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Conformation, Structure, and UV–Visible and Circular Dichroism Spectra of Cobalt(III) Complexes of 1-Phenyl-2-amino-1,3-dihydroxypropanes

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The ligands (1*S*,2*S*)-(+)-1-phenyl-2-amino-1,3-dihydroxypropane, $C_6H_5CH(OH)CH(NH_2)CH_2OH$, (+)-PAHPH, and (1*R*,2*R*)-(−)-1-phenyl-2-amino-1,3-dihydroxypropane upon reaction with hexanitrocobaltate(III) ion yielded Co(PAHPH)(PAHP)$_2$(NO$_2$). Treatment of this complex with ethylenediamine plus chloride or iodide ion yielded green crystals of *trans*-Co(PAHP)$_2$(en)Cl·4H$_2$O and purple crystals of the cis isomer. The latter compound was converted to Co(PAHP)$_2$(en)I·H$_2$O. Crystals of this compound are orthorhombic with a = 6.786 (2) Å, b = 14.469 (2) Å, c = 24.807 (4) Å, and Z = 4. The space group is $P2_12_12_1$. Intensity data (2677 reflections above background) were obtained with an automated counter diffractometer (CAD-4) by using the θ–2θ scan technique. The structure was solved by a combination of Patterson and Fourier methods. Refinement by full-matrix least-squares procedures led to a final R of 0.029 and weighted R_w of 0.042. The amino alcohol coordinates through the amino group and the O$^-$ on C1. Cobalt is octahedrally coordinated with the two ethylenediamine nitrogens and the alcohol oxygens forming the equatorial plane. The conformation is $\Delta(\delta\delta\lambda)$. Spectral data are presented for all the compounds and used to delineate their conformations as well as provide information on protonation–deprotonation equilibria.

Introduction

Derivatives of 2-aminoethanol can act as chelating ligands forming five-membered chelate rings similar to ethylenediamine. The alcohol group is a relatively weak donor moiety[1] and thus an amino alcohol molecule may coordinate as a monodentate ligand through the amine, as a neutral chelating ligand, or as a uninegative chelating ligand via ionization of the alcoholic proton. Despite a wide interest in complexes of this type of ligand, very little is known about the structural details of these complexes. Many of the structures which have been determined involve polynuclear complexes which are associated through hydrogen bonds between the oxygens or involve bridging oxygens.[1] In contrast, only a few structures of mononuclear complexes containing coordinated alcoholate functions have been reported.[1-4]

During the study of the coordinating properties of the ligand (1*S*,2*S*)-(+)$_D$-1-phenyl-2-amino-1,3-dihydroxypropane, (+)-PAHPH (I), the serendipitous isolation of two diastereomeric crystalline mixed-ligand cobalt(III) complexes containing two (+)-PAHP-1 ligands and an ethylenediamine group was effected. The observation of their unusual spectroscopic properties prompted a more detailed characterization of these complexes. A crystal structure determination was undertaken to answer two questions, (1) which of two possible cis complexes (with respect to placement of the two oxygen donors), vide infra, had been isolated and (2) which of the alcoholic functions was involved in chelation to the cobalt?

Experimental Section

Materials. The ligands (1*S*,2*S*)-(+)-1-phenyl-2-amino-1,3-dihydroxypropane, (+)-PAHPH, and (1*R*,2*R*)-(−)-1-phenyl-2-amino-1,3-dihydroxypropane, (−)-PAHPH, were obtained from Parke-Davis Pharmaceutical Co. and were recrystallized to a constant optical rotation from acetonitrile: mp 112–113 °C; $[\alpha]_D$ = ±27°. All other chemicals were reagent grade materials and were used without further purification.

Preparation of Complexes. To a solution of 25 g of (+)- or (−)-PAHPH in 600 mL of a 3:1 methanol–water solution was added 12.4 g of solid sodium hexanitrocobaltate(III) in small portions with rapid stirring. The mixture was allowed to stir ca. 5 min and filtered. The red-brown filtrate was allowed to react overnight at ambient temperature. The brown product which formed was filtered, washed thoroughly with water, and air-dried. The yield was 9.5 g, 51%. Anal. Calcd for $Co(C_9H_{12}NO_2)_2(C_9H_{13}NO_2)(NO_2)$: C, 53.6; H, 6.12; N, 9.26; Co, 9.74. Found: C, 51.3; H, 5.88; N, 9.38; Co, 9.97. Mol wt calcd 604; found 583 (CH$_3$OH).

The entire yield of this brown material was dissolved in 450 mL of a 2:1 methanol–water solution and treated with 10 g of ethylenediamine. The mixture was warmed to 60 °C for 20 min and filtered, and a sodium chloride solution (18 g in 75 mL of H$_2$O) was added to the filtrate. Upon cooling of the mixture under ambient conditions, green crystals of the trans product formed. These were filtered, washed with ethanol, and air-dried; yield 2.25 g, 26%. The product was recrystallized to constant optical rotation and visible molar extinction coefficients by dissolving the complex in warm water (60 °C) and adding 2.0 M potassium chloride to initiate crystallization. Anal. Calcd for $Co(C_9H_{12}NO_2)_2(C_2H_8N_2)Cl\cdot 4H_2O$: C, 43.0; H, 7.15; N, 10.0; Co, 10.5; Cl, 6.32. Found: C, 43.3; H, 7.15; N, 10.2; Co, 10.4; Cl, 6.36. Optical rotation: $[\alpha]_D$ ±900°.

A second complex was isolated upon further evaporation of the reaction mixture at room temperature. This purple material was isolated in the same manner as the first product. This material was converted to the iodide salt by recrystallizing twice from potassium iodide solution; yield 0.90 g, 10%. Anal. Calcd for $Co(C_9H_{12}NO_2)_2(C_2H_8N_2)I\cdot H_2O$; C, 40.3; H, 5.70; N, 9.39; Co; 9.88; I, 21.3. Found: C, 40.3; H, 5.89; N, 9.32; Co, 9.99; I, 21.3. Optical rotation: $[\alpha]_D$ ±450°.

Crystals of the purple complex were obtained by recrystallizing from potassium iodide solution.

The acid-dissociation constants of the complexes were determined spectrophotometrically at an ionic strength of 0.10 with HCl, formate, acetate, and phosphate buffers over the pH range of ca. 1–8 at 23 ± 1 °C. Absorbance measurements were made at 400 nm. Measurement of pH was done on a Fisher Accumet Model 420 digital pH meter. The hydrogen ion activity was converted to concentration for calculation of the pK_a values. Both absorbance values and pH values were found to remain constant within the time of the experiment.

Physical Measurements. Electronic absorption spectra were obtained with a Cary 14 spectrophotometer. The circular dichroism (CD) spectra were determined on a Model J-20 Japan Spectroscopic Co. CD-Ord spectrophotometer. Elemental analysis and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, TN.

Crystal Data. A crystal 0.25 × 0.25 × 0.5 mm^3 was mounted with the long axis almost parallel to the ϕ axis of the goniometer. Accurate unit cell dimensions were determined from 25 reflections at high and moderate 2θ angles. A graphite-crystal incident-beam monochromator was used with Mo Kα radiation (λ(Mo Kα_1) 0.70930 Å). The results were a = 6.786 (2) Å, b = 14.469 (2) Å, c = 24.807 (4) Å, and V = 2435.7 (14) Å^3. The calculated density based upon Z = 4 is 1.626 g cm^{-3} which compares to a value of 1.627 g cm^{-3} obtained by flotation in a *sym*-tetrabromoethane–methylene chloride mixture. The space group was shown to be $P2_12_12_1$ from the systematic absences $h00$ with $h = 2n + 1$, $0k0$ with $k = 2n + 1$ and $00l$ with $l = 2n + 1$ which were observed in the intensity data set.

Intensity data were collected at room temperature (23 ± 2 °C) by using an automated four-circle counter diffractometer (CAD-4, Enraf-Nonius) under the following conditions: Crystal to counter distance was 21 mm and the crystal to aperture distance 17.3 mm, and a θ–2θ scan rate ranged from 20°/min for the most intense

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0.25182 (6)	0.21046 (2)	0.20186 (1)	0.02370 (8)	0.00388 (1)	0.00167 (1)	−0.00228 (8)	−0.00237 (5)	0.00087 (2)
Co	0.28577 (8)	0.56308 (4)	0.17380 (2)	0.00721 (9)	0.00200 (2)	0.00093 (1)	0.00014 (9)	−0.00022 (5)	−0.00036 (2)
O1	0.1949 (4)	0.6691 (2)	0.1380 (1)	0.0056 (5)	0.0023 (1)	0.00114 (5)	0.0001 (5)	−0.0004 (3)	0.0000 (1)
O2	0.3570 (4)	0.5030 (2)	0.1086 (1)	0.0066 (5)	0.0029 (1)	0.00113 (5)	−0.0010 (5)	0.0002 (3)	−0.0009 (1)
O3	0.8188 (6)	0.6824 (3)	0.1022 (2)	0.0123 (7)	0.0046 (2)	0.00191 (7)	−0.0018 (7)	0.0006 (4)	−0.0013 (2)
O4	−0.3160 (4)	0.4169 (2)	0.1285 (1)	0.0070 (6)	0.0044 (2)	0.00133 (5)	0.0005 (6)	−0.0002 (3)	−0.0003 (2)
O5	0.1823 (8)	0.8517 (4)	0.2726 (2)	0.0275 (14)	0.0099 (3)	0.00224 (9)	−0.0015 (13)	0.0004 (6)	−0.0026 (3)
N1	0.2169 (6)	0.6177 (2)	0.2438 (1)	0.0141 (9)	0.0030 (2)	0.00112 (5)	0.0008 (8)	0.0005 (4)	−0.0007 (2)
N2	0.5410 (5)	0.6234 (2)	0.1733 (2)	0.0097 (7)	0.0024 (2)	0.00111 (6)	0.0007 (6)	−0.0016 (4)	−0.0006 (2)
N3	0.3766 (6)	0.4571 (3)	0.2175 (2)	0.0131 (8)	0.0027 (2)	0.00134 (7)	0.0003 (7)	−0.0006 (4)	0.0000 (2)
N4	0.0244 (5)	0.5105 (2)	0.1623 (1)	0.0089 (7)	0.0025 (2)	0.00088 (6)	0.0001 (6)	0.0002 (3)	−0.0002 (2)
C1	0.3523 (6)	0.7153 (3)	0.1119 (2)	0.0090 (8)	0.0022 (2)	0.00100 (6)	−0.0009 (7)	−0.0000 (4)	−0.0004 (2)
C2	0.5232 (6)	0.7190 (3)	0.1523 (2)	0.0080 (7)	0.0021 (2)	0.00111 (6)	0.0006 (7)	−0.0007 (4)	−0.0005 (2)
C3	0.7226 (7)	0.7535 (3)	0.1314 (2)	0.0107 (9)	0.0028 (2)	0.00173 (8)	−0.0017 (8)	−0.0004 (5)	0.0003 (2)
C4	0.1863 (6)	0.4897 (3)	0.0770 (2)	0.0077 (8)	0.0024 (2)	0.00099 (6)	−0.0003 (7)	0.0001 (4)	−0.0006 (2)
C5	0.0269 (6)	0.4486 (3)	0.1140 (2)	0.0081 (7)	0.0020 (2)	0.00100 (6)	−0.0004 (7)	−0.0003 (4)	−0.0006 (2)
C6	−0.1752 (6)	0.4425 (3)	0.0888 (2)	0.0087 (8)	0.0034 (2)	0.00090 (6)	0.0001 (8)	−0.0002 (4)	−0.0004 (2)
C7	0.2271 (13)	0.5477 (5)	0.2861 (2)	0.0481 (23)	0.0073 (3)	0.00106 (7)	0.0146 (17)	0.0060 (8)	0.0016 (3)
C8	0.3545 (17)	0.4747 (5)	0.2744 (2)	0.0821 (40)	0.0051 (3)	0.00115 (9)	0.0197 (18)	−0.0014 (11)	0.0007 (3)
C9	0.2216 (7)	0.4293 (3)	0.0281 (2)	0.0102 (8)	0.0028 (2)	0.00093 (6)	−0.0016 (8)	0.0013 (4)	−0.0005 (2)
C10	0.1238 (8)	0.4498 (4)	−0.0198 (2)	0.0141 (10)	0.0043 (2)	0.00115 (7)	0.0022 (10)	0.0003 (5)	−0.0001 (2)
C11	0.1419 (10)	0.3922 (4)	−0.0642 (2)	0.0233 (14)	0.0059 (3)	0.00089 (7)	0.0019 (13)	0.0001 (6)	−0.0005 (3)
C12	0.2655 (10)	0.3169 (4)	−0.0623 (2)	0.0221 (14)	0.0051 (2)	0.00124 (7)	0.0004 (12)	0.0011 (6)	−0.0019 (2)
C13	0.3627 (8)	0.2962 (3)	−0.0155 (2)	0.0173 (11)	0.0035 (2)	0.00169 (9)	0.0019 (10)	0.0005 (6)	−0.0017 (3)
C14	0.3385 (8)	0.3510 (3)	0.0298 (2)	0.0132 (10)	0.0027 (2)	0.00136 (8)	0.0005 (8)	−0.0013 (5)	−0.0007 (2)
C15	0.2784 (7)	0.8080 (3)	0.0932 (2)	0.0104 (9)	0.0029 (2)	0.00100 (6)	−0.0008 (8)	0.0006 (4)	0.0002 (2)
C16	0.2475 (9)	0.8803 (3)	0.1284 (2)	0.0193 (11)	0.0033 (2)	0.00144 (7)	0.0061 (10)	−0.0021 (6)	−0.0003 (2)
C17	0.1693 (10)	0.9629 (4)	0.1107 (3)	0.0235 (14)	0.0035 (2)	0.00196 (11)	0.0059 (10)	−0.0001 (7)	−0.0006 (3)
C18	0.1142 (10)	0.9734 (4)	0.0574 (3)	0.0177 (13)	0.0036 (2)	0.00247 (12)	0.0012 (10)	−0.0014 (7)	0.0020 (3)
C19	0.1405 (10)	0.9019 (4)	0.0226 (2)	0.0254 (15)	0.0053 (3)	0.00142 (9)	−0.0021 (13)	−0.0019 (7)	0.0018 (3)
C20	0.2245 (9)	0.8196 (3)	0.0397 (2)	0.0232 (14)	0.0040 (2)	0.00096 (6)	−0.0027 (11)	−0.0013 (6)	0.0005 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1	0.398 (7)	0.682 (3)	0.083 (2)	1.5 (9)	H16	0.264 (15)	0.863 (5)	0.163 (4)	10.0 (25)
H2	0.488 (6)	0.754 (3)	0.183 (2)	0.6 (7)	H17	0.146 (9)	1.008 (3)	0.134 (2)	4.0 (13)
H3	0.683 (10)	0.803 (4)	0.106 (2)	4.6 (14)	H18	0.064 (11)	1.030 (4)	0.051 (2)	5.4 (16)
H3′	0.839 (6)	0.760 (3)	0.161 (1)	0.6 (7)	H19	0.115 (12)	0.909 (4)	−0.017 (3)	7.1 (20)
H4	0.140 (6)	0.547 (2)	0.065 (2)	0.7 (7)	H20	0.218 (9)	0.771 (3)	0.012 (2)	4.0 (13)
H5	0.069 (7)	0.388 (3)	0.125 (2)	1.6 (9)	H21	0.105 (8)	0.643 (3)	0.247 (2)	2.6 (10)
H6	−0.206 (7)	0.507 (3)	0.075 (2)	1.6 (9)	H21′	0.262 (11)	0.659 (4)	0.251 (3)	6.0 (16)
H6′	−0.163 (12)	0.400 (4)	0.056 (3)	6.8 (19)	H22	0.587 (6)	0.625 (2)	0.198 (1)	0.5 (7)
H7	0.206 (10)	0.573 (4)	0.322 (2)	4.7 (14)	H22′	0.586 (6)	0.600 (2)	0.153 (2)	0.8 (8)
H7′	0.058 (13)	0.504 (5)	0.277 (3)	6.8 (21)	H23	0.333 (9)	0.402 (3)	0.206 (2)	3.2 (11)
H8	0.342 (11)	0.417 (4)	0.298 (3)	6.7 (18)	H23′	0.455 (8)	0.449 (3)	0.214 (2)	3.3 (11)
H8′	0.495 (28)	0.556 (10)	0.291 (5)	28.1 (69)	H24	−0.030 (8)	0.485 (3)	0.187 (2)	2.4 (11)
H10	0.060 (8)	0.492 (3)	−0.024 (2)	2.5 (11)	H24′	−0.054 (7)	0.559 (3)	0.154 (2)	2.1 (9)
H11	0.070 (9)	0.421 (4)	−0.097 (2)	4.2 (13)	H26	0.945 (9)	0.687 (3)	0.113 (2)	3.5 (13)
H12	0.250 (9)	0.271 (4)	−0.094 (2)	4.5 (13)	H27	−0.412 (7)	0.434 (3)	0.117 (2)	2.5 (10)
H13	0.437 (9)	0.244 (4)	−0.015 (2)	3.7 (13)	H25	0.086 (18)	0.833 (7)	0.267 (4)	10.9 (36)
H14	0.401 (10)	0.335 (3)	0.061 (2)	3.1 (12)	H25′	0.238 (14)	0.842 (7)	0.306 (4)	13.1 (30)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

reflections to 2°/min for the weak ones. The angular scan width was variable and amounted to 0.6° before 2θ(Mo Kα_1) and 0.60 after 2θ(Mo Kα_1). Right and left backgrounds were each scanned for 25% of total scan time. Three standard reflections were recorded every 100 reflections and used to place the data on a common scale. Least-squares analysis of the standard intensities showed no significant variation. A total of 3215 reflections were scanned out to $2\theta = 55°$. Of these 2677 had intensities with $I \geq 3\sigma(I)$ and were considered to be observed. Here $\sigma(I) = [S^2(C + R^2B) + (pI)^2]$ and $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background time, and $p = 0.05$. These data were corrected for Lorentz and double polarization factors but not absorption. With $\mu = 20.53$ ($\mu R \simeq 0.26$) and the near-cylindrical shape of the crystal due to beveled edges, the absorption error was deemed not to be serious. This was borne out by the high level of refinement achieved ($R = 0.029$).

Structure Solution and Refinement. A three-dimensional Patterson map revealed the positions of the cobalt and iodine atoms. Subsequent Fourier and difference maps yielded the positions of all the nonhydrogen atoms.[5] Full-matrix least-squares refinement with anisotropic temperature factors reduce R, defined as $\sum(||F_o| - |F_c||)/\sum|F_o|$, to 0.049 and the weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 0.065. A difference synthesis revealed the positions of all hydrogens except H(3)′, H(6)′, H(8)′, H(22)′, and H(24)′. Positional parameters for these atoms were calculated with program hydrogen in idealized positions.[5] Inclusion of the hydrogen atoms with isotropic temperature factors in the refinement reduced R to 0.029 and R_w to 0.042 at convergence. The esd of an observation of unit weight was 1.324. In the final cycle of refinement all shifts for the nonhydrogen atom parameters were less than 0.1 their esd's (except for those of the water oxygen which were slightly higher) and for hydrogen the shifts were less than 0.3 their esd's except for H(7)′, and H(8)′. These hydrogen atoms are attached to C7 and C8, respectively, of the ethylenediamine ligand which it turns out is disordered. In order to determine the absolute configuration, refinement was also carried out on the structure in which all the signs of the positional parameters were reversed. R in this case was 0.036, R_w was 0.051, and the esd of an observation of unit weight was 1.607. Thus the original choice was correct.

The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ with weights, w, assigned by the expression $w = 1/\sigma^2(F_o) = 4F_o^2/[\sigma(F_o^2)]^2$ where $\sigma(F_o^2) = [\sigma(I)^2 + (0.05I^2)^2]^{1/2}/LP$. Neutral atom scattering factors for all nonhydrogen atoms were those of Cromer and Waber[6] and were corrected for anomalous dispersion. Scattering factors for hydrogen were taken from Stewart et al.[7] Positional and thermal parameters are presented in Table I. A listing of the observed and calculated structure factors is given as supplementary material.

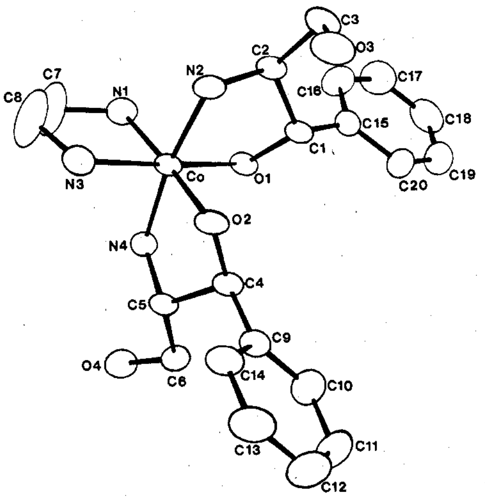


Figure 1. A perspective view of the complex together with the numbering scheme used in the tables.

Table II. Bond Distances (Å) and Angles (deg) within the Cobalt Coordination Sphere[a]

	Bond Distances		
Co-O1	1.877 (3)	Co-N2	1.940 (4)
Co-O2	1.900 (3)	Co-N3	1.976 (5)
Co-N1	1.963 (4)	Co-N4	1.951 (4)
	Angles		
O1-Co-O2	93.1 (1)	O2-Co-N4	85.9 (1)
O1-Co-N1	90.7 (2)	N1-Co-N2	92.1 (2)
O1-Co-N2	85.6 (1)	N1-Co-N3	84.3 (2)
O1-Co-N3	175.0 (2)	N1-Co-N4	94.0 (2)
O1-Co-N4	87.2 (1)	N2-Co-N3	94.2 (2)
O2-Co-N1	176.2 (2)	N2-Co-N4	170.6 (2)
O2-Co-N2	88.5 (2)	N3-Co-N4	93.5 (2)
O2-Co-N3	91.9 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Results

Crystal Structure. Figure 1 gives a perspective view of the complex cobalt ion together with the numbering scheme used in the tables. Each of the aminopropanediol ligands chelate cobalt through the amino nitrogen and the hydroxyl groups on carbon 1. Together with the ethylenediamine nitrogens they form a slightly distorted octahedral coordination group about the cobalt. Table II gives the bond distances and angles in the coordination sphere. The equatorial plane is formed by the two hydroxyl oxygens and the ethylenediamine nitrogens, while the two nitrogens of the aminopropanediol ligands occupy the axial positions. Each of the interior angles of the five-membered rings subtended at the cobalt is smaller than 90°. The cobalt–oxygen and cobalt–nitrogen bond distances fall well within the expected range.[8] Interestingly the Co–N distances to diol nitrogens are slightly less than these distances with the ethylenediamine nitrogens but this may stem from the disorder exhibited by the ethylenediamine group.

Bond distances and angles for the remainder of the molecule are given in Table III. These parameters are quite regular except for the ethylenediamine ring. Here the C7–C8 bond distance is quite short and the thermal parameters of these atoms are very large. In addition, one of the carbon–hydrogen bond distances to each of the ring carbons is long. These discrepancies may be indicative of some type of disorder in the ethylenediamine ring. However, none could be detected. This result should be tempered by the fact that very few data were observable at the high angle range and hence any resolution below 0.2–0.3 Å may not be detectable. In any case, the atoms refined with large temperature factors in a normal fashion and left no unaccounted for electron density in the final difference map.

Table III. Bond Distances (Å) and Angles (deg)

	Bond Distances		
O1-C1	1.417 (5)	O2-C4	1.412 (5)
C1-C2	1.535 (5)	C4-C5	1.539 (6)
C2-N2	1.482 (6)	C5-N4	1.497 (5)
C2-C3	1.533 (6)	C5-C6	1.509 (5)
C3-O3	1.417 (6)	C6-O4	1.422 (5)
C1-C15	1.505 (6)	C4-C9	1.514 (5)
C15-C16	1.378 (6)	C9-C10	1.392 (7)
C16-C17	1.381 (7)	C10-C11	1.386 (7)
C17-C18	1.382 (9)	C11-C12	1.375 (8)
C18-C19	1.359 (9)	C12-C13	1.369 (8)
C19-C20	1.387 (8)	C13-C14	1.385 (7)
C20-C15	1.389 (6)	C14-C9	1.384 (6)
N1-C7	1.461 (7)	N3-C8	1.442 (8)
C7-C8	1.395 (10)	C8-H8	1.03 (8)
C7-H7	0.96 (6)	C8-H8′	1.57 (22)
C7-H7′	1.33 (9)		
	Angles		
Co-O1-C1	110.7 (2)	Co-O2-C4	109.0 (2)
Co-N2-C2	110.4 (3)	Co-N4-C5	109.9 (3)
O1-C1-C2	106.7 (3)	O2-C4-C5	107.3 (3)
C1-C2-N2	105.0 (3)	C4-C5-N4	104.8 (3)
C1-C2-C3	117.2 (4)	C4-C5-C6	114.5 (4)
N2-C2-C3	110.5 (3)	N4-C5-C6	110.9 (3)
C2-C3-C3	110.0 (4)	C5-C6-C4	109.8 (3)
O1-C1-C15	108.0 (3)	O2-C4-C9	113.2 (3)
C2-C1-C15	114.9 (3)	C5-C4-C9	111.5 (3)
C1-C15-C16	122.2 (4)	C4-C9-C10	119.0 (4)
C1-C15-C20	119.3 (4)	C4-C9-C14	122.6 (4)
C15-C16-C17	121.0 (5)	C9-C10-C11	120.5 (5)
C16-C17-C18	120.2 (5)	C10-C11-C12	120.2 (5)
C17-C18-C19	119.3 (5)	C11-C12-C13	119.7 (4)
C18-C19-C20	120.9 (5)	C12-C13-C14	120.4 (5)
C19-C20-C15	120.3 (5)	C13-C14-C9	120.8 (5)
C20-C15-C16	118.3 (4)	C14-C9-C10	118.3 (4)
Co-N1-C7	110.2 (3)	Co-N3-C8	111.6 (4)
N1-C7-C8	113.8 (5)	N3-C8-C7	113.7 (6)

Mean plane equations are presented in Table IV. From the deviations of atoms from the planes and Figure 1, one can deduce that the conformation is $\Delta(\delta\delta\lambda)$. Even though the ethylenediamine grouping is disordered, the atoms were defined accurately enough to classify the ring conformation as δ. Phenyl ring 7 makes a dihedral angle of about 70° with the five-membered ring to which it is attached while with phenyl ring 8, the angle is slightly higher.

Possible hydrogen bonds are shown in Table V. Each of the uncoordinated hydroxyls form two short contacts. In each case, the hydroxyl oxygen acts as both acceptor and donor. O3 donates its proton to O1 of an adjacent complex in the *X* direction and in turn interacts with the N2 proton in an intramolecular interaction. O4 hydrogen bonds with O2 which is in a complex one unit cell away along the *X* axis. However, it in turn accepts a proton from the water molecule. N4, while only 2.81 Å away, makes a bond angle of 95 (4)° and thus is not considered as forming a hydrogen bond. However, there is also a weak intermolecular interaction with the N3–H23′ group.

The water molecule forms a hydrogen bond with the iodide ion which in turn forms three additional H bonds with N1, N2, and N3 as donors. Two other close contacts are included in the table of possible hydrogen bonds, N4–H24···O5 at 3.14 Å and N4–H24′···O3 at 3.22 Å. With the inclusion of the latter two values all the electronegative atoms partake of hydrogen bonding. The hydroxyl groups link molecules in the *X* direction while the water and iodide serve to bind molecules in the *X* and *Y* directions (see Figure 2).

Spectral Characterization. The reaction of (+)- or (−)-PAHPH with sodium hexanitrocobaltate(III) produces a water-insoluble material which is formulated [Co(PAHP)$_2$-

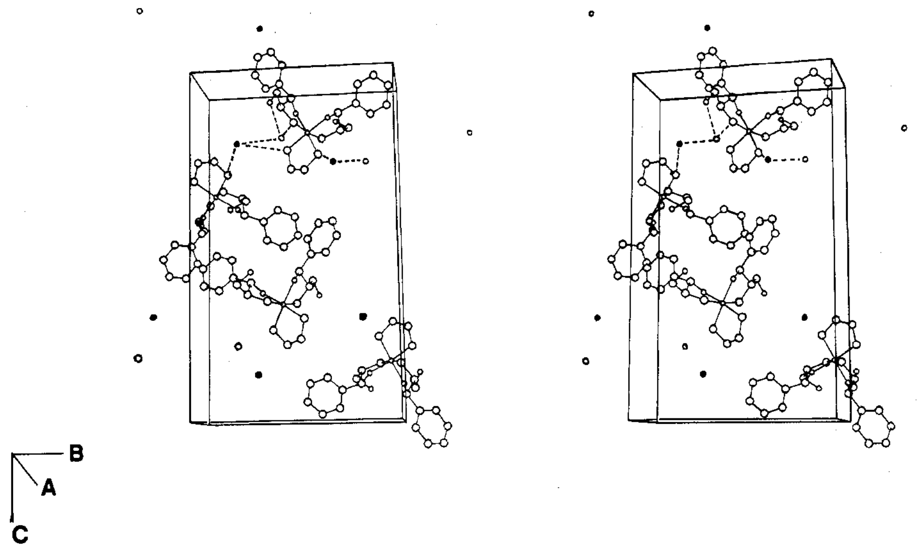
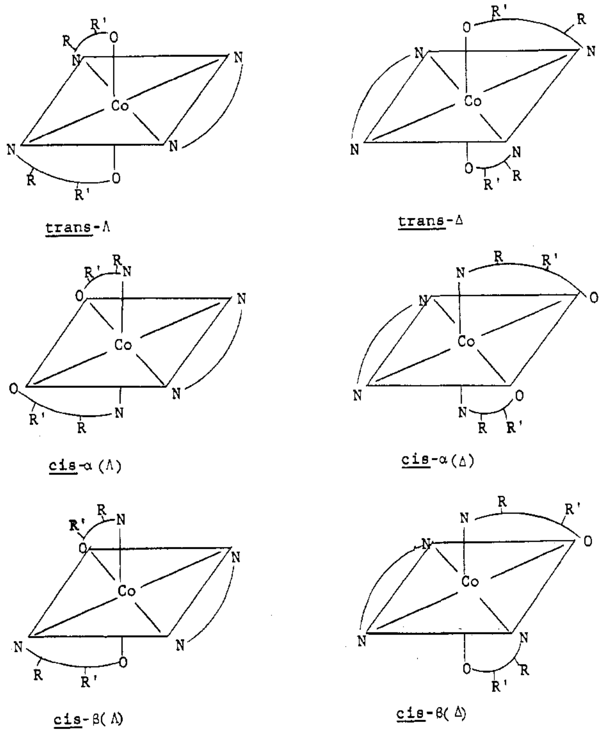


Figure 2. Stereoscopic view of the unit cell contents showing the crystal packing. Dashed lines give the hydrogen bonding of the water molecule and iodide ion. Open circle is water and filled circle is I^- outside the complex.



trans-Λ trans-Δ

cis-α (Λ) cis-α(Δ)

cis-β(Λ) cis-β(Δ)

Figure 3. Possible conformations of $[Co(PAHP)_2(en)]^+$: R = CH_2OH, R′ = C_6H_5.

$(PAHPH)(NO_2)]$. With the exception of the irreproducible and low carbon percentage, the elemental analysis and spectral data support this formulation. This substance is monomeric in methanol and a nonelectrolyte. Infrared absorption bands at 1395, 1300, and 818 cm^{-1} indicate the presence of coordinated nitrite.[9] The absorption spectrum of this complex is given in Table VI. It behaves as a monobasic acid with a pK_a value ca. 3.68. This complex has not been further characterized but has been used to prepare the complexes of interest by its reaction with ethylenediamine. Fractional crystallization of the products from the reaction mixture gave the less soluble green *trans*-$[Co(PAHP)_2(en)]Cl\cdot4H_2O$ followed by a purple cis isomer. For a given enantiomer of PAHPH, six diastereomeric complexes with this formulation are possible (Figure 3) in which the chelated oxygens may occupy either cis or trans positions. The cis complex obtained with the (+)-PAHPH is now known to be the *cis*-α-Δ-$(-)_{589}$-$[Co\{(+)\text{-}PAHP\}_2en$-$\delta\delta\lambda]^+$, *cis*-α(Δ), diastereomer on the basis of its crystal structure. The trans isomer can be assigned the Λ configuration on the basis of its circular dichroism spectra (vide infra). The enantiomeric complexes, the *trans*-Δ and the *cis*-α(Λ), have also been prepared from (−)-PAHPH.

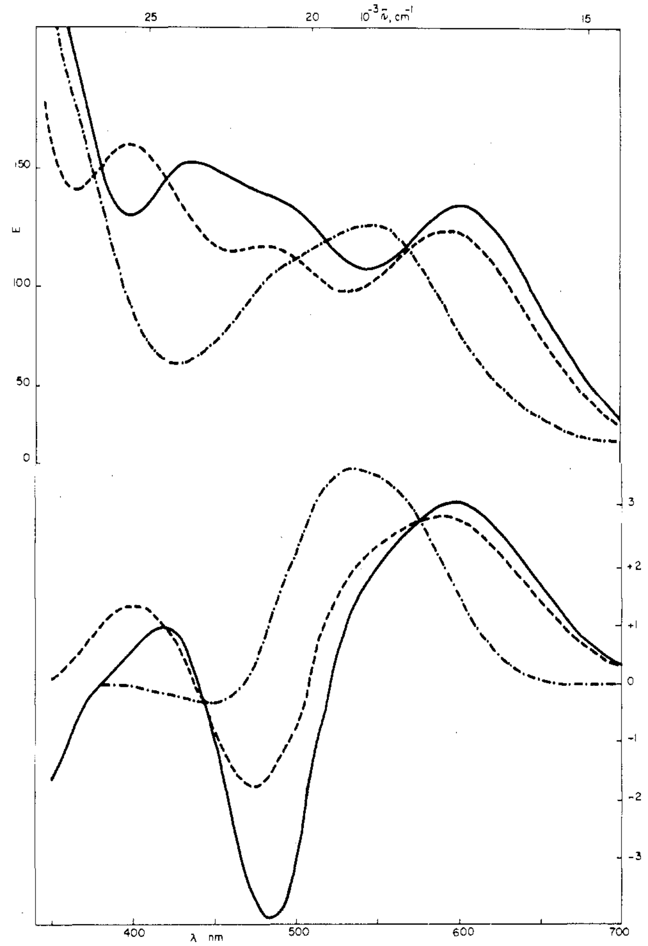


Figure 4. Visible absorption and circular dichroism spectra of the *trans*-Λ complex: pH 8.60, —; pH 4.50, ---; 0.6 M HCl, ····.

These complexes are dibasic and undergo protonation reversibly, adding two protons. The two protonation steps are accompanied by dramatic changes in the visible absorption spectra and the circular dichroism (CD) spectra of these

Table IV

Least-Squares Mean Planes for Various Groupings in the Complex

plane no.	atoms[a]	dist from plane, Å	atoms[a]	dist from plane, Å
1	Co*	−0.024	N4*	0.100
	N1*	−0.081	O2*	−0.094
	N2*	0.100		
	O1	1.852	N3	−1.996
2	Co*	−0.005	N3*	−0.080
	O1*	−0.097	N4*	0.090
	N2*	0.092		
	N1	−1.964	O2	1.894
3	Co*	0.000	N1*	0.006
	O1*	−0.005	N3*	−0.006
	O2*	0.005		
	N2	−1.933	N4	1.944
4	N1*	−0.069	C7*	0.134
	N3*	0.070	C8*	−0.134
	Co	0.136	O2	0.342
	O1	0.171		
5	O1*	−0.151	C1*	0.264
	N2*	0.140	C2*	−0.254
	Co	0.167	C3	0.228
	N3	0.330	O3	1.543
	N4	0.354	C15	−0.252
6	O2*	−0.155	C4*	0.273
	N4*	0.141	C5*	−0.260
	Co	0.216	O4	−0.121
	N1	0.471	C6	0.268
	N2	0.503	C9	−0.169
7	C9*	0.007	C12*	0.012
	C10*	0.013	C13*	0.008
	C11*	−0.022	C14*	−0.018
	C4	−0.059		
8	C15*	0.003	C18*	0.001
	C16*	−0.012	C19*	−0.010
	C17*	0.010	C20*	0.008
	C1	−0.101		

Selected Dihedral Angles between Planes

planes	angles, deg	planes	angles, deg
1-7	70.7	6-7	68.0
2-8	73.9	5-8	77.8

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.3370	0.8042	−0.4895	3.8128
2	0.2736	−0.4442	−0.8531	−6.7615
3	−0.9126	−0.4046	−0.0584	−5.3181
4	−0.8887	−0.4289	−0.1622	−6.0532
5	0.2605	−0.5586	−0.7874	−7.6081
6	−0.2883	0.8958	−0.3384	5.0641
7	0.7763	0.5540	−0.3007	4.3922
8	0.9139	0.3462	−0.2121	5.2800

[a] Atoms defining planes are indicated by asterisks.

Table V. Possible A-H· · ·B Hydrogen Bonds

A	H	B	A–H, Å	H· · ·B, Å	A· · ·B, Å	angle, deg
O3	H26	O1[d]	0.90 (6)	1.83 (7)	2.71	168 (6)
N2	H22′	O3	0.68 (8)	2.34 (5)	2.72	117 (4)
O4	H27	O2[e]	0.75 (5)	1.87 (6)	2.59	161 (6)
O5	H25′	O4[a]	0.93 (4)	2.01 (12)	2.78	138 (10)
N3	H23′	O4[c]	0.55 (6)	2.68 (7)	3.09	135 (9)
O5	H25	I[a]	0.72 (14)	3.00 (15)	3.64	151 (14)
N1	H21	I[a]	0.85 (6)	2.91 (6)	3.71	158 (5)
N2	H22	I[b]	0.68 (5)	3.00 (5)	3.63	157 (4)
N3	H23	I	0.90 (6)	2.82 (6)	3.69	161 (4)
N4	H24	O5	0.81 (6)	2.40 (6)	3.14	151 (5)
N4	H24′	O3	0.90 (5)	2.36 (5)	3.22	158 (4)

[a] Atom at $\bar{x}$, $^1/_2 + y$, $^1/_2 - z$. [b] Atom at $1 - x$, $^1/_2 + y$, $^1/_2 - z$. [c] Atom at $1 - x, y, z$. [d] Atom at $1 + x, y, z$. [e] Atom at $x - 1, y, z$.

complexes, the diprotonated forms being bright pink. The spectra are tabulated in Table VI and shown in Figures 4 and 5. The pK_a values for the two protonation steps for the *trans*-Λ and *cis*-$\alpha(\Delta)$ complexes have been determined spectrophotometrically and are given in Table VII.

$$[Co(PAHPH)_2en]^{3+} \rightleftarrows [Co(PAHP)(PAHPH)]^{2+} + H^+ \quad pK_1 \quad (1)$$

$$[Co(PAHP)(PAHPH)en]^{2+} \rightleftarrows [Co(PAHP)_2en]^+ + H^+ \quad pK_2 \quad (2)$$

The observation of isosbestic points in each pH region (Table VII) confirms the presence of only the two acid–base forms for each step.

The enantiomeric complexes obtained with (−)-PAHPH were found to have identical spectroscopic properties and identical but reverse optical rotations and CD spectra. These are also included in Table VI. Because of limited quantities of these complexes absorption spectra for all protonated forms were not obtained.

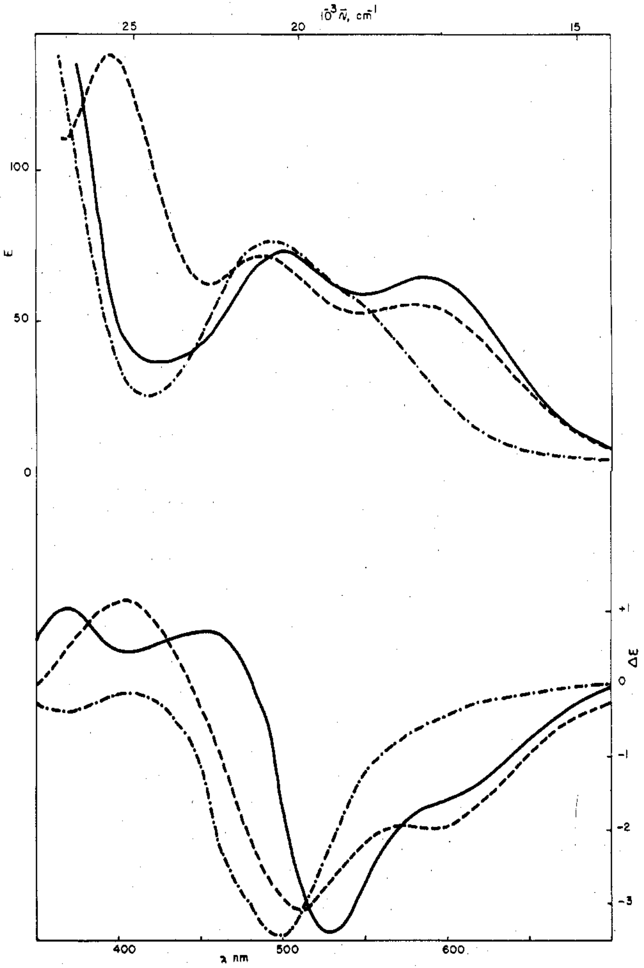


Figure 5. Visible absorption and circular dichroism spectra of the *cis*-$\alpha(\Delta)$ complex: pH 8.60, —; pH 3.30, - - -; 0.6 M HCl.

Discussion

The complexes reported here represent, so far as we know, the first characterization of mixed-ligand cobalt(III) complexes containing two chelated amino alcoholate ligands. The PAHP$^-$ ligand surprisingly is seen to chelate using the more sterically crowded secondary alcohol rather than the primary alcoholic group. The ligands chelate as uninegative anions, the protons being lost from the coordinated alcohol groups. Both complexes add two protons reversibly in acidic solution. Evidence that protonation is occurring on the coordinated alcoholate groups comes from the absorption and CD spectral changes in the region of the cobalt d–d electronic transitions. The

Table VI. Visible Absorption and Circular Dichroism Spectral Data for Co^{III}–PAHPH Complexes[a]

		$A_{1g} \rightarrow T_{1g}$		$A_{1g} \rightarrow T_{2g}$	
complex	medium	abs $\bar{\nu}$ (E)	CD $\bar{\nu}$ (ΔE)	abs $\bar{\nu}$ (E)	CD $\bar{\nu}$ (ΔE)
$[Co(PAHP)_2(PAHPH)NO_2]$	0.2 M HCl	21.0 (125)		29.4 (sh)[d]	
	H_2O/CH_3OH	19.3 (138)			
[*trans*-Λ]$^{3+}$	0.6 M HCl	18.5 (135)	18.7 (3.54)		
		18.9 (sh)	22.2 (−0.35)		
[*trans*-Λ]$^{2+}$	pH 4.50[b]	16.9 (109)	16.9 (+2.80)	25.1 (157)	25.0 (+1.24)
			18.2 (+sh)		
		20.6 (100)	21.1 (−1.67)		
[*trans*-Λ]$^{+}$	pH 8.60[c]	16.6 (134)	16.7 (+3.03)	22.5 (166)	23.8 (+0.93)
		20.0 (sh)	20.7 (−3.77)		
[*cis*-α-Δ]$^{3+}$	0.6 M HCl	18.5 (sh)	20.1 (−3.69)		27.0 (−0.39)
		20.2 (72.1)			
[*cis*-α-Δ]$^{2+}$	pH 3.47[b]	17.2 (55.2)	16.9 (−2.04)	25.4 (136)	24.7 (+1.25)
		20.6 (70.9)	19.6 (−3.26)		
[*cis*-α-Δ]$^{+}$	pH 8.6[c]	17.0 (61.9)	16.9 (sh)		
		20.0 (72.6)	18.9 (−3.58)		27.2 (+1.22)
			22.0 (+0.82)		
[*trans*-Δ]$^{3+}$	0.6 M HCl	18.2 (135)	18.6 (−3.58)		
		18.9 (sh)	22.2 (+0.34)		
[*trans*-Δ]$^{2+}$	pH 4.50[b]		16.9 (−2.82)		25.0 (−1.30)
			18.2 (−sh)		
			21.1 (+1.67)		
[*trans*-Δ]$^{+}$	pH 8.6	16.6 (134)	16.7 (−3.04)	22.5 (166)	23.8 (−0.91)
[*cis*-α-Λ]$^{3+}$	0.6 M HCl	18.5 (sh)	20.1 (+3.70)		27.1 (+0.40)
		20.0 (71.3)			
[*cis*-α-Λ]$^{2+}$	pH 3.47[b]	17.2 (54.2)	16.9 (+2.03)	25.4 (136)	24.7 (−1.27)
		20.5 (68.3)	19.7 (+3.26)		
[*cis*-α-Λ]$^{+}$	pH 8.6	17.0 (62.7)	16.9 (+sh)		
		20.0 (72.8)	19.0 (+3.62)		27.2 (−1.20)
			21.9 (−0.83)		

[a] In 10^3 cm^{-1}. [b] Acetate buffer. [c] Borate buffer. [d] Phenyl ring $\pi \rightarrow \pi^*$, 40 000 cm^{-1} (9.3 × 10^3 cm^{-1}).

Table VII. Acid Dissociation Constants of $[Co(PAHP)_2en]^+$ Complexes (23 ± 1 °C, $\mu = 0.10$)

complex	pK_1 (isosbestic points, nm)	pK_2 (isosbestic points, nm)
trans-Λ	2.14 ± 0.02 (522, 500, 377)	6.22 ± 0.02 (421, 380)
cis-α-Δ	1.49 ± 0.03 (511, 495, 375)	5.16 ± 0.01 (418, 378)

enhanced acidity of chelated amino alcohol ligands has been recognized[10-14] as have changes in the absorption and CD spectra of the complexes upon protonation.[12,13,15-17] The effect of protonation is to shift the spectral bands to higher frequencies. The effect of the first protonation step (pK_2) of the *trans*-Λ and *cis*-α(Δ) complexes is a shift of the spectra to higher frequencies by ca. 200–300 cm^{-1} (Table VI). The second protonation step, however, results in a much greater shift, ca. 2000 cm^{-1}. The observation of several isosbestic points (Table VII) associated with each protonation step confirms the presence of only two absorbing species, i.e., the acidic complex and its conjugate base in each region. The pK_a's are separated by at least 4 units in both complexes allowing the separate determination of the spectra of the intermediate monoprotonated forms of each complex. These complexes are among the most acidic reported[10] with the *cis*-α(Δ) complex being more acidic than the *trans*-Λ complex (Table VII).

Octahedral complexes of cobalt(III) exhibit two bands in their absorption spectra corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions in order of increasing energy. The $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is observed to split to give two bands in the spectra of *trans*-CoN_4X_2 (D_{4h} symmetry) complexes. These are known to correspond to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ electronic transitions with the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition occurring near the same frequency of the parent CoN_6 complex[18,19] and the $^1A_{1g} \rightarrow {}^1E_g$ band appearing at lower frequencies when N > X in the spectrochemical series. The energy difference of the levels in the second transition $^1A_{1g} \rightarrow {}^1T_{2g}$ is not as great and splitting of the second band is not normally observed. The absorption spectrum of the less soluble green diastereomer shows the expected splitting for a D_{4h} coordination symmetry in which the chelated oxygens are trans to each other (Table VI) with the $^1A_{1g} \rightarrow {}^1A_{2g}$ band occurring at 20 700 cm^{-1}, quite close to the absorption maximum of the parent CoN_6 complex ($Co(en)_3^{3+}$, 21 470 cm^{-1}) and the $^1A_{1g} \rightarrow {}^1E_g$ transition occurring at 16 700 cm^{-1}. The effect of protonation is seen to shift the position of the $^1A_{1g} \rightarrow {}^1E_g$ band to higher frequencies while the position of the $^1A_{1g} \rightarrow {}^1A_{2g}$ band remains almost invariant throughout the series of protonated complexes. Calculation of Dq' from crystal field theory[19] for the chelated alcohol and alcoholate functions by using the trans 3+ and trans 1+ complexes respectively gives the results for ROH, $Dq' = 1947$ cm^{-1}, and for RO$^-$, $Dq' = 1567$ cm^{-1}. This is the expected spectrochemical order and places chelated ROH close to H_2O (ca. 1900 cm^{-1}) and RO$^-$ near Cl$^-$ (1559 cm^{-1}). The $^1A_{1g} \rightarrow {}^1T_{2g}$ band is also seen to shift to higher frequencies upon protonation so that in the trans 3+ complexes it becomes hidden under the bands in the UV region.

A fourth low-intensity band of uncertain origin at 28 600 cm^{-1} (Table VI) is also observed in the spectrum of the *trans*-Λ$^+$ complex.

The CD spectra of the protonated forms of the trans complexes containing (+)-PAHP$^-$ are consistent with the Λ configuration consisting of a major positive component at lower energies in the region of the $^1A_{1g} \rightarrow {}^1E_g$ absorption maximum and a negative component near the $^1A_{1g} \rightarrow {}^1A_{2g}$ absorption transition. This is the expected pattern for a cobalt(III) complex having the Λ configuration and has been observed in other *trans*-CoN_4O_2 complexes.[20] The low-frequency CD band is also observed to shift to higher frequencies upon protonation. This band is observed to have a shoulder on the high-frequency side indicating a slight splitting of the two levels under the ^1E_g transition in which both components have a positive rotational strength.

The intensity of the negative $^1A_{1g} \rightarrow {}^1A_{2g}$ CD band decreases upon protonation (Figure 4). A similar effect has been observed in the CD spectra of several bis(ethylenediamine)(amino alcoholato)cobalt(III) complexes[13,16,17] and has been attributed to the vicinal effect due to the ring conformation of the dissymmetric amino alcohol ligand.[13] Vicinal effects may arise from the presence of asymmetric atoms in the ring and also the ring conformation. The (+)-PAHP$^-$ ligand in the *cis*-α(Δ) complex adopts the δ conformation, which places the C_6H_5 and CH_2OH substituents in equatorial positions. It is reasonable to expect that the (+)-PAHP$^-$ ligand will also adopt the δ conformation in the *trans*-Λ complexes. Because of the steric bulk of these substituents it seems unlikely that protonation would cause changes in the ligand conformation. The conformation of the five-membered amino alcoholate chelate ring has been shown to contribute more significantly to the enhancement of the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ CD band upon deprotonation than the asymmetric atoms in the chelate ring.[13] If no significant conformational changes occur upon protonation, the observed decrease in intensity upon protonation must be a result of the changing donor properties of the alcoholate group upon protonation.

The absorption spectra of the *cis*-α(Δ) complexes are unusual in that significant splitting of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) transition occurs producing two bands in the spectrum of the *cis*-$\alpha(\Delta)^+$ complex at 17 000 and 20 000 cm^{-1} (Table VI and Figure 5). It is unlikely that these bands correspond respectively to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h) transitions as the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ does not normally occur at such a low frequency. The intensity of the corresponding CD bands in this region supports the assignment, as the CD bands under the ${}^1T_{2g}$ level are normally weak.

For cis cobalt(III) complexes with C_2 symmetry (e.g., *cis*-$\mathrm{Co(en)_2L_2}$) the ${}^1T_{1g}$ (O_h) state is decomposed into a component of A symmetry and two of B symmetry. The A component has been shown to be derived from the E_a level of the parent trigonal (D_3) complex and hence the rotation strength of the ${}^1A \rightarrow {}^1A$ (E_a) transition should correlate with the configuration of the complex.[21] Experimentally, such complexes are observed to give a major and a minor band under the ${}^1T_{1g}$ (O_h) envelope. The major band is observed to be closer to the center of gravity of the E_a (D_3) and A_1 (D_3) bands of the parent trigonal complex. The major band was suggested to be due to the combined ${}^1A(A_2)$ and ${}^1B(B_2)$ components of the ${}^1T_{1g}$ (O_h) state and hence this band should correlate with the configuration of the complex. The minor band therefore was considered to arise from the ${}^1B(B_1)$ state. Two independent criteria thus are available for assigning these transitions, relative displacement and relative band areas. While this was developed rigorously for *cis*-$\mathrm{Co(en)_2L_2}$ complexes with L being a unidentate ligand, other complexes such as $\mathrm{Co(en)_2(ox)^+}$ and $\mathrm{Co(en)_2(acac)^{2+}}$ have been interpreted via this scheme.[17] The *cis*-$\alpha(\Delta)^+$ complex is of C_2 symmetry and the CD spectrum of this complex is quite similar, containing a major band at 18 900 cm^{-1} and a minor band at 16,900 cm^{-1} with the major band being displaced less from the parent $\mathrm{Co(en)_3}^{3+}$ ${}^1T_{1g}$ band than the minor component. The major band therefore is assigned to the ${}^1A \rightarrow \{{}^1A(A_2), {}^1B(B_2)\}$ transition and the negative rotational strength of this band is consistent with the observed Δ configuration of this complex. This ordering of levels indicates an axial field which is stronger than the equatorial field.[18,21] The assignments of the CD bands support the assignments in the absorption spectra. The observed splitting of the ${}^1T_{1g}$ (O_h) level in the absorption spectrum of the *cis*-$\alpha(\Delta)^+$ complex can be interpreted on the basis of the structure of this complex which shows that the cobalt–nitrogen bonds trans to an oxygen are lengthened by comparison with the cobalt–nitrogen bond cis to the oxygens. In an acetylacetonato–ethylenediamine complex[8] and a dimethylglyoximato complex[23] of Co(III), the Co–N bond lengths in the equatorial plane averaged 1.907 (4) Å as compared to 1.965 (7) Å for the axial ones. Thus, the equatorial Co–N bonds in the present compound have increased relative to the axial bonds. This may result from the disorder exhibited by the ethylenediamine ligand. In any case, the axial ligand field should be somewhat stronger than the equatorial ligand field with two nitrogen and two alcoholate oxygen donor atoms. This difference in field strengths is apparently great enough to cause the splitting of the ${}^1T_{1g}$ (O_h) band.

The CD spectrum of the *cis*-$\alpha(\Delta)^+$ complex is of interest because both CD bands in the long-wavelength absorption band region are of the same sign. McCaffery et al.[21] have shown that the rotational strengths of the bands in this region of complexes with approximate C_{2v} symmetry can be dominated by the rotational strength of the parent E_a (D_3) transition and therefore have the same signs. The extent to which this analysis applies depends on the magnitude of the vicinal effects due to the (+)-PAHP$^-$ chelate ring which are as yet unknown.

As in the *trans*-Λ series, both the absorption maxima and the CD maxima shift to higher frequencies upon protonation. The absorption spectrum of the monoprotonated *cis*-$\alpha(\Delta)^{2+}$ complex exhibits a third band at 25 400 cm^{-1}, and a corresponding CD maximum at 24 700 cm^{-1} is also observed. A similar band has been reported in the CD spectra of the deprotonated form of several $\mathrm{Co(en)_2(amino\ alcoholato)^{2+}}$ complexes and has been attributed to the conformation of the amino alcoholate chelate ring.[13] The positive CD maximum at 25 000 cm^{-1} observed here for the δ-(+)-PAHP conformation is consistent with the results obtained for the $\mathrm{Co(en)_2(amino\ alcoholato)^{2+}}$ complexes. These bands are observed in the absorption and CD spectra of both the *trans*-Λ^{2+} and the *cis*-$\alpha(\Delta)^{2+}$ complexes and interestingly are seen only in the spectra of these intermediate monoprotonated forms of each complex.

The crystal structure of the *trans*-Λ^+ as the chloride salt is currently under investigation to further characterize these complexes.

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Registry No. $\mathrm{Co(PAHP)_2(PAHPH)NO_2}$, 69726-68-7; *trans*-$\Lambda$-$(+)_{589}$-[Co{(+)-PAHP}$_2$en]Cl, 69726-69-8; *trans*-Δ-$(-)_{589}$-[Co{(−)-PAHP}$_2$en]Cl, 69779-31-3; *cis*-α-Λ-$(+)_{589}$-[Co{(−)-PAHP}$_2$en]I, 69779-32-4; *cis*-α-Δ-$(-)_{589}$-[Co{(+)-PAHP}$_2$en]I·H$_2$O, 69779-33-5; *trans*-Λ^{3+}, 69726-70-1; *trans*-Λ^{2+}, 69726-71-2; *cis*-α-Δ^{3+}, 69779-34-6; *cis*-α-Δ^{2+}, 69779-35-7; *trans*-Δ^{3+}, 69779-36-8; *trans*-Δ^{2+}, 69779-37-9; *cis*-α-Λ^{3+}, 69779-38-0; *cis*-α-Λ^{2+}, 69779-39-1; sodium hexanitrocobaltate(III), 13600-98-1.

Supplementary Material Available: Table of structure factors (12 pages). Ordering information is given on any current masthead page.

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Structures of Five-Coordinate Dinitrosyls of Manganese. 2. The Triclinic Form of Dinitrosylbis(dimethyl phenylphosphonite)manganese(I) Chloride, $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$

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The crystal structure of the second polymorph of dinitrosylbis(dimethyl phenylphosphonite)manganese(I) chloride, $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$, has been determined by X-ray diffraction. This form crystallizes from C_2H_5OH/CH_2Cl_2 in the triclinic space group $P\bar{1}$, with $a = 15.727$ (5) Å, $b = 15.198$ (5) Å, $c = 9.405$ (5) Å, $\alpha = 90.97$ (5)°, $\beta = 89.04$ (5)°, $\gamma = 97.21$ (5)°, $V = 2229.6$ Å^3, $\rho_{obsd} = 1.45$ g cm^{-3}, and $Z = 4$ (two molecules per asymmetric unit). The structure was solved by direct methods and refined by block-diagonal least squares to a conventional R of 0.040 for 3711 reflections with $I > 1.65\sigma(I)$. The coordination about the manganese is trigonal bipyramidal in both molecules; however, the relative conformation of phosphonite ligands in the two molecules is not the same. One molecule has symmetry 2, while the other has symmetry m. In both isomers the NO groups are ordered, and the atoms of the $\{Mn(NO)_2Cl\}$ groups are coplanar with the two NO groups bent in toward each other. Bond lengths and angles of interest are as follows. Molecule "2": Mn–P = 2.285, 2.295 (5) Å; Mn–Cl = 2.360 (5) Å; Mn–N = 1.657, 1.644 (10) Å; N–O = 1.19, 1.18 (1) Å; P–Mn–P = 163.9 (5)°; N–Mn–N = 113.5 (5)°; O–Mn–O = 101.9 (5)°; Cl–Mn–P = 82.3, 82.4 (5)°; Cl–Mn–N = 129.2, 117.3 (5)°; Mn–N–O = 167, 165 (1)°. Molecule "M": Mn–P = 2.298, 2.297 (5) Å; Mn–Cl = 2.352 (5) Å; Mn–N = 1.633, 1.642 (10) Å; N–O = 1.19, 1.19 (1) Å; P–Mn–P = 167.6 (5)°; N–Mn–N = 112.1 (5)°; O–Mn–O = 99.8 (5)°; Cl–Mn–P = 83.4, 84.5 (5)°; Cl–Mn–N = 123.0, 124.9 (5)°; Mn–N–O = 166, 165 (1)°.

Introduction

A large number of solvents were tried before crystals of $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$ of quality suitable for X-ray analysis could be obtained.[1] The combination of ethanol/methylene dichloride was found to yield a second polymorph, triclinic with two molecules per asymmetric unit. The first structure determination had shown that the two Mn–N–O groups were nonlinear, in contrast to the results reported[2] for the series $[Mn(NO)(CO)_{4-x}\{P(C_6H_5)_3\}_x]$ ($x = 0, 1, 2$). The two molecules per asymmetric unit in this second form offered the chance of getting four independent measures of the Mn–N–O angle and the Mn–N and N–O bond lengths, and for this reason the crystal structure was determined. Preliminary results have been published.[3]

Experimental Section

The compound was prepared as described previously,[4] and crystals were obtained from C_2H_5OH/CH_2Cl_2. Preliminary oscillation and Weissenberg photographs showed that the crystals were triclinic; satisfactory elucidation of the structure confirmed that the space group was centrosymmetric, $P\bar{1}$.

Crystal data: $C_{16}H_{22}MnClN_2O_6P_2$, mol wt 490.4, triclinic space group $P\bar{1}$, $a = 15.727$ (5) Å, $b = 15.198$ (5) Å, $c = 9.405$ (5) Å, $\alpha = 90.97$ (5)°, $\beta = 89.04$ (5)°, $\gamma = 97.21$ (5)°, $V = 2229.6$ Å^3, $\rho_{obsd} = 1.45$ (3) g cm^{-3}, $Z = 4$, μ(Mo Kα) = 9.2 cm^{-1}; two independent molecules per asymmetric unit.

Accurate unit cell dimensions were determined from least-squares refinement of the 2θ, χ, and ϕ angles of 25 reflections measured on a Philips PW 1100 four-circle diffractometer (C.S.I.R., Pretoria) with graphite-monochromated Mo Kα radiation (λ 0.7107 Å). Intensity data were collected for θ between 3 and 20°. Three reflections were used as intensity standards and remeasured after every 60 reflections; no decomposition of the crystal was detectable. The diffractometer was operated in the standard mode; the ω–2θ scan technique was used; the scan width was 1.2°, each peak was scanned over 40 s, and the background was counted for 40 s. Of the 4135 reflections measured, 3711 were classed as observed: $I > 1.65\sigma(I)$. Only Lorentz–polarization corrections were applied.

Table I

	triclinic $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$	ideal centrosymmetric distribution
$\lvert E\rvert$	0.805	0.798
$\lvert E^2 - 1\rvert$	0.973	0.968
$\lvert E^2\rvert$	1.014	1.00
%$E > 3.0$	0.3	0.3
%$E > 2.0$	4.6	4.6
%$E > 1.0$	26.6	31.7
Probk	0.0973	

Starting Set of Reflections

hkl	*E*	cor soln	*hkl*	*E*	cor soln
623	2.83[a]	+	522	2.96[b]	–
332	3.50[a]	+	580	3.40[b]	–
$1\bar{4}3$	3.02[a]	+	$\bar{4}\bar{3}8$	3.09[b]	–
$\bar{1}\bar{3}3$	3.21[b]	–	$\bar{6}\bar{5}7$	2.95[b]	+

[a] Origin definers. [b] Variables.

A three-dimensional Patterson map showed that the two molecules, A and B, in the asymmetric unit were aligned so that the Mn–Cl vector

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