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Notes

A Seven Coordinate Co−EDTA Complex. Crystal and Molecular Structure of Aquo(ethylenediaminetriacetatoacetic acid)cobalt(III) Dihydrate

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Introduction

There is continuing interest in the complexes of ethylenediaminetetraacetic acid, EDTA, with various transition metals. A large number of such heavy-metal−organic compound systems are increasingly being postulated and studied as components in environmental waste, thus making a detailed understanding of their chemical properties and reaction chemistry highly desirable. In analytically-related investigations, metal−EDTA chemical systems have been used as model systems for studying reversed phase ion-pair liquid chromatography to separate heavy metals such as cadmium, nickel, iron, and copper.[1] Proton nuclear magnetic resonance (NMR) has been used to study such paramagnetic metal ions as copper(II), nickel(II), iron(II,III), and gadolinium(III) that have been chelated to EDTA,[2] while the determination of transition and alkaline earth metal anionic complexes of EDTA was effected using dual-column ion chromatography.[3] Ligand substitution reaction chemistry between EDTA and metal−cupferron complexes of copper, iron, nickel, zirconium, titanium, and aluminum ions have been studied using conductometric titrations,[4] while similar studies were also conducted using EDTA and metal−8-quinolinol chelates.[5] The formation constants of many six-coordinate metal−EDTA complexes are known and EDTA is the reagent of choice in most complexometric titrations[6] in addition to those mentioned above.

The reaction between a range of metal salts and EDTA salts can produce different compounds, depending upon reaction conditions. Octahedral, hexadentate EDTA−cobalt compounds, for example, have been well characterized; among them are, $[NH_4][Co^{III}(EDTA)]$,[7] $[Co(H_2O)_4][Co^{II}(EDTA)]\cdot 2H_2O$,[8] Co^{II}_2EDTA)$\cdot 2H_2O$,[9] and $[Co(H_2O)_6][Co^{II}(EDTAH)(H_2O)]_2\cdot 2H_2O$.[10] Several other metal ions also form compounds containing a coordinated water; they are either seven coordinate with a hexadentate EDTA [M = Mn,[11] Ti,[12] and Fe[13]] or six coordinate with a pentadentate EDTA, with one acetate group unattached and a coordinated water molecule completing the octahedron, [M = Ni(II),[14] Co(III),[15] Cu(II),[16] and Fe(III)[17]]. Herein, we report the synthesis and structural characterization of a seven-coordinate cobalt−aquo−EDTA complex.

Experimental Section

All chemicals used were reagent grade and used as received without further purification. Fourier transformed infrared spectra were obtained on a Nicolet Model 5PC spectrometer, and the observed vibrational bands were in excellent agreement with those reported for other transition metal-EDTA complexes.[18]

Synthesis of $[Co(H_2O)(C_{10}H_{13}N_2O_8)]\cdot 2H_2O$. A 0.291 g sample of $Co(NO_3)_2\cdot 6H_2O$ (0.1 mmol) was combined with 0.416 g (0.1 mmol) of Na_4EDTA in distilled, deionized water at room temperature. On dissolution of the two reactants, 3% hydrogen peroxide was added with stirring until the color change of the solution was complete. The volume of water was very slowly (over a period of several days) reduced by evaporation, leaving large crystals of the compound. The purity of the product and quality of the crystals were found to be heavily dependent on the rate at which they came out of solution. If the rate was too fast, the result was sometimes a mixture of products as evidenced by different colors, incomplete dehydration of the product, and powders rather than crystals. IR (KBr, cm^{-1}): 1732 (s), 1640 (m), 1593 (vs), 1437, 1404, 1391, 1321 (m), 1273 (w), 1217, 1121, 1109, 1100 (m), 968, 938, 866, 808, 758, 718, 640, and 380 (w).

X-ray Crystallography. Data were collected on a Siemens R3m/V automated diffractometer fitted with a molybdenum source and a graphite monochromator (wavelength = Kα 0.710 73).[19]

Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.

The structure was found by location of the cobalt atom in a Patterson function map, and the remaining atoms were located from subsequent difference Fourier calculation maps. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic vibrational amplitude, features were found corresponding to the positions of the hydrogen atoms for the waters and the acetic acid group. Their positions and isotropic vibrational amplitudes were

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Table 1. Crystallographic Data for $[Co(H_2O)(C_{10}H_{13}N_2O_8]\cdot 2H_2O$

chem formula: $C_{10}H_{19}CoN_2O_{11}$	fw = 402.2
space group: $P\bar{1}$ (No. 2)	$Z = 2$
$a = 7.436(2)$ Å	density(calcd) = 1.732 Mg/m^3
$b = 7.751(2)$ Å	μ (Mo Kα) = 1.176 mm^{-1}
$c = 13.807(3)$ Å	$\lambda = 0.710\,73$ Å
$\alpha = 79.52(3)°$	temp = 22 °C
$\beta = 82.96(3)°$	$R^a = 0.0378$
$\gamma = 82.04(3)°$	$R_w{}^b = 0.0760$
$V = 771.1(3)$ Å^3	

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum(w|F_o| - |F_c|)^2/\sum(wF_o{}^2)]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Co(H_2O)(EDTAH]\cdot 2H_2O$

	x	y	z	U(eq)
Co(1)	934(1)	2383(1)	2575(1)	25(1)
O(1)	427(3)	1728(3)	1213(2)	48(1)
O(7)	1417(3)	2909(2)	3937(1)	37(1)
O(5)	3180(2)	3622(2)	1525(1)	31(1)
N(2)	308(2)	5311(2)	2418(1)	22(1)
N(1)	−2137(2)	2705(2)	2629(1)	22(1)
O(2)	−1386(3)	306(2)	563(1)	37(1)
O(3)	−352(2)	−10(2)	3773(1)	34(1)
O(4)	−2823(2)	−373(3)	4859(1)	40(1)
C(1)	−2615(3)	1566(3)	1978(2)	27(1)
C(6)	−1677(3)	5766(3)	2673(2)	25(1)
O(8)	2541(4)	4787(3)	4672(2)	53(1)
O(6)	3558(3)	5842(3)	273(2)	51(1)
C(3)	−2950(3)	2160(3)	3650(2)	27(1)
C(5)	−2736(3)	4586(3)	2257(2)	25(1)
C(10)	2682(3)	5075(3)	1048(2)	28(1)
C(8)	1805(3)	4443(3)	3993(2)	30(1)
C(2)	−1065(3)	1209(3)	1200(2)	27(1)
C(4)	−1896(3)	456(3)	4106(2)	25(1)
C(9)	907(3)	6089(3)	1391(2)	29(1)
C(7)	1372(3)	5880(3)	3119(2)	28(1)
O(1W)	3005(3)	291(3)	2631(2)	58(1)
O(2W)	5116(5)	−1269(4)	1057(2)	78(1)
O(3W)	4676(3)	−2509(3)	3877(2)	50(1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

refined. Hydrogen atom positions on carbons in the ligand were assigned idealized locations. These atoms were included in structure factor calculations, but not refined. Selected crystal data for the complex are given in Table 1. Table 2 gives the non-hydrogen atomic coordinates and isotropic displacement coefficients.

Scattering factors were taken from ref 20.

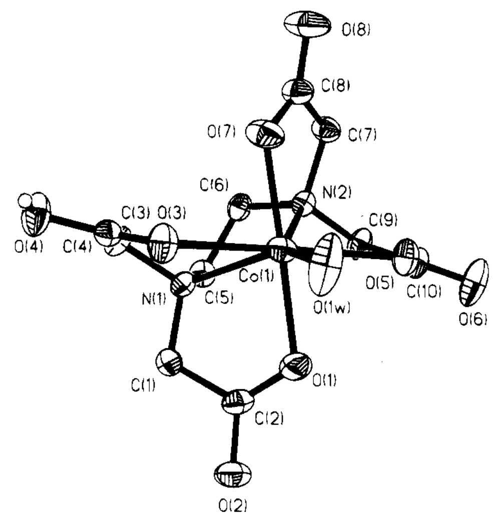

Figure 1. Co(EDTAH)(H_2O) viewed down the Co−water bond. This view shows the distortion in the pentagonal plane. ORTEP (50% ellipsoids).

Table 3. Selected Bond Lengths (Å) and Bond Angle (deg) for $[Co(H_2O)(EDTAH]\cdot 2H_2O$

Co(1)−O(1)	2.124(2)	Co(1)−O(7)	2.078(2)
Co(1)−O(5)	2.272(2)	Co(1)−N(2)	2.229(2)
Co(1)−O(3)	2.465(3)	Co(1)−N(1)	2.256(2)
Co(1)−O(1W)	2.073(2)	C(2)−O(1)	1.234(3)
C(4)−O(3)	1.215(3)	C(2)−O(2)	1.281(3)
C(4)−O(4)	1.294(3)	C(8)−O(7)	1.279(3)
C(10)−O(5)	1.230(3)	C(8)−O(8)	1.220(4)
C(10)−O(6)	1.275(3)		
O(1)−Co(1)−O(7)	177.5(1)	O(1)−Co(1)−O(5)	78.9(1)
O(7)−Co(1)−O(5)	102.9(1)	O(1)−Co(1)−N(2)	105.9(1)
O(7)−Co(1)−N(2)	76.5(1)	O(5)−Co(1)−N(2)	71.8(1)
O(1)−Co(1)−N(1)	75.8(1)	O(7)−Co(1)−N(1)	103.9(1)
O(5)−Co(1)−N(1)	134.0(1)	N(2)−Co(1)−N(1)	79.0(1)
O(1)−Co(1)−O(1W)	86.6(1)	O(7)−Co(1)−O(1W)	92.0(1)
O(5)−Co(1)−O(1W)	78.8(1)	N(2)−Co(1)−O(1W)	144.8(1)
N(1)−Co(1)−O(1W)	136.2(1)	O(4)−Co(1)−O(1)	105.9(1)
O(4)−Co(1)−O(7)	72.3(1)	O(4)−Co(1)−O(5)	172.2(1)
O(4)−Co(1)−N(2)	112.2(1)	O(4)−Co(1)−N(1)	53.8(1)
O(4)−Co(1)−O(1W)	95.2(1)		

Results and Discussion

Structure of $[Co(H_2O)(EDTAH)]\cdot 2H_2O$. The structure of the cobalt cation, shown in Figure 1, is best approximated as a distorted pentagonal bipyramid. Table 3 summarizes the bond distances and interbond angles.

Cobalt is coordinated to the nitrogen donors and oxygens of three acetate groups and one acetic acid group of an $EDTAH^{3-}$ ligand and one oxygen from a water molecule. Two oxygen donors from different acetate groups occupy the axial positions. The two nitrogen donors, one acetato oxygen, one oxygen in the protonated acetic acid group and the water oxygen are situated in the pentagonal plane. The hydrogens for the acetic acid group and the coordinated water molecule were located in the diffrence map. This position is supported by the C−O bond lengths in the acetate groups.[21] The carbon−oxygen distance for the protonated O(4) is 1.294(3) Å, compared to an average of 1.2610(4) Å for the three other carbon to noncoordinated oxygen bonds. The coordinated O(3)−C(4) distance is 1.215(3) Å compared to an average distance of 1.2477(3) Å. Bond lengths of the coordinated ligand average longer than in other cobalt−EDTA compounds. Hexadentate EDTA complexes have an average Co−N bond distance of 2.17 Å and an average Co−O bond distance of 2.08 Å. Comparable bond distances in the octahedral compound, $[Co(EDTAH)(H_2O)]^-$, are as follows: Co−N, 2.145(2) and 2.221(2) Å; Co−O, 2.118(1), 2.082(1), and 2.123(2) Å; Co−O(water), 2.040(2) Å.[10] With a fifth donor atom within a bonding contact distance a weakening of the other bonds, as evidenced by an increase in bond distance, would be expected. The bond distances are similar to $[Co(II)EDTA]^{2-}$ (Co−N, 2.158(3) and 2.161(4) Å; Co−O, 2.039(3), 2.087(3), 2.082(3), and 2.123(2) Å).[8] The geometry of the Co(II) complex is significantly distorted away from an octahedral geometry.

Bond angles suggest the pentagonal bipyramidal structure for **1**. Only the axial ligands have a trans bond angle near the expected 180° {177.5(1)° for O(7)−Co−O(1)}. Similar geometries are adopted by $[Mn(H_2O)(EDTAH)]^{2-}$, contained in $Mn_3(EDTAH)_2\cdot 10H_2O$,[13] by $M[Fe(H_2O)(EDTA)]\cdot H_2O$, (M = Rb and Li),[14] and $[Ti(H_2O)(EDTA)]$.[15] These compounds are described as possessing roughly pentagonal bipyramidal shapes with a pseudo 2-fold axis passing through the midpoint of the

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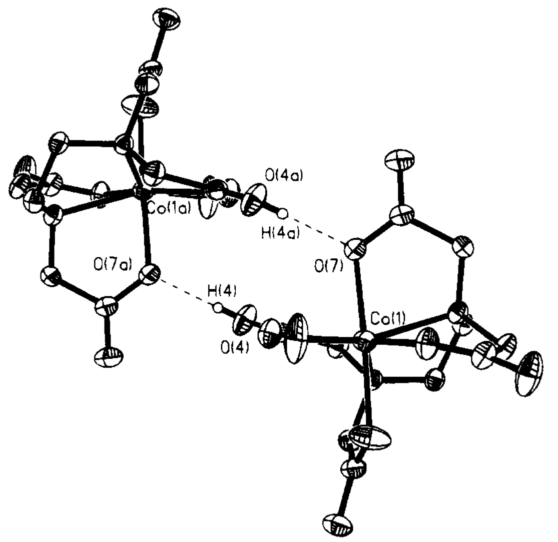

Figure 2. Hydrogen-bonded dimers. Interaction occurs between the protonated carboxylic acid group, O(4)−H(4) to the neighboring O(7a).

ethylene group, the metal atom, and the oxygen of the water molecule. The plane is distorted in an alternating up and down relationship. The mean deviation for the pentagonal plane is 0.34 Å for Co, 0.21 Å for Fe, 0.34 Å for Mn, and 0.15 Å for Ti complexes. The *trans*-O−Co−O in **1** is the most linear at 177.5(1)°. The average bond angle in the pentagonal plane is74.9°, distorted from the ideal angle of 72.0° and represents the largest deviation, with 74.4° for Fe and Mn and 72.4° for Ti complexes.

Hydrogen-Bonding Scheme. The cobalt centers are related in a dimeric fashion. The protonated carboxylic group forms a hydrogen bond using H(4) to a coordinated oxygen, O(7a), Figure 2. The O(4)···O(7a) distance is 2.524(2) Å with the O(4)−H(4)···O(7a) angle 116.5(2)°. H(4)a forms a hydrogen bond to O(7), completing the dimeric unit. [Mn(H_2O)(EDTAH)]$^{2-}$ forms anionic chains parallel to the *b*-axis through the crystal.[13]

The coordinated water, O(1w), is hydrogen bonded to both water molecules associated with the cobalt center. The water molecules also form intermolecular hydrogen bonds. O(3w) is bonded to O(8b) and weakly to O(4a). O(2w) forms one hydrogen bond to O(2a). The acetic acid groups hydrogen bond pairwise from O(4) to O(7c) (and O(7) to O(4)). A complete listing of the oxygen−oxygen distances and a figure illustrating the hydrogen bonding network are included in the supplemental material.

Ring Strain. Hoard proposed that the strain of the chelate rings could be measured by the sum of the angles of the five-membered rings.[7] The "ideal" angle sum for the ethylenediamine backbone (E-ring) is 527.9°. Two rings are used for the carboxylate ligands, the R-ring for the more relaxed axial rings (O trans to O) and the G-ring for the in-plane (N trans to O) rings. The "ideal" angle sum is 538.9°. Using the method of Hoard,[7] compound **1** is a strained compound with E-ring, R-ring, and G-ring sums of 515.3, 531.0, and 522.9°, respectively. For **1** the G-rings and E-ring defined the pentagonal plane. The E-ring exhibits a "strain" similar to those in comparison compounds. This could be an explanation of the longer Co(1)−O(3) bond distance of 2.4 Å. By comparison the related values for Ti(H_2O)(EDTA) are 515.3, 533.9, and 520.9° [12] and for Li[Fe(EDTA)H_2O] are 514.1, 535.1, and 522.8°.[14] A full discussion of structural features for M(III)−EDTA compounds has appeared.[22]

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Supporting Information Available: Tables containing a full summary of the structure determination, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates with isotropic displacement coefficients, and hydrogen bonding distances and angles and figures showing unit cell, packing, and stereoscopic views are available (17 pages). Ordering information is given on any current masthead page.

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