 7800, 14 700, and 26 700 cm^{-1}, typical of a square-pyramidal low-spin configuration (Figure 3).[10,12] These spectra are almost superimposable with that of the α analogue, which has the chromophore $[CoOP_4]$.[3] On the other hand, the γ-$[18]aneP_4O_2$ isomer fails to give pure tetraphenylborate complexes with cobalt(II) but, unique among the series of five isomers, it gives the mixed-anion compound $[CoCl(\gamma\text{-}[18]aneP_4O_2)][BPh_4]$. The electronic spectra of this complex, both in MeCN solution and in the solid state, are indicative of a low-spin square-pyramidal configuration showing bands at 6000, 13 500, and 23 500 cm^{-1} (Figure 3). Coordination of the chloride anion to cobalt is proved by the electric conductivity value, which is typical of 1:1 electrolytes (Table I). The occurrence of the CoP_4Cl chromophore also accounts for the red shifts of the electronic absorption bands with respect

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(8) Benzo-15-P_4 is 1,4,8,11-tetraphenyl-13,14-benzo-1,4,8,11-tetraphosphacyclopentadecane: DelDonno, T. A.; Rosen, W. *Inorg. Chem.* **1978**, *17*, 3714.

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(11) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *Inorg. Chim. Acta* **1980**, *45*, L239.

(12) Orioli, P. L. *Coord. Chem. Rev.* **1971**, *6*, 285. Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227. Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.

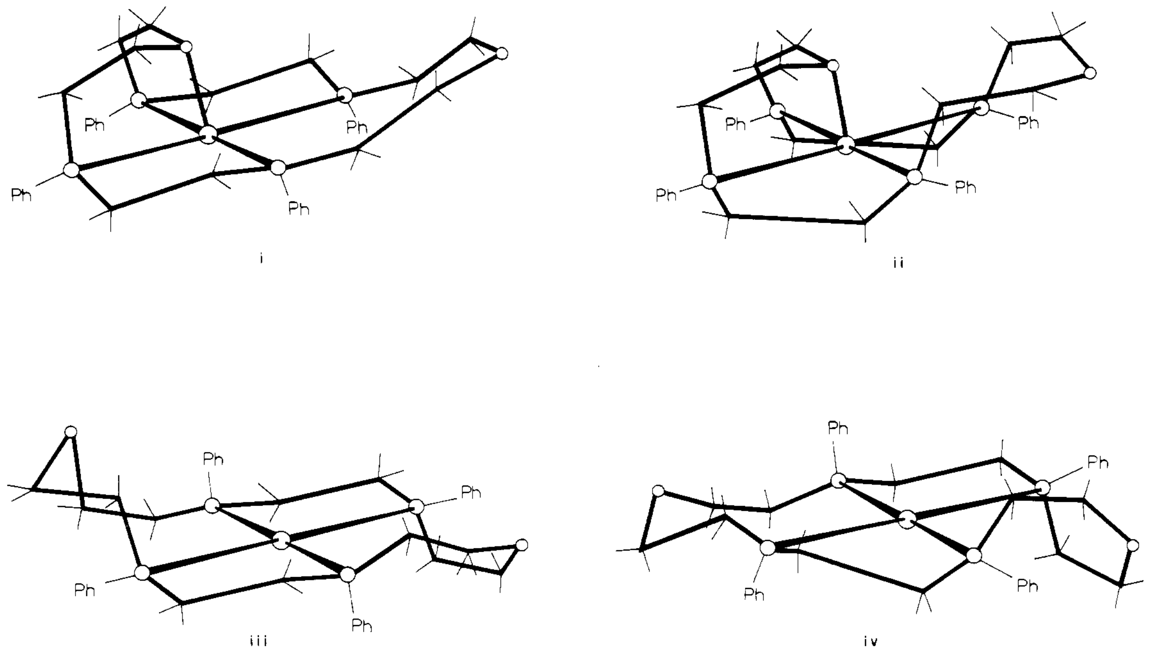

Figure 5. Proposed conformational structures for metal complexes of (i) 4*RS*,7*SR*,13*RS*,16*SR*-[18]aneP_4O_2 ($\delta\lambda$), (ii) 4*RS*,7*SR*,13*RS*,16*SR*-[18]aneP_4O_2 (eclipsed), (iii) 4*RS*,7*SR*,13*SR*,16*RS*-[18]aneP_4O_2 ($\delta\lambda$), and (iv) 4*RS*,7*SR*,13*SR*,16*RS*-[18]aneP_4O_2 ($\lambda\lambda$). (iv) 4*RS*,7*SR*,13*SR*,16*RS*-[18]aneP_4O_2 ($\lambda\lambda$).

to those of the CoP_4O chromophores with α- and ϵ-cobalt analogues. It appears, therefore, that the γ- and ϵ-[18]aneP_4O_2 isomers behave toward cobalt(II) respectively as tetradentate and pentadentate ligands.

The considerations that were extensively reported in ref 3 lead to the expectation of such a behavior for the remaining two isomers. In fact, the 4*RS*,7*SR*,13*RS*,16*SR* isomer has both $P(CH_2)_2O(CH_2)_2P$ moieties available for tridentate facial coordination. Nonetheless, the two moieties are linked by CH_2CH_2 chains in a syn arrangement so that both ethereal oxygens do compete with each other for the same apical positions of a square pyramid (Figure 5i,ii). Such an isomer, therefore, is expected to act as a pentadentate ligand, and it should be identified with the ϵ-[18]aneP_4O_2 diastereoisomer. On the contrary, the 4*RS*,7*SR*,13*SR*,16*RS* isomer does not allow the facial coordination of $P(CH_2)_2O(CH_2)_2P$ moieties (Figure 5iii,iv), whereas the meridional coordination is incompatible with a P_4 planar arrangement. This isomer, therefore, should act as a tetradentate ligand, and it is reasonably assigned as the γ isomer.

The nickel(II) tetraphenylborate complexes of the γ- and ϵ-[18]aneP_4O_2 isomers exhibit solid-state electronic spectra that agree with the ligand coordinative behaviors found for the cobalt complexes. In fact, solid $[Ni(\epsilon\text{-}[18]aneP_4O_2)][BPh_4]_2\cdot 2Me_2CO$ shows the first absorption maximum at 24 100 cm^{-1} (Figure 4) in accord with a weak axial interaction between nickel and an ethereal oxygen.[13] On the other hand, $[Ni(\gamma\text{-}[18]aneP_4O_2)][BPh_4]_2$ exhibits a steadily increasing absorption in the ultraviolet region with no definite maximum up to about 28 000 cm^{-1}, the upper limit of our reflectance measurements. This suggests a square-planar NiP_4 chromophore, the ethereal oxygens not interacting with nickel. Accordingly, the absorption spectra of this complex vary with the coordinative nature of the solvent: for example, they remain indicative of square-planar coordination in Me_2CO but they show occurrence of a weak axial interaction in MeCN (ν_{max} = 23 600 cm^{-1}). The mixed-anion complex $[NiCl(\gamma\text{-}[18]aneP_4O_2)][BPh_4]$ can also be isolated in the solid state. This complex has a pentacoordinated structure with coordinated chloride as is shown by its electric conductivity value (Table I) as well as by its electronic spectrum (ν_{max} = 21 900 cm^{-1}).

Conclusions

The series of the five [18]aneP_4O_2 isomers exhibits a marked configurational and coordinative interdependence. Because of planar or a pseudoplanar arrangement of the four phosphorus atoms and internal requirements due to the annular nature of the ligand, they behave toward cobalt(II) as hexadentate (β and δ isomers), pentadentate (α and ϵ isomers), and tetradentate (γ isomer) ligands.

Molecular models, however, show that the ligating behavior of these macrocycles might change if the planar disposition of the four phosphorus atoms would not hold true. Thus also α and ϵ isomers might act as hexadentate ligands, giving cis-octahedral complexes. On the other hand, the γ isomer might act as a pentadentate ligand, a phosphorus atom being not coordinated. Such behavior might be exhibited by [18]ane macrocycles having donors of higher coordinating strength substituted for oxygen atoms. We are presently carrying out the synthesis and characterization of [18]aneP_4S_2[11] and [18]aneP_4N_2 analogues in order to test this hypothesis.

Acknowledgment. We thank Mr. G. Vignozzi for microanalyses.

Registry No. $[CoCl(\gamma\text{-}[18]aneP_4O_2)][BPh_4]$, 83269-50-5; $[NiCl(\gamma\text{-}[18]aneP_4O_2)][BPh_4]$, 83269-52-7; $[Ni(\gamma\text{-}[18]aneP_4O_2)][BPh_4]_2$, 83269-54-9; $[Co(\delta\text{-}[18]aneP_4O_2)][BPh_4]_2\cdot 2Me_2CO$, 83348-96-3; $[Ni(\delta\text{-}[18]aneP_4O_2)]Cl_2$, 83348-97-4; $[Ni(\delta\text{-}[18]aneP_4O_2)][BPh_4]_2$, 83376-12-9; $[Co(\epsilon\text{-}[18]aneP_4O_2)][BPh_4]_2$, 83348-99-6; $[Ni(\epsilon\text{-}[18]aneP_4O_2)][BPh_4]_2$, 83349-01-3.

Supplementary Material Available: A listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[13] Metal coordination by Me_2CO molecules is ruled out due to IR data. Actually, the C=O stretching frequency falls at 1715 cm^{-1} with the three acetone adducts of Table I, showing no red shift with respect to the free solvent. For IR spectra of coordinated acetone, see, e.g.: Driessen, W. L.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 258. Wilkins, J. D. *J. Organomet. Chem.* **1974**, *80*, 357.