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Registry No. $(Mn(DAPSC)(H_2O)(Cl))^+Cl^-\cdot 2H_2O$, 65484-11-9; $(Fe(DAPSC)(H_2O)(Cl))^+Cl^-\cdot 2H_2O$, 43010-80-6; $(Co(DAPSC)(H_2O)(Cl))^+Cl^-\cdot 2H_2O$, 43010-81-7; $(Zn(DAPSC)(H_2O)(Cl))^+Cl^-\cdot 2H_2O$, 42936-39-0.

Supplementary Material Available: Listings of structure factor amplitudes (39 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This paper is abstracted from a dissertation submitted by D.W.W. to the Graduate School of the University of Florida in partial fulfillment of the requirements of the Ph.D. degree in Chemistry.
(2) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).
(3) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 32 (1964).
(4) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, **88**, 3228 (1966).
(5) A comparison of the stereochemistry in the seven-coordinate complexes of EDTA with Mg(II), Mn(II), and Fe(III) has been given by J. J. Stezowski, R. Countryman, and J. L. Hoard, *Inorg. Chem.*, **12**, 1749 (1973).
(6) (a) J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964); (b) S. M. Nelson and D. H. Busch, *Inorg. Chem.*, **8**, 1859 (1969).
(7) E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, **89**, 720 (1967).
(8) M. G. B. Drew, G. W. A. Fowles, and D. F. Lewis, *Chem. Commun.*, 876 (1969).
(9) (a) R. L. R. Towns and R. A. Levenson, *J. Am. Chem. Soc.*, **94**, 4345 (1972); (b) R. A. Levenson and R. L. R. Towns, *Inorg. Chem.*, **13**, 105 (1974).
(10) G. J. Palenik, D. F. Rendle, and W. S. Carter, *Acta Crystallogr., Sect. B*, **30**, 2390 (1974), and references therein.
(11) D. V. Naik and G. J. Palenik, *Acta Crystallogr., Sect. B*, **30**, 2396 (1974).
(12) D. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 6505 (1973).
(13) D. Wester and G. J. Palenik, in preparation.
(14) D. F. Lewis and R. C. Fay, *J. Am. Chem. Soc.*, **96**, 3843 (1974).
(15) N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 727 (1974).
(16) (a) M. G. B. Drew, A. H. bin Othman, S. C. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans*, 438 (1977); (b) *ibid.*, 1173 (1973).
(17) M. Nardelli, C. Pelizzi, and G. Pelizzi, *Transition Met. Chem.*, **2**, 40 (1977).
(18) M. G. B. Drew, A. H. bin Othman, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1394 (1976).
(19) M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *Acta Crystallogr., Sect. B*, **32**, 1029 (1976).
(20) M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 2507 (1975).
(21) F. Mathieu and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 816 (1973).
(22) M. G. B. Drew and S. M. Nelson, *Acta Crystallogr., Sect. A*, S140 (1975).
(23) D. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, **96**, 7565 (1974).
(24) (a) U. Rychlewska, R. C. Palenik, R. W. King, and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 799 (1975); (b) G. J. Palenik, D. W. Wester, U. Rychlewska, and R. C. Palenik, *Inorg. Chem.*, **15**, 1814 (1976).
(25) D. McRitchie, G. J. Palenik, and R. C. Palenik, *Inorg. Chim. Acta*, **20**, L27 (1976).
(26) (a) D. Wester and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 74 (1975); (b) *Inorg. Chem.*, **15**, 755 (1976).
(27) (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); (b) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968); (c) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(28) See paragraph at end of paper regarding supplementary material.
(29) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, discusses the electroneutrality principle which could be applicable in this case.
(30) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976), gives revised ionic radii for most elements. The high-spin Fe(II) is approximately 0.14 Å larger than high-spin Fe(III) for coordination numbers six and eight.
(31) R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.*, **16**, 511 (1977), and references therein.
(32) H. A. Jahn and E. Teller, *Proc. R. Soc. London*, **161**, 200 (1937).
(33) A. H. White and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1377 (1977).
(34) M. G. B. Drew, *Acta Crystallogr., Sect. A*, **31**, S140 (1975), reported the crystal structure of PBP zinc complex but no distances were given.
(35) J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, N.Y., 1972, p 310. There are numerous other textbooks where similar plots can be found.

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Selenite Complexes with Pentaamminecobalt(III): O- and Se-Bound Forms[1]

R. C. ELDER* and PAUL E. ELLIS, JR.

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The reaction of sodium selenite with aquopentaamminecobalt(III) chloride in ammoniacal solution leads to the formation of oxygen-bound selenitopentaamminecobalt(III) chloride-$^5/_2$-water. The x-ray structure of this complex which crystallizes in the monoclinic system [space group $I2/a$; $a = 17.490$ (3), $b = 6.887$ (1), $c = 19.987$ (2) Å; $\beta = 94.19$ (1)°; $Z = 8$] has been refined to $R_1 = 0.024$ and $R_2 = 0.032$. The six-coordinate cobalt atom binds five ammonia ligands and an oxygen atom of the selenite anion. The selenite geometry is pyramidal with the longest Se–O bond, 1.707 (4) Å, being that to the oxygen atom coordinated to cobalt. There is a marginally significant negative trans effect in that the trans Co–N distance, 1.951 (3) Å, is 0.011 (5) Å less than the average cis Co–N distance 1.962 (4) Å. The reaction of sodium selenite with (dimethyl sulfoxide)pentaamminecobalt(III) perchlorate in methanol leads to a product whose chemical characterization and IR spectrum provide evidence that it is the selenium-bound selenitopentaamminecobalt(III) perchlorate.

Introduction

Following our discovery of a large ground-state structural trans effect in sulfitopentaamminecobalt(III) chloride[2] and our subsequent finding[3] that coordinated selenium seems to cause a larger trans effect than coordinated sulfur, we decided to prepare and study the selenium analogue of sulfitopentaamminecobalt(III). Our first attempts led to the formation of the oxygen-bound selenitopentaamminecobalt(III) cation, the structure of which we have determined by x-ray crystallography. Subsequent attempts appear to have produced the selenium-bound isomer of the complex cation, although we have not yet obtained a suitable material for x-ray studies. We report here the synthesis and characterization, including the crystal structure, of the oxygen-bound selenitopentaamminecobalt(III) chloride and the synthesis and partial characterization of selenium-bound selenitopentaamminecobalt(III) perchlorate.

Experimental Section

General Data. Common laboratory chemicals were of reagent grade. Visible–UV spectra were recorded on a Cary 14 spectrophotometer.

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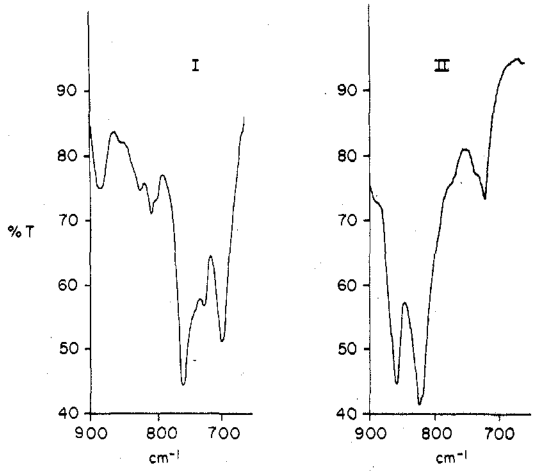

Figure 1. IR spectra of oxygen-bound selenitopentaamminecobalt(III) chloride-$^5/_2$-water, $[(NH_3)_5CoOSeO_2]Cl\cdot{}^5/_2H_2O$, I, and of selenium-bound selenitopentaamminecobalt(III) perchlorate, $[(NH_3)_5CoSeO_3]ClO_4$, II, in the Se–O stretching region, 900–660 cm^{-1}.

IR spectra were run as mineral oil mulls on KBr plates using a Beckman IR12 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

(Selenito-*O*)pentaamminecobalt(III) Chloride-$^5/_2$-Water, $[(NH_3)_5CoOSeO_2]Cl\cdot{}^5/_2H_2O$, I. Essentially, the synthetic method[4] consists of substitution of selenite for water in $[(NH_3)_5CoH_2O]Cl_3$ to yield the oxygen-bound selenito complex as the chloride salt. Convenient conditions for this reaction are as follows. Two grams of freshly prepared[6] $[(NH_3)_5CoH_2O]Cl_3$ is dissolved in 12 mL of ~3 M ammonia by warming to 40 °C, and the solution is filtered to remove any undissolved $[(NH_3)_5CoCl]Cl_2$. A filtered solution of 1.68 g of Na_2SeO_3 dissolved in 2 mL of H_2O and 1 mL of concentrated ammonia is added. The mixture is then warmed to 60 °C, slowly cooled to 5 °C, and filtered. Three milliliters of absolute ethanol is added to the cooled, deep ruby red solution. A dark red oil separates and slowly converts into deep red crystals. Crystals suitable for x-ray diffraction studies were grown by dissolving the crude crystals in a minimal amount of 3 M ammonia at room temperature and adding ethanol dropwise until the first stubborn cloudiness appeared. The solution beaker was then placed in a Dewar flask and the covered Dewar placed in a refrigerator. After 6–12 h the solution had cooled to 5 °C and well-formed, deep red crystals had precipitated. The crystals were filtered, washed with 60% (v/v) ethanol/water, and air-dried. The yield was ~75%. Anal. Calcd for $CoN_5H_{15}O_3SeCl\cdot{}^5/_2H_2O$: Co, 16.76; N, 19.92; H, 5.73; Se, 22.46; Cl, 10.09. Found: Co, 17.18; N, 20.68; H, 5.28; Se, 23.30; Cl, 10.39. The IR spectrum of this material indicated that it contained water of crystallization. The spectrum in the region from 900 to 660 cm^{-1}, which is expected to span the Se–O stretching frequencies,[7] is presented in Figure 1. The visible–UV spectral parameters are listed in Table I.

Attempted Synthesis of (Selenito-*Se*)pentaamminecobalt(III) Perchlorate, $[(NH_3)_5CoSeO_3]ClO_4$, II. An attempt to form the selenium-bound isomer via the substitution of SeO_3^{2-} for dimethyl sulfoxide, Me_2SO, in $[(NH_3)_5Co(Me_2SO)](ClO_4)_3$[8] was made using methanol as the solvent. A filtered solution of 0.332 g of Na_2SeO_3 in 50 mL of methanol was added to a filtered solution of 1.00 g of $[(NH_3)_5CoMe_2SO](ClO_4)_3$ in 150 mL of methanol. The mixture was heated, first at 35 °C for 24 h and then at 45 °C for 48 h. At this point a small amount (~20 mg) of purple precipitate was filtered as a fine powder and discarded. The 200 mL of pale red-violet solution was reduced in volume to ~20 mL on a rotary evaporator giving a solution of deep red color. On standing, this liquid produced a white precipitate (~10 mg) which was also filtered and discarded. Further evaporation led to a red oil. This was redissolved in hot methanol and a small amount (~100 mg) of a light red-pink powdery solid precipitated by the addition of chloroform. The material, II, was filtered and washed with a cold mixture of methanol and chloroform. We were unsuccessful in attempts to recrystallize II for x-ray studies. A few crystals were obtained from the wall of the reaction vessel on one occasion. Most of these, although exhibiting well-developed faces, were rather opaque. Five of the clearer crystals were mounted on glass fibers and examined using a Syntex $P\bar{1}$ diffractometer. All five of the crystals were found to be twinned and further x-ray studies of the perchlorate salt were abandoned. The powdery material was further characterized in several experiments. Analysis by energy-dispersive x-ray fluorescence (EDAX Model 707) indicated a 1:1 atom ratio for Co:Se, with an error estimated to be less than 20%. Cation-exchange chromatographic experiments using 3 M ammonia and various concentrations of ammonium nitrate gave behavior very similar to that of the oxygen-bound selenito complex, indicating a 1+ charge on the cobalt complex. No separation was observed on elution from the column. The IR spectrum of II indicated that it was an anhydrous perchlorate salt. The portion of the spectrum from 900 to 660 cm^{-1} which is expected to span the Se–O stretching region is presented in Figure 1. The visible–UV spectral results obtained from II are given in Table I. Since we were unable to effect purification of this compound by recrystallization, we did not perform an elemental analysis.

Table I. Absorption Spectra[a]

Complex	λ_{max} (ϵ)	λ_{max} (ϵ)	Solvent	Ref
$[A_5CoOSeO_2]^+$	520 (60)	285 sh (1100)	H_2O	*b*
$[A_5CoO_2CCH_3]^{2+}$	502 (77)		H_2O	*c*
$[A_5CoSeO_3]^+$	515 (60)	285 sh (1800)	H_2O	*d*
$[A_5CoSeO_3]^+$	520 (60)	265 sh (13 000)	MeOH	*d*
$[A_5CoSO_3]^+$	457 (148)	279 (17 800)	1 M NH_3	*e*
$[A_5CoS(O)_2R]^{2+}$	463 (221)	303 (13 500)	1 M $HClO_4$	*e*
$[(en)_2Co(SC_2H_4NH_2)]^{2+}$	482 (140)	282 (14 000)	1 M $HClO_4$	*f*
$[(en)_2Co(SeC_2H_4NH_2)]^{2+}$	490 (170)	297 (18 500)	1 M $HClO_4$	*f*

[a] Entries headed λ_{max} are peak positions in nm; following values in parentheses are molar extinction coefficients in M^{-1} cm^{-1}. [b] This work: $[(NH_3)CoOSeO_2]Cl\cdot{}^5/_2H_2O$. [c] E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967: $[(NH_3)_5CoO_2CCH_3]ClO_4$. [d] This work: $[(NH_3)_5CoSeO_3]ClO_4$. The entries for these extinction coefficients have an additional uncertainty due to the approximate formulation of the compound. [e] R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula, and E. A. Deutsch, *Inorg. Chem.*, 17, 431 (1978). [f] Reference 3.

X-Ray Characterization of $[(NH_3)_5CoOSeO_2]Cl\cdot{}^5/_2H_2O$. A dark red crystal of the oxygen-bound selenito complex was mounted on a glass fiber and precession photographs of the *hk*0, *hk*1, 0*kl*, 1*kl*, and 2*kl* layers were taken using Cu Kα radiation. The systematic absences were for *hkl*, *h* + *k* + *l* odd, and for *h*0*l*, *h* odd (*l* odd), suggesting possible choices of space group[9] *Ia* (nonstandard setting of *Cc*, No. 9) or *I*2/*a* (nonstandard setting of *C*2/*c*, No. 15) for the monoclinic cell. The approximate cell constants were a = 17.43 (3) Å, b = 6.86 (3) Å, c = 20.06 (3) Å, and β = 94.2 (2)°. A second, smaller crystal in the form of a rectangular parallelepiped truncated at one end with mean dimensions of 0.18 × 0.19 × 0.23 mm was mounted on a glass fiber with the long dimension parallel to the fiber axis. This crystal was placed on a Syntex $P\bar{1}$ diffractometer and optically centered, and precise cell constants were determined in the usual manner.[10] They are a = 17.490 (3) Å, b = 6.887 (1) Å, c = 19.987 (2) Å, and β = 94.19 (1)°. Partial oscillation photographs (±14°) were taken about each of the crystal axes to check crystal quality and the correctness of indexing. With the assumption of eight formula units per cell, the calculated density is 1.94 g cm^{-3} and the measured density is 1.90 (3) g cm^{-3} (neutral buoyancy in $CHCl_3$/$CHBr_3$). All measurements were made at room temperature.

Intensity measurements were made[10] as previously described, for the 3119 reflections with $2\theta \leq 42°$ in the four forms hkl, $h\bar{k}l$, $\bar{h}kl$, and $\overline{hk}l$. From these data, 1408 unique reflections were obtained by averaging. The average percent discrepancy for multiply measured reflections was 1.06%. The θ–2θ scan for these measurements, using Mo Kα radiation (λ 0.71069 Å) and a graphite monochromator, was from 1.0° below to 1.0° above the reflection in 2θ. Scan rates varied from 2.0 to 8.0°/min depending on the intensity of the reflection. Four standard reflections were used to check stability and to account for long-term drift. The drift correction varied from 1.025 to 0.992. Since μ, the linear absorption correction, was 48.6 cm^{-1}, absorption corrections were applied. The transmission coefficients ranged from 0.497 to 0.432. The correctness[3] of the calculations of transmission coefficients was checked by a series of ψ scans of the standard reflections. Of the set of 1408 unique normalized structure factors,

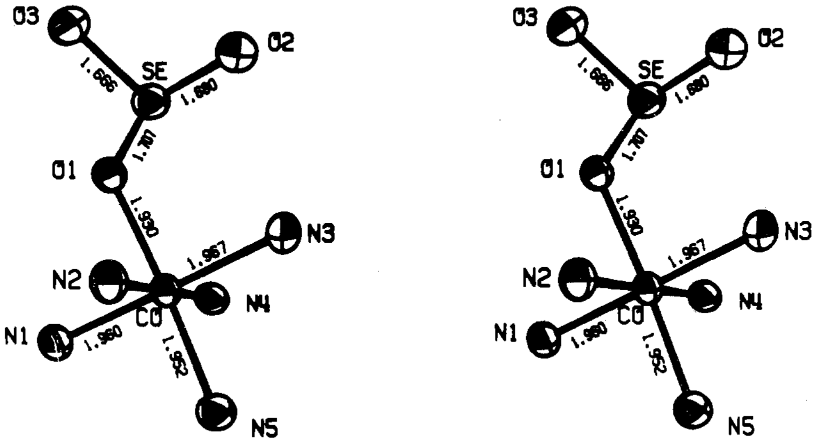

Figure 2. ORTEP stereodiagram of the oxygen-bound selenitopentaamminecobalt(III) complex cation, $[(NH_3)_5CoOSeO_2]^+$.

Table II. Fractional Atomic Positional Parameters[a-c]

Atom	*x*	*y*	*z*
Co	0.355 53 (3)	0.293 73 (7)	0.096 31 (3)
Se	0.263 71 (3)	−0.068 18 (6)	0.155 52 (2)
O(1)	0.293 4 (2)	0.061 5 (3)	0.089 3 (1)
O(2)	0.344 0 (2)	−0.189 2 (4)	0.181 1 (2)
O(3)	0.209 5 (2)	−0.233 2 (4)	0.113 6 (2)
N(1)	0.270 2 (2)	0.428 8 (4)	0.047 3 (2)
N(2)	0.395 9 (2)	0.208 5 (5)	0.011 8 (2)
N(3)	0.439 0 (2)	0.154 9 (4)	0.147 3 (2)
N(4)	0.313 2 (2)	0.380 4 (5)	0.179 4 (2)
N(5)	0.419 2 (2)	0.526 9 (5)	0.095 5 (2)
O(4)[d]	0.500 0	0.467 5 (8)	0.250 0
O(5)	0.138 3 (2)	0.329 7 (5)	0.196 4 (2)
O(6)	0.086 3 (2)	0.731 9 (6)	0.193 1 (2)
Cl	0.084 83 (7)	0.221 4 (2)	0.050 46 (6)

[a] The estimated error in the last digit is given in parentheses. This form is used throughout. [b] The numbering scheme is shown in Figure 2. [c] The equivalent positions for the space group *I*2/*a* are $x, y, z; \bar{x}, \bar{y}, \bar{z}; {}^1/_2 + x, {}^1/_2 - y, z;$ and ${}^1/_2 - x, {}^1/_2 + y, z$ (0, 0, 0 and ${}^1/_2, {}^1/_2, {}^1/_2$). [d] This atom lies on a twofold axis and thus has no errors in *x* or *z*.

Table III. Root-Mean-Square Displacements (Å)

Atom	Min	Mean	Max
Co	0.124	0.145	0.155
Se	0.156	0.164	0.190
O(1)	0.130	0.153	0.192
O(2)	0.172	0.183	0.213
O(3)	0.164	0.190	0.202
N(1)	0.144	0.157	0.184
N(2)	0.152	0.163	0.175
N(3)	0.146	0.163	0.175
N(4)	0.142	0.148	0.184
N(5)	0.157	0.164	0.193
O(4)	0.213	0.232	0.236
O(5)	0.176	0.220	0.268
O(6)	0.195	0.238	0.294
Cl	0.177	0.185	0.247

Table IV. Bond Lengths (Å) and Bond Angles (deg)

Co-O(1)	1.930 (3)	Co-N(3)	1.967 (5)
Co-N(1)	1.960 (5)	Co-N(4)	1.958 (5)
Co-N(2)	1.965 (5)	Co-N(5)	1.952 (3)
Se-O(1)	1.707 (4)	Se-O(3)	1.666 (4)
Se-O(2)	1.680 (4)		
O(1)-Co-N(1)	87.1 (1)	O(1)-Co-N(3)	91.7 (1)
O(1)-Co-N(2)	85.7 (2)	O(1)-Co-N(4)	93.9 (1)
N(1)-Co-N(2)	91.0 (1)	N(1)-Co-N(4)	87.7 (1)
N(1)-Co-N(5)	91.3 (1)	N(2)-Co-N(3)	90.2 (1)
N(2)-Co-N(5)	89.9 (2)	N(3)-Co-N(4)	91.1 (1)
N(3)-Co-N(5)	90.0 (1)	N(4)-Co-N(5)	90.4 (1)
O(1)-Co-N(5)	175.3 (1)	N(1)-Co-N(3)	178.3 (3)
N(2)-Co-N(4)	178.7 (3)		
Co-O(1)-Se	125.2 (2)	O(1)-Se-O(2)	101.6 (1)
O(1)-Se-O(3)	99.1 (1)	O(2)-Se-O(3)	104.5 (1)

1342 had $F_o^2 \geq 3\sigma(F_o^2)$, where a value of 0.02 was used for *p*, the ignorance factor,[10] in calculating $\sigma(F_o^2)$.

The statistical distribution[11] of *E* values strongly suggested that the centric space group *I*2/*a* was the correct choice. A sharpened, origin-removed Patterson map indicated positions for the selenium and cobalt atoms compatible with the centric space group. An electron density synthesis based on signs derived from the selenium and cobalt positions revealed the positions of the remaining nonhydrogen atoms except for the oxygen atoms of the water molecules. A subsequent difference electron density map based on those atoms above indicated positions for the oxygen atoms of the water molecules, one of which lies on a twofold axis and thus leads to the formulation with $^5/_2$ water molecules. Refinement of atomic positional and isotropic thermal parameters yielded $R_1 = 0.062$.[12] A difference electron density map showed 19 distinct peaks corresponding to 19 of the 20 hydrogen atoms. Two models were refined to convergence. In the first model, hydrogen positional and isotropic thermal parameters were refined as well as positional and anisotropic thermal parameters for nonhydrogen atoms. Convergence was reached at $R_1 = 0.023$ and $R_2 = 0.029$. One N–H bond in this model led to an unreasonable distance, 0.53 (6) Å. In the second model, the ammonia hydrogen atoms were located at the tetrahedral angles and a fixed distance (1.00 Å) to give the minimal deviation from those positions found from the difference map, the positions of the hydrogen atoms of the water molecules were refined, and positional and anisotropic thermal parameters were refined for the nonhydrogen atoms. This model converged to $R_1 = 0.024$ and $R_2 = 0.032$. The Hamilton *R* factor test[13] did not indicate significant improvement of fit for the first model and so we discuss the results of the second model below. In the final cycle of refinement the average shift per error was 0.038. Two positional parameters of hydrogen atoms of water molecules changed by 0.41 and 0.37 times their estimated standard deviations. A total of 1408 reflections was used to refine 139 variables. A final difference map was essentially featureless with the highest peak less than 0.3 e Å^{-3}. Examination of groups of reflections ordered on $(\sin\theta)/\lambda$ or on $|F_o|$ revealed no significant trends in disagreement with the model. Zerovalent scattering curves from Cromer[14] were used for Se, Co, Cl, O, and N. Those for hydrogen were taken from Stewart.[15] Corrections for anomalous dispersion[16] were made using the following values: Co, $\Delta f' = 0.4$, $\Delta f'' = 1.1$; Se, $\Delta f' = -0.1$, $\Delta f'' = 2.4$; Cl, $\Delta f' = 0.1$, $\Delta f'' = 0.2$. The values of $|F_o|$ and F_c are listed in Table A.[17]

Results and Discussion

Description of Crystal Structure. Fractional atomic positional parameters for nonhydrogen atoms from the last cycle of least-squares refinement are presented in Table II. Those used for the hydrogen atoms are to be found in Table B. Anisotropic thermal parameters are listed in Table C, the root-mean-square displacements derived therefrom are given in Table III and the associated thermal ellipsoids (50% probability) are illustrated in Figure 2. The bond distances and angles for the complex cation have been gathered in Table

Table V. Possible Hydrogen Bonds

Atoms A, H, B	A···B, Å	H···B, Å	A–H···B, deg
N(1), H(1a), O(3)[a]	2.911	2.030	165.8
N(1), H(1b), O(1)[b]	3.015	2.359	129.6
N(2), H(2a), O(3)[b]	3.031	2.186	156.6
N(3), H(3a), O(2)	2.994	2.139	157.7
N(3), H(3b), O(4)	3.108	2.255	158.0
N(4), H(4a), O(2)[a]	3.006	2.108	171.5
N(4), H(4b), O(5)	3.120	2.240	166.0
N(4), H(4c), O(5)[c]	2.946	2.074	163.5
N(5), H(5b), O(2)[a]	2.963	2.078	167.9
N(5), H(5c), Cl[b]	3.206	2.305	175.5
O(4), H(O4), O(6)	2.842	2.053	158.9
O(5), H(O5a), Cl	3.090	2.224	176.8
O(5), H(O5b), O(6)	2.909	2.267	154.6
O(6), H(O6a), O(3)[a]	2.777	1.746	158.4
O(6), H(O6b), O(2)[d]	2.732	2.062	167.6

[a] Transformed to $x, 1 + y, z$. [b] Transformed to $^1/_2 - x, {}^1/_2 + y, -z$. [c] Transformed to $-^1/_2 + x, -^1/_2 + y, -^1/_2 + z$. [d] Transformed to $^1/_2 - x, {}^1/_2 - y, {}^1/_2 - z$.

IV. The crystal consists of six-coordinate "octahedral" cobalt cations, chloride anions, and water molecules linked together through a network of hydrogen bonds. These hydrogen bonds are listed in Table V. The complex cation is formed by coordination of five ammonia molecules and a selenite anion bound through oxygen to the cobalt(III) center. The selenito ligand is pyramidal. The longest Se–O bond, Se–O(1), involves the oxygen atom which is bound to cobalt.

Crystal Structure of $[(NH_3)_5CoOSeO_2]Cl\cdot{}^5/_2H_2O$. The structure of this compound is as expected for the oxygen-bound selenite. "Octahedral" coordination of the cobalt center is effected by five nitrogen atoms from ammonia ligands and an oxygen atom from the selenite anion. The major distortion from the ideal 90° angles expected about the cobalt atom results from bending O(1) toward N(2), 85.7°, and away from N(4), 93.9°. Also, the Co–O(1)–Se angle is 125.2 (2)°, somewhat larger than the expected tetrahedral value. These distortions all relieve the steric interaction between the selenium atom and N(4) as may be seen in Figure 2. The selenito ligand has the expected pyramidal geometry. We have not found any other examples of selenite coordinated as a monodentate oxygen-bound ligand. The selenite ligand[18] is tridentate in $CuSeO_3\cdot 2H_2O$ with each oxygen atom binding to a different copper atom. There, the Se–O distances are 1.701 (4), 1.702 (5), and 1.712 (4) Å and the O–Se–O angles are 98.1 (2), 100.2 (2), and 100.4 (2)°. In the structure[19] of $[Mg(H_2O)_6]SeO_3$, the selenite counterion has threefold symmetry with the Se–O distance 1.69 (1) Å and the O–Se–O angle 100.7 (5)°. In a neutron diffraction study[20] of selenious acid, H_2SeO_3, Larsen and co-workers found that the two selenium–oxygen bonds involving protonated oxygen atoms were 1.735 (2) and 1.743 (2) Å, whereas the third Se–O distance was 1.643 (2) Å. Similarly, in this study, the oxygen atom O(1) bound to cobalt has a longer Se–O bond, 1.707 (4) Å, than either of the Se–O bonds of the free oxygen atoms, 1.680 (4) and 1.666 (4) Å.

Our interest in the selenite ligand stems in part from our anticipation that selenium-bound selenitopentaamminecobalt(III) will exhibit a large trans effect. In the case of the oxygen-bound form reported here, there may be a small negative trans effect, i.e., a shortening of the trans Co–N bond relative to the normal cis Co–N bonds. The average cis Co–N bond, 1.962 (4) Å, is of normal length when compared to 1.966 (4), 1.965 (9), and 1.974 (2) Å found for $[(NH_3)_5CoSO_3]Cl\cdot H_2O$,[2] $(NH_3)_5CoNCCo(CN)_5\cdot H_2O$,[21] and $(NH_3)_5CoCNCo(CN)_5\cdot H_2O$,[22] respectively. Fronczek and Schaefer[22] quoted the value found here of 1.962 Å as normal for cis Co–N distances in pentaamminecobalt(III) structures. The trans Co–N distance in this study is slightly shorter, 1.952 (3) Å, giving a difference of –0.010 (5) Å, which appears marginally significant. A negative trans effect is not unknown.[21] A difference of –0.030 (9) Å has been found for $(NH_3)_5CoNCCo(CN)_5\cdot H_2O$. The hydrogen bonds (Table V) in this structure seem relatively weak and do not appear to have a significant influence on the cation geometry.

Selenite Linkage Isomers. There is a striking difference in the course of the reaction of aquopentaamminecobalt(III) with the sulfite and selenite anions. In the former case, the sulfur-bound sulfitopentaamminecobalt(III) cation appears to be the only product, whereas in the latter case, the oxygen-bound selenitopentaamminecobalt(III) cation is the only product which we have been able to isolate. Although the sulfito and selenito ligands with their relatively simple structures and similar types of atoms (all atoms are chalcogens) are appealing candidates with which to attempt the formation of linkage isomers, we find no such claim[23] in the literature. Different choices of central metal ion can lead to a change in binding mode for the sulfite anion. Thus Carlyle and King[24] have studied the formation and reactions of sulfitopentaaquochromium(III) and found evidence only for the oxygen-bound species.

When we discovered that the product of the reaction of aquopentaamminecobalt(III) with selenite was the oxygen-bound species, we assumed, following King, that the substitution reaction took place without breaking the cobalt–oxygen bond[25] of the aquopentaamminecobalt(III) starting material. In an attempt to avoid this type of reaction, we used (dimethyl sulfoxide)pentaamminecobalt(III) perchlorate as a source of the pentaamminecobalt(III) and reacted it with sodium selenite in methanol. We anticipated that the selenium-bound isomer would have a brown-yellow color much the same as (2-selenolatoethylamine-*N*,*Se*)bis(ethylenediamine)cobalt(III),[3] due to the tailing of the selenium-to-cobalt charge-transfer absorption into the visible spectrum. No brown product was observed. The pink-red product which we obtained appears to contain the selenium-bound isomer. However, due to our current failure to obtain suitable single crystals for x-ray analysis, we have not been able to determine unequivocally its structure. The evidence in hand is somewhat contradictory. The x-ray fluorescence experiment establishes a Co:Se ratio of 1:1. Spot tests indicate the selenium is still present as selenite. The elution characteristics on a cation-exchange column suggest that the complex cation has a 1+ charge, indicating that the selenite is bound to cobalt. The lack of significant absorption above 3400 cm^{-1} in the IR spectrum ($[(NH_3)_5CoOSeO_2]Cl\cdot{}^5/_2H_2O$ has a broad band centered at 3460 cm^{-1}) indicates that the material is anhydrous. Based on this evidence, there appear to be three most likely formulations for the cation: $[(NH_3)_5CoSeO_3]^+$, $[(NH_3)_5CoOSeO_2]^+$, and $[(NH_3)_4CoO_2SeO]^+$, where SeO_3 refers to monodentate, selenium-bound selenite, $OSeO_2$ refers to monodentate, oxygen-bound selenite, and O_2SeO refers to bidentate selenite, bound through two oxygen atoms.

Short of an x-ray structure determination, analysis of the Se–O stretching region of the IR spectrum of II provides the best method of assigning the binding mode of the selenite anion. The free SeO_3^{2-} ion, which has C_{3v} symmetry, exhibits[5] a symmetric stretch (ν_1—A) at 810 cm^{-1} and a degenerate asymmetric stretch (ν_3—E) at 740 cm^{-1}. If the local symmetry of the selenite is lowered on coordination through oxygen and the threefold axis is lost, then the degenerate asymmetric stretch must split into two bands. Analysis based on the number of bands is complicated by the fact that the ammine rocking modes are expected[26] also to occur in the same region. Recently, Fowless and Stranks[5] reported the IR spectrum of $[(NH_3)_5CoOSeO_2]Br\cdot H_2O$ and by deuteration of the ammonia hydrogen atoms were able to assign the observed bands at 805, 755, 695, and 520 cm^{-1} as ν_1', ν_2', ν_5', and ν_3' of the oxygen-bound selenite moiety. In I, the analogous chloride salt, we observe bands at 807, 758, 697, and 523 cm^{-1}. Thus there can be no doubt that the binding mode of selenite in the bromide salt is the same, namely, monodentate oxygen bound, as that in the chloride salt whose structure we have established via an x-ray crystal structure determination. Fowless and Stranks also have isolated $[(en)_2CoO_2SeO]ClO_4\cdot H_2O$ which they formulated as containing bidentate (two oxygen atoms bound) selenite. The band positions for this complex are 830, 752, 678, and 515 cm^{-1}, quite similar to those for monodentate oxygen-bound selenite.

The spectrum of II is strikingly different from those for monodentate or bidentate oxygen-bound selenite. Newman and Powell,[27] following an argument of Cotton,[28] have analyzed the binding mode of coordinated sulfite and have pointed out that on coordination through sulfur the S–O stretching frequencies should shift to higher energy, whereas on oxygen coordination they are expected to shift to lower frequencies than found in the free ion. This argument applied to the Se–O stretches of II leads to the assignment of the band at 860 cm^{-1} to ν_1 and the band at 823 cm^{-1} to the unsplit ν_3 with local C_{3v} symmetry. Thus, the IR spectrum on the basis of both the number of bands and their energies leads to the description of II as the selenium-bound isomer $[(NH_3)_5CoSeO_3]ClO_4$.

The visible–UV spectrum of II is somewhat surprising based on this description. Sulfur or selenium donors bound to cobalt(III) routinely have a ligand-to-metal charge-transfer absorption band at ~285 nm with extinction coefficients on the order of 18 000 $M^{-1}\,cm^{-1}$ (see Table I). On the other hand, pentaamminecobalt(III) species with an oxygen donor as the sixth ligand, for example, acetatopentaamminecobalt(III), do not. The spectrum of II dissolved in methanol shows a charge-transfer band at 265 nm with an extinction coefficient of ~13 000 $M^{-1}\,cm^{-1}$. However, when II is dissolved in water, its spectrum is very similar to that of I.[29] A possible explanation of this behavior is that II rapidly converts to an equilibrium mixture consisting in large part of I and a small amount of II. This would also explain the otherwise confusing shoulder at 285 nm observed in the spectrum of I as due to a small (<10%) concentration of II in solution. Since these spectra do not appear to change with time, we must assume that such an equilibrium is relatively rapidly attained. The speed of this reaction would then explain our inability to separate the isomers on a cation-exchange column.

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Registry No. I, 65484-07-3; II, 65484-04-0; $[(NH_3)_5CoH_2O]Cl_3$, 13820-80-9; $[(NH_3)_5Co(Me_2SO)](ClO_4)_3$, 38246-85-4.

Supplementary Material Available: Tables A–C, listing structure factor amplitudes, H atom positional parameters, and anisotropic temperature parameters of nonhydrogen atoms (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1975; see Abstracts, No. INOR 168.
(2) R. C. Elder and M. Trkula, *J. Am. Chem. Soc.*, **96**, 2635 (1974).
(3) C. A. Stein, P. E. Ellis, Jr., R. C. Elder, and E. A. Deutsch, *Inorg. Chem.*, **15**, 1618 (1976).
(4) Since our development of this synthesis, Fowless and Stranks[5] have published the syntheses of several other cobalt(III) complexes containing oxygen-bound selenite.
(5) A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, **16**, 1271, 1276, 1282 (1977).
(6) G. G. Schlesinger, "Inorganic Laboratory Preparations", Chemical Publishing Co., New York, N.Y., 1962, p 207.
(7) K. Sathiananden, L. D. McCory and J. L. Margrave, *Spectrochim. Acta*, **20**, 957 (1964).
(8) C. R. P. Mac-Coll and L. Beyer, *Inorg. Chem.*, **12**, 7 (1973).
(9) "International Tables for X-Ray Crystallography", Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965. The nonstandard setting was chosen to give an angle β near 90°.
(10) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
(11) All computations were performed using a local version of X-RAY67: J. M. Stewart, University of Maryland, crystallographic computer system.
(12) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.
(13) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(14) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(15) R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, England, 1962, p 215.
(17) Supplementary material. This includes all tables designated by alphabetic characters.
(18) T. Asai and R. Kiriyama, *Bull. Chem. Soc. Jpn.*, **46**, 2395 (1973).
(19) R. Weies, J.-P. Wendling, and D. Grandjean, *Acta Crystallogr.*, **20**, 563 (1966).
(20) F. K. Larsen, M. S. Lehmann, and I. Søtofte, *Acta Chem. Scand.*, **25**, 1233 (1971).
(21) B.-C. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).
(22) F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, **13**, 727 (1974).
(23) Various authors have postulated the formation of an oxygen-bound sulfito–cobalt(III) intermediate to explain reaction kinetics. See, for example, S. M. Farrell and R. S. Murray, *J. Chem. Soc., Dalton Trans.*, 322 (1977). Stranks[5] quoted Murray (R. S. Murray, *J. Chem. Soc., Dalton Trans.*, in press) that an oxygen-bound sulfito–cobalt intermediate has been identified spectroscopically.
(24) D. W. Carlyle and E. L. King, *Inorg. Chem.*, **9**, 2333 (1970).
(25) This assumption has recently been shown to be correct by Fowless and Stranks.[5]
(26) S. D. Ross and N. A. Thomas, *Spectrochim. Acta, Part A*, **26**, 971 (1970).
(27) G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).
(28) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).
(29) Fowless and Stranks[5] reported that for $[(NH_3)_5CoOSeO_2]^+$ λ_{max} is 519 nm and ϵ is 62 $M^{-1}\,cm^{-1}$. Our values agree well with these. Stranks made no mention of the shoulder at 285 nm.