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cation has square-planar geometry typical for complexes of platinum(II). While the estimated standard deviations in the bond lengths and angles are large by comparison to those in compound **1**, the geometry of the platinum coordination sphere is normal. The Pt–N and Pt–Cl bond lengths and interbond angles are comparable to those found in compounds **1** and **2**. The four ligands attached to the platinum define a plane with a rms deviation of 0.017 Å, and the platinum atom lies in the plane (0.001 Å displacement). The platinum coordination plane makes a dihedral angle of 56.8° with the plane of the 2-hydroxypyridine ligand. This angle is $\sim$15° smaller than the corresponding angle in compound **1**.

The geometry of the 2-hydroxypyridine ligand in compound **3** is equivalent to that found in compound **1**. Although an accurate comparison is precluded by the large errors in **3**, the largest difference ($<2\sigma$) is found in the C3–C4 bond length. The small dihedral angle between the plane of the ring and platinum coordination plane may be a result of an intramolecular hydrogen bond between the exocyclic oxygen (O2) and the ammine ligand (N3). While hydrogen atoms were not located in the structure, the short N3–O2 distance, 2.93 (3) Å, is suggestive of a hydrogen bond between these two groups.

A stereoview of the unit-cell packing of compound **3** is given in ref 23. As suggested by the length of the crystallographic *c* axis, 4.151 (1) Å, the relatively flat cations stack in columns along the [001] direction. The shortest interaction Pt–Pt′ distance is 5.68 Å (between cations stacked along *c*). The planar nitrate anions also stack in channels along the crystallographic *c* axis. The plane of the nitrate anion makes a dihedral angle of 35.9° with the platinum coordination plane. The nitrate anion is involved in three possible hydrogen-bond contacts to neighboring cations. The oxygen atoms O41 and O42 lie close to the ammine nitrogen atoms N2 and N3 (Table VII), and consequently the nitrate anion appears to form a hydrogen-bonded bridge between adjacent ammines of the same cation. The remaining nitrate oxygen atom (O43) lies 2.62 (3) Å from the 2-hydroxyl group of a neighboring cation.

Conclusion

The structures of three mononuclear *cis*-diammineplatinum complexes of α-pyridone have been determined crystallographically. The mono- and bis(α-pyridone) complexes of *cis*-diammineplatinum(II) contain 2-hydroxypyridine ligands bound to platinum through the heterocyclic nitrogen atom. Recrystallization of the mono(2-hydroxypyridine) complex *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ from 1M HCl provides small quantities of the α-pyridonate complex of Pt(IV) *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$. Deprotonation of the α-pyridone ligand in this last complex is promoted by the high electrostatic Lewis acid strength of Pt(IV),[26] despite the acidic conditions of the medium. Knowledge of the structures of each of these mononuclear complexes is valuable in assessing the chemistry of *cis*-diammineplatinum(II) complexes with nucleic acid bases and their analogues.

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Registry No. **1**, 76761-67-6; **2**, 86471-90-1; **3**, 86471-92-3; *cis*-$[Pt(NH_3)_2Cl_2]$, 15663-27-1; *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]Cl$, 85336-86-3; $[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2$, 76775-76-3; *cis*-$[Pt(NH_3)_2Cl(H_2O)]^{2+}$, 53861-42-0.

Supplementary Material Available: Atomic positional and thermal parameters for compounds **1**–**3** (Tables S1–S3) as well as final observed and calculated structure factors (Tables S4–S6) (26 pages). Ordering information is given on any current masthead page.

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[26] Zhang, Y. *Inorg. Chem.* **1982**, *21*, 3889 and references cited therein.

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Cobalt(III) Complexes of Amino Alcohols. Structural Consequences of Protonation

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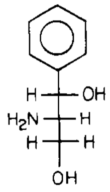
The crystal structure of the diprotonated form of *cis*-α-Δ-$(-)_{589}$-$[Co\{(+)\text{-PAHP}\}_2\text{en-}\delta\delta\gamma]^+$ (PAHP = monoanion of 1-phenyl-2-amino-1,3-dihydroxypropane), $Co(C_9H_{12}NO_2H)_2(C_2N_2H_8)Cl_3\cdot 2H_2O$, has been determined by single-crystal X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 14.113$ (2) Å, $b = 18.782$ (5) Å, $c = 10.175$ (2) Å, and $Z = 4$. Full-matrix least-squares refinement gave an R index of 0.044 for 2060 observed reflections with intensities greater than 3σ. The absolute configuration was determined by refinement of both enantiomorphs. The protonation sites were inferred to be the alcohol oxygens bonded to cobalt from the very short Cl–O interatomic distances. As a consequence, the Co–O and C–O bonds are lengthened. The effect of protonation upon other structural features is described.

Introduction

As part of a study of complexes containing substituted 2-aminoethanol ligands, we have recently reported the characterization of several isomeric complexes of cobalt(III) containing ethylenediamine and either (1*S*,2*S*)- or (1*R*,2*R*)-1-phenyl-2-amino-1,3-dihydroxypropane (PAHPH) (structure I).[1] The complexes $[Co(PAHP)_2en]^+$ are strongly acidic (diprotic) and were isolated containing the chelated amino alcoholate ligand $PAHP^-$. As part of this characterization, the crystal structure of the complex shown to be



I

cis-α-Δ-$(-)_{589}$-$[Co\{(+)\text{-PAHP}\}_2\text{en-}\delta\delta\gamma]^+$, the *cis*-$\alpha(\Delta)^+$ isomer, was reported.[1] This showed that the $PAHP^-$ chelates via the amine and the secondary alcoholate groups. In acid solution this complex and its isomers reversibly add two protons, the site of protonation presumably being the coordinated alcoholate

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moieties. We have now isolated the diprotonated form of the *cis*-$\alpha(\Delta)^+$ isomer and report herein its crystal structure. This provides a unique opportunity to examine the structural consequences of protonation of a coordinated ligand group and represents the third crystal structure reported of a complex containing this ligand; the structure of a copper(II) complex has also been reported.[2]

Experimental Section

Preparation of Complexes. The preparation of the complex is described in the previous paper.[1] The crystals of the diprotonated form of the cis-$\alpha(\Delta)^+$ complex were obtained by dissolving the chloride salt in 12 M hydrochloric acid and allowing the solution to stand several days at ambient temperature. The crystals lose HCl upon removal from the mother liquor. For this reason elemental analysis for the diprotonated complex is not reported.

Crystal Data. A dark red prismatic crystal with approximate dimensions 0.3 × 0.3 × 0.25 mm was mounted in a glass capillary under 12 M HCl to keep it from decomposing. Accurate unit cell parameters were determined from 25 reflections at moderate to high 2θ angles. A graphite-crystal incident beam monochromator was used with Mo Kα radiation ($\lambda = 0.70930$ Å for Mo Kα_1). The orthorhombic parameters were determined as $a = 14.113$ (2) Å, $b = 18.782$ (5) Å, $c = 10.175$ (2) Å, and $V = 2697.1$ (16) Å^3. The calculated density, based upon $Z = 4$, is 1.457 g cm^{-3}. No measured density was obtained because of the difficulty of maintaining the crystals outside 12 M HCl. The systematic absences were $h00$ with $h = 2n + 1$, $0k0$ with $k = 2n + 1$, and $00l$ with $l = 2n + 1$, fixing the space group as $P2_12_12_1$.

Intensity data were collected at 24 ± 2 °C with an automated four-circle diffractometer (Enraf-Nonius CAD-4) under the same conditions reported earlier.[1] A total of 2570 unique reflections were collected of which 2060 had intensities greater than $3\sigma(I)$ and were used in the least-squares refinement. Lorentz and double polarization corrections were applied to the data, but an absorption correction was not. The low linear absorption coefficient, $\mu = 10.0$ cm^{-1} for Mo Kα, coupled with the almost equal dimensions of the crystal, suggests that neglect of this correlation would not introduce an appreciable error.

Structure Solution and Refinement. A three-dimensional Patterson map revealed the positional parameters for the cobalt and for one chlorine atom. Subsequent difference Fourier maps yielded the positions of all the non-hydrogen atoms.[3] Full-matrix least-squares refinement with anisotropic temperature factors reduced R_F, defined as $\sum(||F_o| - |F_c||)/\sum|F_o|$, to 0.063. At this point, positional parameters for all the hydrogen atoms except those of the alcohol and bonded solvent were calculated and entered into the refinement as fixed contributions. This reduced R_F to 0.054. In order to determine the absolute configuration, refinement was also carried out on the enantiomorph. This procedure reduced R_F to 0.047. A difference map revealed the positions of the remaining non-water and possible chloride-bonded hydrogens. Refinement was carried to completion (307 variables) as judged by a shift to error ratio of less than 0.5 for all non-solvent atoms and a value of about 1.0 for O1 and O6. The final R_F was 0.044, and the weighted function, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.060. The esd of an observation of unit weight was 1.674.

The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ with weights, w, assigned by the expression $w = 1/\sigma(F_o)^2$ where $\sigma(F_o)^2 = [\sigma(I)^2 + (pI^2)^2]^{1/2}$. A value of 0.05 was assigned to p. Neutral-atom scattering factors[4] were used for all non-hydrogen atoms, and the cobalt and chlorine atom values were corrected for anomalous dispersion (both real and imaginary terms). Scattering factors for hydrogen atoms were those of Stewart et al.[5]

The final difference map contained several peaks at a height of 0.3–0.4 e Å^{-3}. Some of these were close to water oxygens or chlorines, but outside good bonding ranges, and thus were not included in the calculation. The hydrogen-bond scheme was then deduced from close contacts of the heavy atoms involved in hydrogen bonding.

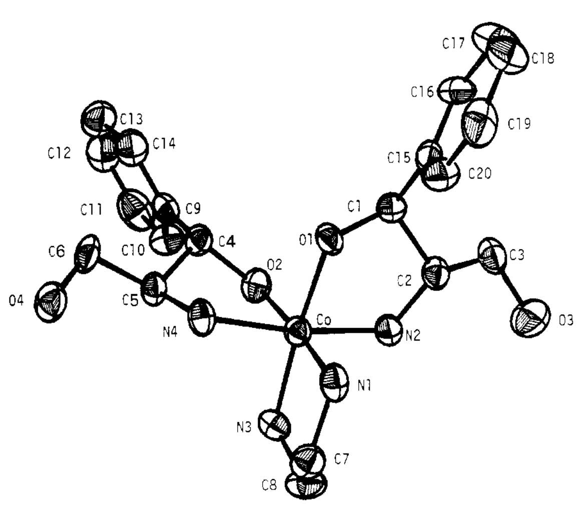

Figure 1. ORTEP diagram of the title complex with the labeling scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

A listing of the observed and calculated structure factors as well as thermal parameters is given as supplementary material.

Results

Table I lists the positional parameters for all the atoms included in the final refinement. The four water hydrogens and the two hydrogens required to neutralize the charges of two chloride ions are not listed in the table.

A perspective view of the cation is shown in Figure 1, together with the numbering scheme used in the tables. As before, each of the aminopropanediol ligands chelates cobalt through the amino nitrogen and the hydroxyl groups on the carbon bonded to the phenyl groups. Together with the ethylenediamine nitrogens, they form a slightly distorted octahedron about the cobalt atom. Bond distances and angles in the coordination sphere are given in Table II. They are, with several exceptions to be noted below, almost identical with those obtained previously for $Co(PAHP)_2I\cdot4H_2O$. The ethylenediamine Co–N bonds are slightly shorter. This may stem from the fact that the ethylenediamine in the latter structure was disordered. Also, the Co–N(ethylenediamine) distances are smaller than the Co–N(amino alcohol) values, as expected. The interior angles of the five-membered rings subtended at the cobalt atom are each smaller than 90° and constitute the smallest angles in the coordination sphere.

Bond distances and angles for the remainder of the molecule are given in Table III. These parameters are quite regular. Mean-plane equations are presented in Table IV as supplementary material. From the deviations of atoms from the planes and Figure 1, it is deduced that the conformation is $\Delta(\delta\delta\lambda)$. Phenyl ring 7 makes a dihedral angle of 52.4° with the five-membered ring to which it is attached, while the dihedral angle between phenyl ring 8 and plane 5 is 73.1°.

Possible hydrogen bonds are shown in Table V. Cl1 and Cl2 form short hydrogen bonds with O1 and O2, respectively. These oxygens are also part of the five-membered rings chelating the cobalt and are the sites of protonation. This fact, together with the shortness of the O-Cl distances, strongly indicates that the oxygens act as donor atoms, forming O–H---Cl type hydrogen bonds. Atom Cl1 then acts as the acceptor for hydrogen bonds from O6, N2, and N3. The Cl1 atom thus serves to link two adjacent complexes through hydrogen bonds along the *a* direction. The second Cl ion acts as the acceptor for an H bond from N2 in the same complex that contains O2 and also from N1 in an adjacent complex, again linking complexes along the *a* direction. The remaining

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(2) A. M. M. Lanfredi, A. Tiripicchio, and M. T. Camellini, *Acta Crystallogr., Sect. B*, **B35**, 349 (1979).

(3) All programs used for this study, unless otherwise specified, were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, revised 1981.

(4) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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Table I. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	−0.27883 (6)	−0.28239 (5)	−0.02374 (9)	H14	−0.3445	−0.0685	−0.3442
Cl1	−0.0071 (1)	−0.3568 (1)	0.0985 (2)	H13	−0.2798	0.0135	−0.4905
Cl2	−0.0652 (1)	−0.1352 (1)	0.0220 (2)	H12	−0.1181	0.0069	−0.5376
Cl3	−0.3225 (2)	−0.3853 (1)	0.3782 (2)	H11	−0.0255	−0.0811	−0.4472
O1	−0.3621 (3)	−0.2129 (3)	0.0553 (4)	H10	−0.0936	−0.1656	−0.3060
O2	−0.2108 (3)	−0.2104 (2)	−0.1278 (5)	H20	−0.4751	−0.2381	0.2501
O3	−0.1351 (4)	−0.2379 (3)	0.3905 (6)	H19	−0.5992	−0.2002	0.3849
O4	−0.4432 (3)	−0.2892 (3)	−0.4308 (5)	H18	−0.5988	−0.0847	0.4676
O5	−0.2980 (4)	−0.4179 (3)	−0.3178 (5)	H17	−0.4746	−0.0082	0.4153
O6	0.1326 (10)	0.0403 (6)	0.2153 (9)	H16	−0.3522	−0.0456	0.2771
N1	−0.3471 (4)	−0.3559 (3)	0.066 4 (5)	H4	−0.3218	−0.1484	−0.1872
N2	−0.2011 (4)	−0.2631 (3)	0.1303 (6)	H5	−0.2722	−0.2665	−0.3394
N3	−0.1969 (4)	−0.3576 (3)	−0.0871 (6)	H1	−0.2908	−0.1296	0.1346
N4	−0.3593 (4)	−0.2875 (3)	−0.1813 (5)	H2	−0.2951	−0.2525	0.2844
C1	−0.3237 (5)	−0.1712 (3)	0.1620 (7)	H3	−0.2260	−0.1595	0.3912
C2	−0.2571 (4)	−0.2216 (4)	0.2324 (6)	H3′	−0.1505	−0.1532	0.2810
C3	−0.1905 (5)	−0.1852 (4)	0.3278 (7)	H6	−0.3660	−0.2051	−0.4646
C4	−0.2744 (5)	−0.1782 (3)	−0.2235 (7)	H6′	−0.4394	−0.1944	−0.3529
C5	−0.3198 (5)	−0.2428 (4)	−0.2897 (6)	H7	−0.3338	−0.4635	0.0789
C6	−0.3947 (5)	−0.2265 (4)	−0.3901 (7)	H7′	−0.3579	−0.4383	−0.0624
C7	−0.3218 (5)	−0.4281 (4)	0.0145 (8)	H8	−0.1999	−0.4637	−0.0724
C8	−0.2167 (5)	−0.4246 (4)	−0.0179 (8)	H8′	−0.1808	−0.4264	0.0610
C9	−0.2257 (5)	−0.1252 (3)	−0.3105 (7)	H21	−0.3320	−0.3541	0.1575
C10	−0.1316 (5)	−0.1288 (4)	−0.3420 (8)	H21′	−0.4132	−0.3483	0.0558
C11	−0.0914 (6)	−0.0786 (4)	−0.4266 (8)	H22	−0.1472	−0.2360	0.1051
C12	−0.1464 (7)	−0.0268 (4)	−0.4799 (9)	H22′	−0.1809	−0.3069	0.1679
C13	−0.2414 (7)	−0.0224 (1)	−0.4523 (8)	H23	−0.1327	−0.3445	−0.0730
C14	−0.2792 (6)	−0.0716 (4)	−0.3663 (8)	H23′	−0.2074	−0.3642	−0.1788
C15	−0.4024 (5)	−0.1462 (4)	0.2479 (6)	H24	−0.4209	−0.2711	−0.1599
C16	−0.4024 (6)	−0.0774 (4)	0.2982 (8)	H24′	−0.3626	−0.3357	−0.2099
C17	−0.4752 (7)	−0.0551 (5)	0.3800 (10)				
C18	−0.5487 (6)	−0.1005 (5)	0.4119 (9)				
C19	−0.5490 (5)	−0.1684 (5)	0.3632 (8)				
C20	−0.4751 (5)	−0.1907 (4)	0.2823 (8)				

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

Bond Distances			
Co-O1	1.932 (4)	Co-N2	1.948 (5)
Co-O2	1.968 (4)	Co-N3	1.937 (5)
Co-N1	1.918 (5)	Co-N4	1.966 (4)
Angles			
O1-Co-O2	93.3 (2)	O2-Co-N3	91.8 (2)
O1-Co-N1	88.9 (2)	O2-Co-N4	82.9 (2)
O1-Co-N2	83.2 (2)	N1-Co-N2	91.8 (2)
O1-Co-N3	174.2 (2)	N1-Co-N3	86.2 (2)
O1-Co-N4	92.2 (2)	N1-Co-N4	93.7 (2)
O2-Co-N1	176.0 (2)	N2-Co-N3	93.9 (2)
O2-Co-N2	91.7 (2)	N2-Co-N4	172.1 (2)

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

Table III. Bond Distances (Å) and Angles (deg) outside the Coordination Sphere

Bond Distances			
O1-C1	1.445 (7)	C7-C8	1.522 (9)
O2-C4	1.456 (7)	C9-C10	1.368 (8)
O3-C3	1.414 (7)	C9-C14	1.380 (9)
O4-C6	1.424 (7)	C10-C11	1.397 (9)
N1-C7	1.498 (8)	C11-C12	1.357 (10)
N2-C2	1.520 (7)	C12-C13	1.373 (11)
N3-C8	1.468 (8)	C13-C14	1.380 (9)
N4-C5	1.494 (7)	C15-C16	1.389 (8)
C1-C2	1.515 (7)	C15-C20	1.369 (8)
C1-C15	1.489 (8)	C16-C17	1.387 (9)
C2-C3	1.515 (8)	C17-C18	1.383 (10)
C4-C5	1.530 (8)	C18-C19	1.368 (10)
C4-C9	1.499 (8)	C19-C20	1.393 (9)
C5-C6	1.502 (8)		
Angles			
Co-O1-C1	116.8 (3)	O4-C6-C5	111.5 (5)
Co-O2-C4	110.2 (3)	N1-C7-C8	105.6 (5)
Co-N1-C7	111.3 (4)	N3-C9-C7	109.0 (5)
Co-N2-C2	110.6 (3)	C4-C9-C10	123.4 (6)
Co-N3-C8	110.6 (4)	C4-C9-C14	118.5 (6)
Co-N4-C5	111.1 (3)	C10-C9-C14	118.1 (6)
O1-C1-C2	104.4 (4)	C9-C10-C11	120.4 (6)
O1-C1-C15	109.4 (4)	C10-C11-C12	119.8 (7)
C2-C1-C15	112.5 (5)	C11-C12-C13	121.4 (7)
N2-C2-C1	108.6 (4)	C12-C13-C14	117.8 (7)
N2-C2-C3	110.3 (4)	C9-C14-C13	122.5 (7)
C1-C2-C3	113.9 (5)	C1-C15-C16	120.6 (5)
O3-C3-C2	108.4 (5)	C1-C15-C20	121.1 (5)
O2-C4-C5	102.9 (4)	C16-C15-C20	118.3 (6)
O2-C4-C9	112.9 (5)	C15-C16-C17	120.2 (6)
C5-C4-C9	117.4 (5)	C16-C17-C18	120.7 (6)
N4-C5-C4	106.1 (4)	C17-C18-C19	119.5 (7)
N4-C5-C6	110.8 (4)	C18-C19-C20	119.5 (7)
C4-C5-C6	115.6 (5)	C15-C20-C19	121.9 (6)

chlorine, Cl3, participates in four hydrogen bonds, acting as the acceptor. Two of the bonds are from N1 and the alcohol group (O4) in the same complex. The other alcohol group (O3) acts as a donor in forming an H bond with the alcohol group (O4) in an adjacent complex ion in the *a* direction. The water molecule O5 accepts hydrogen bonds from N3 and N4, both of which are in the same complex ion. It, in turn, hydrogen bonds to Cl3 and the other water molecule O6. Thus, a network of hydrogen bonds zigzags roughly parallel to *c*. A second network of hydrogen bonds running somewhat parallel to the *a* axis is formed by O3–O4–Cl3–O6.

Discussion

The complex which was isolated from hydrochloric acid and whose structure is reported here is formulated as *cis*-α-Δ-$[\mathrm{Co}\{(+)\text{-PAHPH}\}_2\mathrm{en}\text{-}\delta\delta\lambda]\mathrm{Cl}_3\cdot 2\mathrm{H}_2\mathrm{O}$. Its structure and that reported in the previous paper[1] allow a comparison of structural differences of a conjugate acid/base pair of complexes. As expected, the structures confirm the Δ configuration about the metal ion in both cases. Two structural changes argue for the coordinated alcoholate groups as the sites of protonation: the lengthening of the Co–O and the C–O bond distances of the alcoholates upon addition of two protons. The Co–O1 and Co–O2 bonds are observed to increase from 1.877 (3) and

Table V. Possible Hydrogen Bonds

A···B[a]	dist, A	A···B[a]	dist, Å
Cl1→O1[d]	2.890 (4)	Cl3←O5[b]	3.173 (5)
Cl1←O6[e]	3.234 (8)	Cl3←O6[e]	3.167 (13)
Cl1←N2[b]	3.271 (5)	Cl3←N1[b]	3.238 (5)
Cl1←N3[b]	3.278 (5)	O3→O4[d]	2.786 (6)
Cl2→O2[b]	2.923 (4)	O5→O6[d]	2.708 (10)
Cl2←N1[d]	3.211 (5)	O5←N3[b]	2.971 (7)
Cl2←N2[b]	3.265 (5)	O5←N4[b]	2.945 (6)
Cl3←O4[b]	3.153 (5)		

[a] Position of B atom relative to A at x, y, z and probable donor (→) and acceptor (←) relationship. [b] x, y, z. [c] $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$. [d] $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$. [e] $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

1.900 (3) to 1.932 (4) and 1.968 (4) Å, respectively, upon protonation.

The Co–O bond lengths in the diprotonated complex are similar to reported Co(III)–O bond distances for terminally coordinated water,[6,7] as would be expected on the basis of their similarities in donor properties. The related carbon–oxygen bonds C1–O1 and C4–O2 increase from 1.417 (5) and 1.412 (5) Å in the unprotonated form to 1.445 (7) and 1.456 (7) Å, respectively, in the diprotonated complex. This is in contrast to the C–O bond distances of the two noncoordinated alcohol functions, which show no significant differences between the two structures and which have an average value of 1.419 (5) Å. No other significant changes in bond lengths are observed between the two structures.

The observed Co–O and C–O bond length increases imply some bond weakening of both bonds with protonation. Comparably lengthened amino alcohol C–O bonds have been reported in several structures involving amino alcoholate chelate rings in which the oxygens are extensively hydrogen bonded.[8,9] This may reflect a similar situation in which the effect of the metal ion and hydrogen bond together cause a lengthening of the adjacent C–O bond. The effect of either a metal ion or protonation alone seems to have very little influence on C–O bond distances.[10]

Both structures are extensively hydrogen bonded, with the alcoholate oxygens O1 and O2 acting as acceptor atoms in the unprotonated complex. In the diprotonated complex both of these oxygens are closely associated with a chloride ion. Although the positions of the hydrogens bridging these oxygen–chloride pairs were not located, in light of the acid–base properties of this complex it is assumed the chloride ions are the acceptors.

The increase in the observed Co–O bond distances with protonation is significant in light of the corresponding spectral shift to higher frequencies in the absorption spectrum noted previously.[1] Shifts of similar magnitude were noted for both the cis-α and the trans isomers. The shifts are consistent with the relative positions of ROH ($\sim H_2O$) and RO^- ($\sim Cl^-$) in the spectrochemical series. The alkoxide ligand, like OH^- and Cl^-, has two pairs of electrons, which enable it to act as a stronger π-donor ligand than can a coordinated alcohol group with only one such pair of electrons. According to the angular-overlap model (AOM),[11] the crystal field splitting parameter, Δ_0, is related to the difference in σ- and π-donor abilities of a ligand. Ligands such as OH^- and Cl^-, which produce small splittings, are weak σ donors and strong π donors. In this regard, the combined effects of protonation are consistent with the reduction of the π-donating ability of the coordinated alcoholate/alcohol groups by protonation. The Co–O bond distances observed in the unprotonated complex (1.877, 1.900 Å) represent examples of short cobalt–oxygen bonds. From the covalent radius for sp^3-hybridized N, a covalent radius for cobalt in the present complexes of ca. 1.24 Å can be calculated. This value then allows a value of 0.65 Å to be obtained for the radius of the coordinated alcoholate moiety. This is only slightly less than the value of the covalent radius of oxygen (0.66 Å)[12] and suggests that the degree of π-bonding in this instance is not sufficient to significantly shorten the cobalt–oxygen bond distance.

Registry No. *cis*-α-Δ-$(-)_{589}$-[Co{(+)-PAHPH}$_2$en-$\delta\delta\lambda$]$Cl_3 \cdot 2H_2O$, 86507-86-0.

Supplementary Material Available: A stereoscopic representation of the unit cell contents and listings of least-squares mean planes (Table IV), anisotropic thermal parameters, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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