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Synthesis, Properties, and Crystallographic Characterization of a Dinuclear μ-Carbonato Complex of Cobalt(III): $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$

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The title compound has been synthesized by oxidation of a mixture of cobalt sulfate, ammonium carbonate, and aqueous ammonia at 0 °C. The compound crystallizes from water/ethanol as dark red crystals which have been characterized unambiguously by means of a three-dimensional X-ray diffraction study. The crystals belong to the triclinic space group $P\bar{1}$ (C_i^1; No. 2) with $a = 6.6914$ (14) Å, $b = 11.2847$ (18) Å, $c = 11.8251$ (23) Å, $\alpha = 92.766$ (14)°, $\beta = 99.096$ (15)°, $\gamma = 101.496$ (15)°, $V = 861.1$ (3) Å^3, ρ(calcd) = 1.929 g cm^{-3} for $Z = 2$, and mol wt = 500.21. Difrraction data were collected on a Syntex P2$_1$ automated four-circle diffractometer by using a coupled θ–2θ scan and Mo Kα radiation. The structure was solved by conventional methods and refined by difference Fourier and least-squares techniques to final discrepancy indices of $R_F = 2.9\%$ and $R_{wF} = 2.7\%$ for 2258 reflections in the range $3.5° < 2\theta < 45.0°$. The cation is the first μ-carbonato species of cobalt(III) to be characterized definitively and has approximate C_{2v} symmetry, with two cobalt(III) ions mutually bridged by two hydroxide ions and one carbonate ligand. Each of the cobalt(III) ions is in an approximately octahedral environment and is associated with three NH_3 ligands. Bond lengths of interest are Co(1)–Co(2) = 2.817 (1) Å, Co(1)–(μ-OH) = 1.896 (2) Å and 1.922 (2) Å, Co(2)–(μ-OH) = 1.897 (2) Å and 1.918 (2) Å, Co(1)–O(μ-CO_3) = 1.899 (2) Å, and Co(2)–O(μ-CO_3) = 1.903 (2) Å. The carbonate ligand causes some perturbation in the octahedral environment about the cobalt(III) ions. The angle between the two cobalt-bonded oxygen atoms is increased from 120°, viz., ∠O(3)–C–O(4) = 122.4 (3)°.

Introduction

There have been few reports of binuclear cobalt(III) complexes with carbonate ligands. We recently reported the synthesis and crystallographic characterization of the $[(NH_3)_4Co(\mu\text{-}OH)(\mu\text{-}NH_2)Co(CO_3)_2]$ molecule which contains two chelating carbonate groups associated with one of its cobalt(III) ions.[2] There have, to our knowledge, been no definitive structural studies on binuclear cobalt(III) complexes with bridging carbonate ligands. Golovnya and his co-workers[3] reported the isolation of two binuclear cobalt(III) complex ions $[(NO_2)_4CO_3Co(\mu\text{-}CO_3)CoCO_3(NO_2)_4]^{8-}$ and $[(NO_2)_3CO_3Co(\mu\text{-}CO_3)CoCO_3(NO_2)_3]^{6-}$, each of which has been claimed to contain bridging carbonate without any substantial structural evidence. Baylis and Bailar[4] reported a binuclear diarsine cobalt(III) species with carbonate as a bridging ligand, but the structure of this complex has not been fully ascertained. There have been reports of the isolation of derivatives of the $[(NH_3)_5Co(\mu\text{-}CO_3)Co(NH_3)_5]^{4+}$ ion by several workers,[5] but our attempts to duplicate this work have been unsuccessful. However, modification of the preparative procedure reported by Kranig[5a] for this μ-carbonato complex ion results in the formation of a red crystalline compound containing two hydroxides and one carbonate ligand in bridging positions.

We now report the synthesis, properties, and crystallographic characterization of this cation as the sulfate derivative $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$.

Experimental Section

Preparation of Compounds. Preparation of μ-Carbonato-di-μ-hydroxo-bis[triamminecobalt(III)] Sulfate Pentahydrate. A 7.0-g sample of ammonium carbonate was dissolved completely by stirring, in 200 cm^3 of concentrated ammonia. The solution was cooled to 0 °C, and a concentrated solution of cobalt(II) sulfate (made by dissolving 20.0 g of $CoSO_4\cdot 7H_2O$ in the minimum quantity of water) was added to this solution slowly with stirring. The mixture was kept at 0 °C, and pure oxygen was bubbled into the solution for 24 h. The solution was filtered under suction with use of a sintered Büchner funnel. Dark brown solid was found as a residue. The filtrate was left for ca. 2–3 h at room temperature. By this time the color of the filtrate had changed from reddish brown to intense red. Alcohol (95%) was added slowly to this solution until turbidity appeared. The solution was left in a refrigerator overnight, during which time platelike crystals started to appear. These crystals were filtered, washed thoroughly with dilute alcohol, and kept in a desiccator. The compound was recrystallized twice from water and alcohol. The yield was 5 g. The purity of the complex was checked by microanalysis.[6] Anal. Calcd for $Co_2(NH_3)_6(OH)_2(CO_3)(SO_4)\cdot 5H_2O$: C, 2.40; H, 6.00; N, 16.80; S, 6.40; Co, 23.56. Found: C, 2.24; H, 6.07; N, 16.89; S, 6.52; Co, 23.20.

Preparation of Tri-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate Dihydrate ("Triol"). This red complex was prepared following the procedure of Linhard and Siebert[7] and recrystallized twice from dilute acetic acid containing sodium perchlorate (saturated solution). The purity of the compound was checked by UV–visible spectroscopy.[8]

Materials. All minerals used were of reagent grade. Pure oxygen gas (obtained from JOAL, Jamaica) was used without further treatment. Distilled water, obtained from a Corning all-glass distillation unit, was used for the preparation of complexes. However, ultrapure water, obtained by passing distilled water through a Milli-Q reagent grade water system (Millipore Co., Bedford, Mass.), was used for physical measurements.

Spectra. The absorption spectra in the UV–visible region were obtained by use of a Cary 219 recording spectrophotometer. Extinction coefficients reported are all in M^{-1} cm^{-1}. The infrared spectrum of the bridged carbonato complex was measured with a Perkin-Elmer spectrometer, Model 735B, using the KBr disk technique. The μ-carbonato-di-μ-hydroxo-bis[triamminecobalt(III)] complex ion shows four strong bands at 1600, 1480, 1270, and 825 cm^{-1}. These peaks are comparable to the strong peaks at 1593 cm^{-1} [ν(C–O(II))], 1482 cm^{-1} [ν(C–O(II))], 1265 cm^{-1} [ν(C–O(I)] + δ[O(I)–C–O(II))], and 835 (π) and 850 cm^{-1} (π) for bidentate and monodentate carbonates.[9]

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(1) (a) SUNY at Buffalo. (b) University of the West Indies.

(2) Churchill, M. R.; Harris, G. M.; Lashewycz, R. A.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* **1979**, *18*, 2290–2295.

(3) (a) Golovnya, V. A.; Kokh, L. A.; Sokol, S. K. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 451–453. (b) Golovnya, V. A.; Kokh, L. A. *Ibid.* **1961**, *6*, 906–909.

(4) Baylis, B. K. W.; Bailar, J. C., Jr. *Inorg. Chem.* **1970**, *9*, 641–648.

(5) (a) Kranig, J. *Ann. Chim.* (*Paris*) **1929**, *41*, 87. (b) Kremer, E.; Piriz Mac-coll, C. R. *Inorg. Chem.* **1971**, *10*, 2182–2186. (c) Abedini, M. *Ibid.* **1976**, *15*, 2945.

(6) Microanalysis was done by Dr. Franz Pascher, Microanalytische Laboratorium, D-5300, Bonn 1, West Germany.

(7) Linhard, M.; Siebert, H. *Z. Anorg. Allg. Chim.* **1969**, *24*, 364.

(8) The extinction coefficients of "triol" are 135 and 1667 at 526 and 296 nm, respectively (cf. λ_{max} 526 nm (ϵ 135) and λ_{max} 296 nm (ϵ 1780) in ref 7).

(9) Nakamoto, K. "Infra-red spectra of Inorganic Co-ordination Compounds"; Wiley: New York, 1970; p 170. It is interesting to note that the bridged carbonato complex has all the characteristic bands of bidentate and monodentate carbonato complexes of cobalt(III). We have recently prepared some other bridged carbonato complexes and the infrared spectra of all of them are very similar to the one we reported here. We are now in the process of doing normal-coordinate analysis on this complex to resolve this perplexing behavior.

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Table I. Data for the X-ray Diffraction Study of $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$

(A) Crystal Data

cryst system: triclinic
space group: $P\bar{1}$ [C_i^1; No. 2]
$a = 6.6914\ (14)$ Å[a]
$b = 11.2847\ (18)$ Å
$c = 11.8251\ (23)$ Å
$\alpha = 92.766\ (14)^\circ$
$\beta = 99.096\ (15)^\circ$
$\gamma = 101.496\ (15)^\circ$
$V = 861.1\ (3)$ Å^3
$T = 23$ °C
$Z = 2$
fw = 500.21
ρ(calcd) = 1.929 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda} = 0.710\,730$ Å)
monochromator: highly oriented graphite
reflctns measd: $+h, \pm k, \pm l$
scan type: coupled θ(cryst)–2θ(counter)
2θ range: 3.5–45.0°
scan speed: 4.0°/min
scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$
reflctns collected: 2571 total; 2258 independent
std reflctns: 3 measured every 97 reflections, the $01\bar{7}$, $\bar{1}\bar{7}\bar{1}$, and 411; their intensities decreased steadily by 5.4% (av) over the course of data collection
abs coeff: $\mu = 21.15$ cm^{-1}

(C) Reflections Used for Empirical Absorption Correction[b]

h	k	l	2θ, deg	I_{max}/I_{min}
0	$\bar{2}$	$\bar{4}$	16.39	1.19
0	$\bar{4}$	$\bar{3}$	18.87	1.19
0	$\bar{3}$	$\bar{5}$	21.56	1.16
0	$\bar{6}$	$\bar{5}$	29.63	1.19
0	$\bar{7}$	$\bar{6}$	35.12	1.18
0	6	9	40.77	1.18

[a] Based upon a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 25 reflections. [b] For details of the experimental absorption correction, see: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* 1977, *16*, 2655. Data averaging was accomplished with $R(I) = 1.30\%$ for 232 reflections with two or more contributors.

Collection of X-ray Diffraction Data for $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$. The crystal selected for the structural analysis was of approximately square cross section (0.22 mm in thickness) and 0.27 mm in length. It was mounted in a 0.2-mm diameter glass capillary which was then sealed, set with beeswax into an aluminum pin, and mounted on a eucentric goniometer.

Preliminary precession photographs revealed no symmetry (except for the Friedel condition); the crystal was assumed to be triclinic. The crystal was transferred to a Syntex $P2_1$ automated diffractometer and was accurately centered.

The unit cell dimensions and the orientation matrix were determined and refined as described previously.[10] The crystal quality was checked via a series of θ–2θ and ω scans of reflections along the principal reciprocal axes and was found to be satisfactory. Collection of intensity data was then carried out as described previously;[10] details are given in Table I.

Diffraction data were reduced to net intensities (I) and their estimated standard deviations ($\sigma_c(I)$). The ratio of time taken for the main scan to the total time for background measurement, τ, was 1.50.

Following application of an isotropic linear decay correction, all data were corrected for the effects of absorption [μ(Mo Kα) = 21.15 cm^{-1}] by an empirical method. Several close-to-axial reflections (χ_0 = 76–84°) distributed over the 2θ range used in data collection and each reflection of fairly high intensity ($I/\sigma(I) > 90$) were measured at 10° intervals of Ψ (the diffraction vector) from 0 to 350°. Each reflection was used to define a normalized absorption curve vs. ϕ, corrected for ω and χ. To derive the absorption correction, we interpolated the two curves bracketing the 2θ value of the reflection under consideration both in 2θ and ϕ. The reflections used were all mutually consistent, with similar profiles and maxima and minima at common values; they are listed in Table I.

The check reflections were deleted. The data were averaged according to $\bar{1}$ symmetry, yielding a unique set of 2258 reflections. Intensities were then corrected for Lorentz and polarization effects.

Solution and Refinement of the Crystal Structure. All calculations were performed with the Syntex XTL structure determination system consisting of an in-house Data General Nova 1200 computer with 24K of 16-bit words, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package. The atomic scattering factors of Cromer and Waber[11a] were used for neutral cobalt, oxygen, nitrogen, sulfur, carbon, and hydrogen throughout the analysis. Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms by using the values of Cromer and Liebermann.[11b]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weights used are obtained from counting statistics, modified by the "ignorance factor", p, set at a value of 0.010.

The positions of the cobalt atoms were found from an unsharpened Patterson synthesis. Full-matrix least-squares refinement of the scale factor, along with the positional and isotropic thermal parameters for the two cobalt atoms, using only those data with $|F_o| > \sigma(F_o)$ (i.e., 2172 reflections), led to $R_F = 49.5\%$ and $R_{wF} = 54.7\%$. A difference-Fourier synthesis at this point revealed the positions of all remaining nonhydrogen atoms in the binuclear complex and those of the sulfate ion. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms in the ionic complex and anisotropic thermal parameters for the cobalt atoms gave $R_F = 20.6\%$ and $R_{wF} = 26.5\%$. A difference Fourier synthesis at this time revealed five maxima of peak height 7.06–9.80 e Å^{-3} at distances <2.95 Å from atoms in the molecule. These maxima correspond to the positions of the oxygen atoms of five hydrogen-bonded water molecules and were included in our model. Continued refinement of all nonhydrogen atoms using all data resulted in $R_F = 5.9\%$, $R_{wF} = 7.3\%$, and GOF = 4.40.

A difference-Fourier synthesis based upon all data revealed all the hydrogen atoms present in the $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4$ portion of the structure. Continued refinement including the positional and anisotropic thermal parameters for all nonhydrogen atoms in the molecule, the positional and isotropic thermal parameters for all the hydrogen atoms in the binuclear cobalt cation, and the five oxygen atoms associated with water molecules gave $R_F = 4.7\%$, $R_{wF} = 5.3\%$, and GOF = 3.32.

At this point, all hydrogen atoms associated with the water of crystallization were unambiguously located on a difference-Fourier synthesis using all data.

Least-squares refinement of *all* positional and anisotropic thermal parameters for nonhydrogen atoms and of *all* positional and isotropic thermal parameters for hydrogen atoms resulted in $R_F = 3.7\%$, $R_{wF} = 3.9\%$ and GOF = 2.46.

Careful comparison of observed and calculated structure factor amplitudes indicated that a correction for secondary extinction was necessary. The value of the secondary extinction parameter (k) used was 2.062×10^{-7}. $F_{o,cor}$, the corrected observed structure factor, is given by eq 1.

$$F_{o,cor} = F_o(1.0 + kI_{obsd}) \tag{1}$$

Continued refinement led to final convergence with $R_F = 2.9\%$, $R_{wF} = 2.7\%$, and GOF = 1.72 for all 2258 data; those data with $I < \sigma(I)$ were given zero weight in the refinement process.

A final difference-Fourier synthesis based on all data had only peaks less than 0.35 e Å^{-3} in height.

The average value of $\sum w(|F_o| - |F_c|)^2$ showed no major variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme is therefore acceptable. The final NO:NV ratio was 2258:337 or 6.7:1. Positional and thermal parameters are listed in Tables II and III.

Results and Discussion

Chemical Properties. The red crystalline solid μ-carbonato-di-μ-hydroxo-bis[triamminecobalt(III)] sulfate pentahydrate is very soluble in water but insoluble in nonaqueous solvents. An aqueous solution of the complex ion at pH ~7 is stable for 1 or 2 h, but appreciable decomposition occurs on long standing. The complex solution is comparatively more stable

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(10) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(11) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

Table II. Final Positional Parameters and Isotropic Thermal Parameters (with Esd's) for $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$

atom	*x*	*y*	*z*	B_{iso}, Å^2
Co(1)	0.18887 (6)	0.34783 (3)	0.26449 (3)	
Co(2)	0.08673 (6)	0.09482 (3)	0.21067 (3)	
N(1)	0.2276 (5)	0.3598 (3)	0.4312 (2)	
N(2)	0.0157 (5)	0.4652 (3)	0.2679 (3)	
N(3)	0.4441 (5)	0.4673 (3)	0.2722 (3)	
N(4)	0.0920 (5)	0.0410 (3)	0.3649 (2)	
N(5)	0.2418 (5)	−0.0235 (3)	0.1668 (3)	
N(6)	−0.1745 (5)	−0.0160 (3)	0.1554 (3)	
O(1)	−0.0429 (3)	0.2187 (2)	0.2593 (2)	
O(2)	0.3340 (3)	0.2180 (2)	0.2541 (2)	
C	0.0861 (4)	0.2544 (3)	0.0282 (2)	
O(3)	0.1469 (3)	0.3474 (2)	0.1018 (2)	
O(4)	0.0674 (3)	0.1436 (2)	0.0582 (2)	
O(5)	0.0425 (4)	0.2693 (2)	−0.0772 (2)	
S	0.72217 (12)	0.26977 (6)	0.53165 (6)	
O(11)	0.7513 (3)	0.3789 (2)	0.4686 (2)	
O(12)	0.6973 (4)	0.3007 (2)	0.6493 (2)	
O(13)	0.9001 (3)	0.2107 (2)	0.5332 (2)	
O(14)	0.5328 (3)	0.1830 (2)	0.4727 (2)	
O(10)	0.5830 (4)	0.1778 (2)	0.0947 (3)	
O(20)	0.3930 (5)	1.0266 (4)	0.6448 (3)	
O(30)	−0.2999 (5)	0.4817 (3)	0.0750 (3)	
O(40)	−0.3935 (7)	0.2893 (3)	−0.1107 (3)	
O(50)	0.2254 (5)	0.2699 (3)	−0.2711 (3)	
H(11)	0.119 (7)	0.314 (4)	0.457 (3)	3.3 (10)
H(12)	0.240 (6)	0.426 (4)	0.459 (3)	2.7 (9)
H(13)	0.334 (6)	0.331 (3)	0.473 (3)	3.6 (9)
H(21)	−0.061 (6)	0.448 (4)	0.315 (4)	4.2 (11)
H(22)	0.083 (5)	0.540 (3)	0.286 (3)	1.8 (7)
H(23)	−0.066 (6)	0.462 (3)	0.199 (4)	4.0 (10)
H(31)	0.480 (6)	0.473 (3)	0.205 (4)	4.0 (10)
H(32)	0.537 (6)	0.444 (3)	0.324 (3)	3.1 (9)
H(33)	0.446 (6)	0.536 (4)	0.297 (3)	3.1 (10)
H(41)	−0.024 (8)	0.059 (4)	0.395 (4)	6.6 (13)
H(42)	0.196 (7)	0.067 (4)	0.409 (4)	4.5 (13)
H(43)	0.071 (6)	−0.039 (4)	0.371 (3)	4.1 (10)
H(51)	0.309 (7)	0.001 (4)	0.112 (4)	5.3 (12)
H(52)	0.179 (6)	−0.081 (4)	0.140 (3)	3.0 (11)
H(53)	0.349 (6)	−0.033 (3)	0.222 (3)	3.2 (8)
H(61)	−0.262 (7)	0.019 (4)	0.128 (3)	3.8 (11)
H(62)	−0.163 (6)	−0.062 (4)	0.097 (4)	4.2 (10)
H(63)	−0.234 (7)	−0.042 (4)	0.207 (4)	4.5 (12)
H(1)	−0.134 (5)	0.226 (3)	0.216 (3)	1.7 (9)
H(2)	0.399 (6)	0.213 (3)	0.306 (3)	2.4 (9)
H(101)	0.507 (5)	0.194 (3)	0.131 (3)	1.5 (8)
H(102)	0.569 (6)	0.203 (3)	0.041 (3)	2.3 (10)
H(201)	0.417 (8)	1.080 (4)	0.619 (4)	4.5 (16)
H(202)	0.389 (6)	0.976 (3)	0.613 (3)	1.8 (10)
H(301)	−0.263 (8)	0.531 (4)	0.056 (4)	5.1 (17)
H(302)	−0.322 (8)	0.438 (4)	0.009 (5)	6.7 (15)
H(401)	−0.296 (8)	0.283 (5)	−0.121 (5)	5.2 (17)
H(402)	−0.468 (8)	0.286 (4)	−0.173 (5)	6.5 (15)
H(501)	0.155 (7)	0.284 (4)	−0.216 (4)	5.8 (13)
H(502)	0.148 (8)	0.244 (5)	−0.318 (5)	5.8 (17)

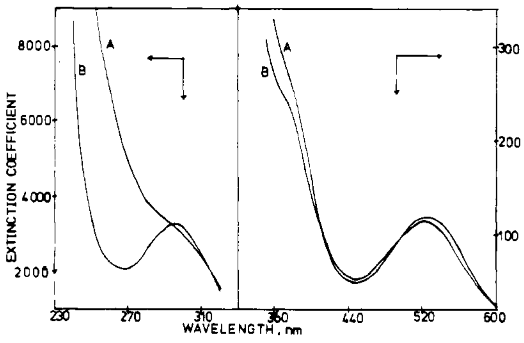

Figure 1. Absorption spectra of $[(NH_3)_3Co(\mu\text{-}CO_3)(\mu\text{-}OH)_2Co(NH_3)_3]^{2+}$ (A) in water and (B) in 0.1 M perchloric acid.

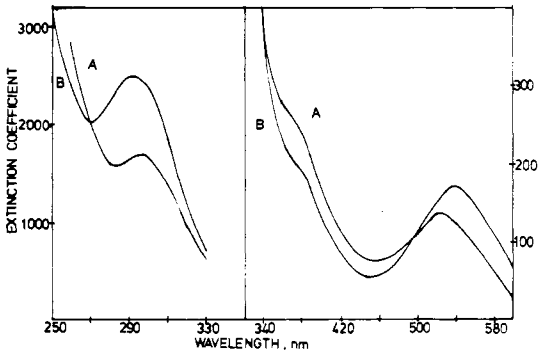

Figure 2. Absorption spectra for $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ (A) in water and (B) in 0.1 M perchloric acid.

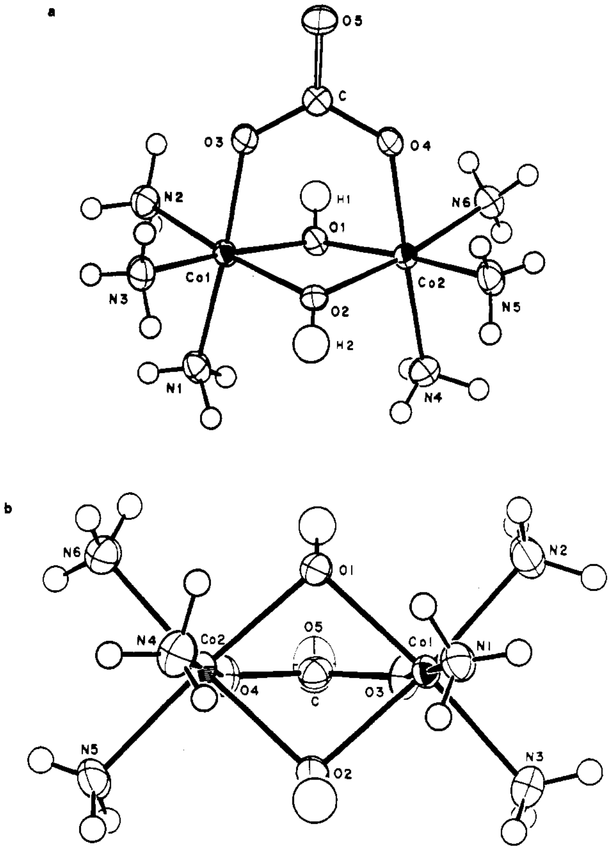

Figure 3. Labeling of atoms in the $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]^{2+}$ cation (ORTEP-II diagram, 50% ellipsoids for all atoms other than ammine hydrogens, which are artificially reduced): (a) "side-on" view showing the bridging carbonate ligand; (b) view down the pseudo-C_2 axis of the cation, showing the approximate C_{2v} symmetry.

in the presence of bicarbonate ions. When a solution of the complex is treated with dilute acid, it aquates rapidly, liberating CO_2 to form the di-μ-hydroxo-bis[aquotriamminecobalt(III)] ion (see Figure 1). The spectrum of this di-μ-hydroxo complex is similar to, but not identical with, that of the aquation product of the tri-μ-hydroxo-bis[triamminecobalt(III)] (triol) ion (see Figure 2). Sykes and co-workers[12] have studied the acid hydrolysis of "triol" and found that one of the μ-hydroxo groups is extremely labile.[12] The product of the acid hydrolysis of "triol" has been characterized as di-μ-hydroxo-*trans*-diaquo-bis[triamminecobalt(III)] on the basis of X-ray diffraction data.[13] Since the hydrolytic product of μ-carbonato-di-μ-hydroxo-bis[triamminecobalt(III)] ion is somewhat different from that of "triol", we believe that the

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[12] Edwards, J. D.; Wieghardt, K.; Sykes, A. G., *J. Chem. Soc., Dalton Trans.* **1974**, 2198–2204. The rate constant for aquation of "triol" is 8.5×10^{-2} s^{-1} at 0.5 M H^+ and $I = 1.0$ M.

Table III. Anisotropic Thermal Parameters[a] (in Å^2) for the Nonhydrogen Atoms in $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4{\cdot}5H_2O$

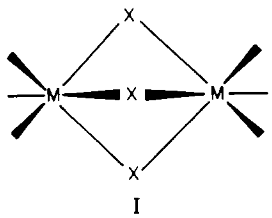
atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	1.234 (18)	1.052 (18)	1.190 (18)	0.266 (13)	0.127 (13)	−0.089 (12)
Co(2)	1.250 (19)	1.038 (17)	1.105 (17)	0.226 (13)	0.193 (13)	0.034 (12)
N(1)	1.81 (13)	1.62 (13)	1.65 (12)	0.45 (11)	0.31 (10)	−0.30 (11)
N(2)	2.15 (14)	1.69 (14)	2.25 (14)	0.82 (11)	−0.06 (12)	−0.23 (11)
N(3)	1.98 (13)	1.40 (13)	2.01 (14)	−0.02 (10)	0.29 (11)	0.06 (11)
N(4)	2.35 (15)	1.81 (14)	1.69 (12)	0.21 (11)	0.24 (12)	0.44 (10)
N(5)	2.00 (14)	1.55 (13)	2.20 (14)	0.60 (12)	0.05 (12)	−0.50 (11)
N(6)	1.64 (13)	1.74 (12)	1.83 (14)	0.20 (10)	0.21 (11)	−0.12 (11)
O(1)	1.23 (9)	1.33 (9)	1.46 (9)	0.23 (7)	0.11 (8)	−0.15 (7)
O(2)	1.36 (9)	1.32 (9)	1.33 (9)	0.40 (7)	−0.15 (8)	0.07 (7)
C	1.31 (13)	1.57 (14)	1.41 (14)	0.23 (11)	0.44 (10)	0.13 (11)
O(3)	2.42 (10)	1.25 (9)	1.34 (9)	0.14 (8)	0.23 (7)	0.14 (7)
O(4)	2.00 (9)	1.29 (9)	1.15 (8)	0.27 (7)	0.23 (7)	−0.11 (7)
O(5)	3.90 (12)	2.31 (10)	1.12 (10)	0.57 (9)	0.28 (8)	0.35 (7)
S	1.56 (3)	1.45 (3)	1.59 (3)	0.23 (3)	0.24 (3)	0.02 (2)
O(11)	3.07 (11)	1.74 (10)	3.19 (11)	0.49 (9)	0.68 (9)	0.71 (8)
O(12)	4.09 (13)	2.99 (11)	2.24 (11)	0.48 (10)	1.41 (9)	−0.36 (8)
O(13)	2.17 (10)	2.56 (10)	2.94 (11)	1.12 (8)	0.61 (8)	0.44 (8)
O(14)	2.08 (10)	2.23 (10)	2.81 (11)	−0.25 (8)	−0.67 (8)	0.40 (8)
O(10)	2.57 (13)	3.66 (13)	3.00 (14)	1.68 (10)	1.32 (11)	1.29 (11)
O(20)	4.17 (15)	2.36 (14)	2.82 (13)	0.53 (12)	1.17 (11)	0.19 (13)
O(30)	3.51 (14)	3.01 (14)	3.19 (14)	0.17 (12)	0.14 (11)	1.20 (13)
O(40)	4.77 (18)	5.41 (17)	2.99 (15)	2.36 (15)	1.28 (14)	1.22 (11)
O(50)	3.29 (15)	6.80 (19)	3.09 (15)	1.54 (14)	0.64 (13)	0.16 (14)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots 2hka^*b^*B_{12} + \ldots)]$.

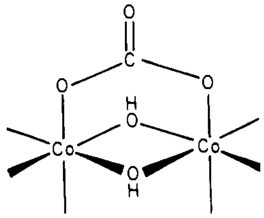
product is a cis rather than trans isomer. (The hydrolyzed product reverts back to a μ-carbonato species on treatment with sodium bicarbonate at pH 8.) We (T.P.D. and K.K.) are now in the process of studying in detail the kinetics of decarboxylation of the μ-carbonate complex and the formation of this ion from di-μ-hydroxo-diaquo species. It is worth mentioning here that Wieghardt and his co-workers[14] recently prepared μ-carbonato complexes of Cr(III) and Rh(III) containing 1,4,7-triazacyclononane. They found that the products of hydrolysis of these compounds are all trans isomers. This suggests that the cobalt(III) complexes behave differently from their Cr(III) and Rh(III) analogues.

Molecular and Crystal Structure. The molecular geometry and atomic labeling scheme for the $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]^{2+}$ cation are shown in Figure 3, while Figure 4 presents a stereoscopic view of this cation. Interatomic distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles are collected in Table V, while important least-squares planes are listed in Table VI.

Each of the cobalt(III) ions is in an approximately octahedral environment. The cobalt(III) ions are each associated with three neutral NH_3 ligands and are mutually bridged by two hydroxide ligands and one carbonate ligand. The resulting stereochemical arrangement is not a confacial bis(octahedron) (I); rather, the ligand arrangement about the two cobalt(III) centers is an edge-shared bis(octahedron) with an axial–axial connection via the bridging carbonate ligand (see II).



I



II

Table IV. Intramolecular Distances with Esd's for $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4{\cdot}5H_2O$

atoms	dist, Å	atoms	dist, Å
(A) Cobalt–(Bridging Ligand) Distances			
Co(1)–O(1)	1.896 (2)	Co(2)–O(1)	1.897 (2)
Co(1)–O(2)	1.922 (2)	Co(2)–O(2)	1.918 (2)
Co(1)–O(3)	1.899 (2)	Co(2)–O(4)	1.903 (2)
(B) Cobalt–Ammine Distances			
Co(1)–N(1)	1.942 (3)	Co(2)–N(4)	1.947 (3)
Co(1)–N(2)	1.929 (3)	Co(2)–N(5)	1.946 (4)
Co(1)–N(3)	1.940 (3)	Co(2)–N(6)	1.933 (3)
(C) Distances within the Bridging Ligands			
O(1)–H(1)	0.75 (4)	O(3)–C	1.286 (3)
O(2)–H(2)	0.70 (4)	O(4)–C	1.303 (3)
		O(5)–C	1.262 (3)
(D) Nitrogen–Hydrogen Distances			
N(1)–H(11)	0.90 (4)	N(4)–H(41)	0.95 (5)
N(1)–H(12)	0.78 (4)	N(4)–H(42)	0.79 (5)
N(1)–H(13)	0.92 (4)	N(4)–H(43)	0.90 (4)
N(2)–H(21)	0.82 (4)	N(5)–H(51)	0.88 (5)
N(2)–H(22)	0.87 (4)	N(5)–H(52)	0.73 (4)
N(2)–H(23)	0.90 (4)	N(5)–H(53)	0.91 (4)
N(3)–H(31)	0.86 (4)	N(6)–H(61)	0.81 (4)
N(3)–H(32)	0.89 (4)	N(6)–H(62)	0.87 (4)
N(3)–H(33)	0.81 (4)	N(6)–H(63)	0.82 (4)
(E) Sulfur–Oxygen Distances			
S–O(11)	1.466 (2)	S–O(13)	1.474 (2)
S–O(12)	1.461 (2)	S–O(14)	1.487 (2)
(F) Distances within the Water Molecules			
O(10)–H(101)	0.75 (4)	O(40)–H(401)	0.70 (5)
O(10)–H(102)	0.71 (4)	O(40)–H(402)	0.82 (6)
O(20)–H(201)	0.69 (5)	O(50)–H(501)	0.89 (5)
O(20)–H(202)	0.66 (4)	O(50)–H(502)	0.70 (5)
O(30)–H(301)	0.63 (5)		
O(30)–H(302)	0.88 (5)		

The bridging hydroxide ligands are in symmetrical locations between the two cobalt ions; however, they appear to be inequivalent, with distances involving O(1) being shorter than those involving O(2), viz., Co(1)–O(1) = 1.896 (2) Å and Co(2)–O(1) = 1.897 (2) Å vs. Co(1)–O(2) = 1.922 (2) Å and Co(2)–O(2) = 1.918 (2) Å. The bridging carbonate ligand also adopts a symmetrical bonding geometry, with Co(1)–O(3)

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(13) Baur, W. H.; Wieghardt, K., *J. Chem. Soc., Dalton Trans.* **1973**, 2669–2674.

(14) Wieghardt, K.; Schmidt, W.; van Eldik, R.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1980**, *19*, 2922.

Table V. Interatomic Angles (Deg) with Esd's for $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot5H_2O$

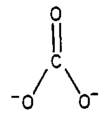
atoms	angle	atoms	angle
	(A) Angles Involving the Bridging Ligands		
Co(1)-O(1)-Co(2)	95.90 (10)	Co(1)-O(2)-Co(2)	94.37 (10)
O(1)-Co(1)···Co(2)	42.08 (7)	O(2)-Co(1)···Co(2)	42.76 (7)
O(1)-Co(2)···Co(1)	42.02 (7)	O(2)-Co(2)···Co(1)	42.87 (7)
O(1)-Co(2)-O(2)	83.24 (9)	O(2)-Co(1)-O(1)	83.17 (9)
O(1)-Co(1)-N(1)	89.64 (11)	O(2)-Co(1)-N(1)	94.68 (11)
O(1)-Co(1)-N(2)	90.91 (12)	O(2)-Co(1)-N(2)	173.66 (12)
O(1)-Co(1)-N(3)	173.93 (12)	O(2)-Co(1)-N(3)	90.87 (12)
O(1)-Co(2)-N(4)	86.95 (12)	O(2)-Co(2)-N(4)	93.77 (12)
O(1)-Co(2)-N(5)	175.18 (12)	O(2)-Co(2)-N(5)	92.04 (12)
O(1)-Co(2)-N(6)	92.95 (12)	O(2)-Co(2)-N(6)	173.30 (12)
O(1)-Co(1)-O(3)	92.10 (9)	O(2)-Co(1)-O(3)	89.30 (9)
O(1)-Co(2)-O(4)	92.45 (9)	O(2)-Co(2)-O(4)	88.90 (9)
Co(1)-O(1)-H(1)	112.5 (5)	Co(1)-O(2)-H(2)	112.8 (5)
Co(2)-O(1)-H(1)	112.7 (5)	Co(2)-O(2)-H(2)	117.2 (5)
Co(1)-O(3)-C	127.16 (19)	Co(2)-O(4)-C	126.54 (18)
O(3)-Co(1)···Co(2)	81.73 (6)	O(4)-Co(2)···Co(1)	81.70 (6)
O(3)-Co(1)-N(1)	175.91 (11)	O(4)-Co(2)-N(4)	177.17 (11)
O(3)-Co(1)-N(2)	88.64 (12)	O(4)-Co(2)-N(5)	88.45 (12)
O(3)-Co(1)-N(3)	89.00 (11)	O(4)-Co(2)-N(6)	85.75 (11)
O(3)-C-O(5)	119.7 (3)	O(4)-C-O(5)	118.0 (3)
O(3)-C-O(4)	122.4 (3)		
	(B) Cobalt-Cobalt-Ligand Angles		
Co(2)···Co(1)-N(1)	102.01 (9)	Co(1)···Co(2)-N(4)	99.64 (10)
Co(2)···Co(1)-N(2)	130.95 (10)	Co(1)···Co(2)-N(5)	133.50 (10)
Co(2)···Co(1)-N(3)	132.37 (10)	Co(1)···Co(2)-N(6)	131.98 (10)
	(C) Ligand-Cobalt-Ligand Angles		
N(1)-Co(1)-N(2)	87.64 (14)	N(4)-Co(2)-N(5)	92.38 (14)
N(1)-Co(1)-N(3)	89.65 (13)	N(4)-Co(2)-N(6)	91.52 (14)
N(2)-Co(1)-N(3)	95.09 (14)	N(5)-Co(2)-N(6)	91.84 (14)
	(D) Other Angles Involving the Ammine Ligands		
Co(1)-N(1)-H(11)	111 (3)	H(11)-N(1)-H(12)	106 (4)
Co(1)-N(1)-H(12)	114 (3)	H(11)-N(1)-H(13)	99 (4)
Co(1)-N(1)-H(13)	120 (2)	H(12)-N(1)-H(13)	106 (4)
Co(1)-N(2)-H(21)	109 (3)	H(21)-N(2)-H(22)	108 (4)
Co(1)-N(2)-H(22)	114 (2)	H(21)-N(2)-H(23)	107 (4)
Co(1)-N(2)-H(23)	110 (3)	H(22)-N(2)-H(23)	108 (3)
Co(1)-N(3)-H(31)	111 (3)	H(31)-N(3)-H(32)	113 (4)
Co(1)-N(3)-H(32)	106 (2)	H(31)-N(3)-H(33)	106 (4)
Co(1)-N(3)-H(33)	118 (3)	H(32)-N(3)-H(33)	103 (4)
Co(2)-N(4)-H(41)	109 (3)	H(41)-N(4)-H(42)	110 (5)
Co(2)-N(4)-H(42)	115 (3)	H(41)-N(4)-H(43)	100 (4)
Co(2)-N(4)-H(43)	117 (3)	H(42)-N(4)-H(43)	104 (4)
Co(2)-N(5)-H(51)	111 (3)	H(51)-N(5)-H(52)	101 (4)
Co(2)-N(5)-H(52)	115 (3)	H(51)-N(5)-H(53)	101 (4)
Co(2)-N(5)-H(53)	115 (2)	H(52)-N(5)-H(53)	113 (4)
Co(2)-N(6)-H(61)	111 (3)	H(61)-N(6)-H(62)	102 (4)
Co(2)-N(6)-H(62)	110 (3)	H(61)-N(6)-H(63)	96 (4)
Co(2)-N(6)-H(63)	113 (3)	H(62)-N(6)-H(63)	123 (4)
	(E) Oxygen-Sulfur-Oxygen Angles		
O(11)-S-O(12)	110.38 (14)	O(12)-S-O(13)	109.74 (14)
O(11)-S-O(13)	110.40 (13)	O(12)-S-O(14)	109.01 (13)
O(11)-S-O(14)	108.88 (13)	O(13)-S-O(14)	108.40 (13)
	(F) Hydrogen-Oxygen-Hydrogen Angles		
H(101)-O(10)-H(102)	110 (4)	H(401)-O(40)-H(402)	108 (6)
H(201)-O(20)-H(202)	116 (5)	H(501)-O(50)-H(502)	104 (6)
H(301)-O(30)-H(302)	95 (6)		

= 1.899 (2) Å and Co(2)–O(4) = 1.903 (2) Å.

The shortest cobalt–nitrogen bond lengths involve the ammine ligands trans to the hydroxide ion associated with the longer Co–O(carbonate) linkages: Co(1)–N(2) = 1.929 (3) Å and Co(2)–N(6) = 1.933 (3) Å. The remaining cobalt–nitrogen bond distances are equivalent, ranging from 1.940 (3) to 1.947 (3) Å.

The intermetallic distance [Co(1)···Co(2) = 2.817 (1) Å], the angles at the bridging hydroxide ligands [Co(1)–O(1)–Co(2) = 95.90 (10)° and Co(1)–O(2)–Co(2) = 94.37 (10)°], as well as the angles at the bridging carbonate ligand [Co(1)–O(3)–C = 127.16 (19)° and Co(2)–O(4)–C = 126.54 (18)°] indicate that (as expected for a binuclear d^6 octahedral species) there is no bonding cobalt–cobalt interaction.

The carbonate ligand causes perturbation in the octahedral environment about the cobalt ions and is itself "stretched" with O(3)–C–O(4) = 122.4 (3)°. It takes up a planar geometry with a contribution from the valence bond structure III. The



III

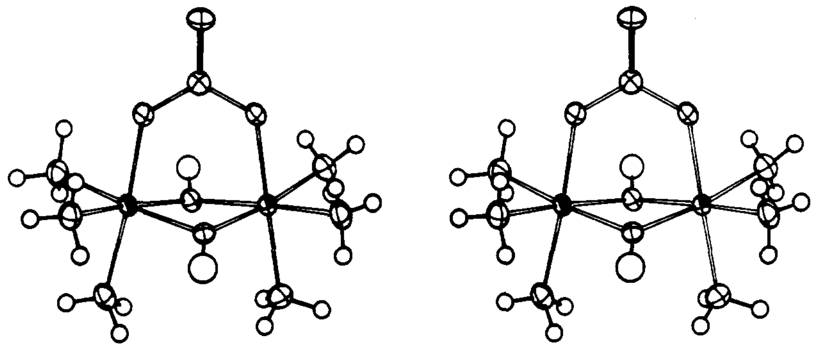


Figure 4. Stereoscopic view of the $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]^{2+}$ cation.

Table VI

Important Least-Squares Planes[a,b] for $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4{\cdot}5H_2O$

atom	dev, Å	atom	dev, Å
Plane I: $0.2032X - 0.2187Y + 0.9544Z = 2.1493$			
Co(1)*	0.0000	N(1)	−1.841 (3)
Co(2)*	0.000	N(2)	0.536 (3)
O(1)*	0.000	N(3)	−0.087 (3)
O(2)	−0.457 (2)	N(4)	−1.849 (3)
O(3)	1.835 (2)	N(5)	−0.072 (3)
O(4)	1.834 (2)	N(6)	0.642 (3)
Plane II: $-0.1525X - 0.2190Y + 0.9637Z = 2.1814$			
Co(1)*	0.000	N(1)	−1.888 (3)
Co(2)*	0.000	N(2)	0.028 (3)
O(2)*	0.000	N(3)	0.419 (3)
O(1)	−0.445 (2)	N(4)	−1.913 (3)
O(3)	1.861 (2)	N(5)	0.426 (3)
O(4)	1.867 (2)	N(6)	0.151 (3)
Plane III: $-0.9998X + 0.0006Y + 0.0182Z = 0.0701$			
Co(1)*	−0.0009 (4)	N(1)	−0.116 (3)
Co(2)*	−0.0017 (4)	N(2)	−1.431 (4)
O(3)*	0.0058 (2)	N(3)	1.421 (3)
O(4)*	0.076 (2)	N(4)	−0.166 (4)
C*	0.014 (3)	N(5)	1.394 (4)
O(5)*	−0.092 (2)	N(6)	−1.385 (3)
O(1)	−1.249 (2)		
O(2)	1.284 (2)		
Plane IV: $-0.9948X - 0.0264Y + 0.0987Z = 0.0067$			
O(3)*	0.00	N(1)	−0.486 (3)
O(4)*	0.00	N(2)	−1.606 (4)
C*	0.00	N(3)	1.228 (3)
O(5)*	0.00	N(4)	−0.568 (4)
Co(1)	−0.2149 (4)	N(5)	1.156 (4)
Co(2)	−0.2394 (4)	N(6)	−1.595 (3)
O(1)	−1.491 (2)		
O(2)	1.035 (2)		
Important Angles (Deg)			
plane I–plane III	100.71	plane II–plane III	80.22

[a] Equations for planes are expressed in orthonormal coordinates. [b] Atoms marked with an asterisk were used in calculating the plane under consideration.

oxygen atom not involved in bonding to the cobalt atoms participates in a shorter carbon–oxygen bond [C–O(5) = 1.262 (3) Å] than the other two oxygen atoms of the carbonate ligand [C–O(3) = 1.286 (3) Å and C–O(4) = 1.303 (3) Å].

It should be noted that, while this paper represents the first structural study on a μ-carbonato complex of cobalt(III), a rather similar μ-acetato species—$[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)Co(NH_3)_3]Br_3{\cdot}3H_2O$—has been examined crystallographically by Mandel, Marsh, Schaefer, Mandel, and Wang.[15]

Each $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]^{2+}$ cation has a SO_4^{2-} anion associated with it. Within this sulfate ion, the oxygen atoms are tetrahedrally arranged around the sulfur atom. The sulfur–oxygen linkages are normal and range from 1.461 (2) to 1.487 (2) Å. The closest contact between the two ions involves one of the bridging hydroxide ligands in the cation: O(2)···O(14) = 2.798 (3) Å with O(2)–H(2) = 0.70 (4) Å, H(2)···O(14) = 2.11 (4) Å, and O(2)–H(2)···O(14) = 167 (14)°.

Hydrogen Bonding in the Crystal. There is an extensive hydrogen-bonding scheme within the crystal. The relevant dimensions are collected in Table VII. All of the hydrogen atoms within the cation and the water molecules are involved.

The shortest involve the systems O(5)···H(501)–O(50), O(2)···H(101)–O(10), O(2)–H(2)···O(14), and O(10)–H(102)···O(40), for which the O···O distances are 2.764 (4), 2.782 (4), 2.798 (3), and 2.802 (5) Å, respectively. All other X–H···Y systems are associated with X···Y distances of 2.85 Å or greater.

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Registry No. $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4{\cdot}5H_2O$, 75476-69-6; "triol", 45976-80-5.

Supplementary Material Available: Listings of data-processing formulas, observed and calculated structure factor amplitudes, and distances and angles involving hydrogen bonding (Table VII) (14 pages). Ordering information is given on any current masthead page.

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(15) Mandel, G. S.; Marsh, R. E.; Schaefer, W. P.; Mandel, N. S.; Wang, B. C. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3185–3188.