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Trichloro(perchlorato)stannate(II), a Dianionic Tin(II) Complex Containing Bound Perchlorate: Crystal Structure of $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$

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Crystals containing the dinegative trichloro(perchlorato)stannate(II) anion may be prepared from a hydrochloric acid solution of stannous chloride and (benzenesulfinato-*S*)pentaamminecobalt(III) perchlorate. The title complex crystallizes in space group $P2_1/n$ with $a = 14.278$ (1) Å, $b = 6.965$ (7) Å, $c = 21.484$ (1) Å, $\beta = 105.29$ (1)°, and $Z = 4$. A total of 3054 unique reflections measured with an automated diffractometer were used to refine the crystal structure to a conventional R factor of 0.038. The cobalt atom is octahedrally coordinated by five ammines and the sulfur atom of the benzenesulfinato ligand. A structural trans effect is apparent. The best value from several studies for the sulfinato trans effect is 0.054 (6) Å. The dianion $[Cl_3SnOClO_3]^{2-}$ is formed from pyramidal $SnCl_3^-$ and perchlorate with a 2.91 (1)-Å bond between tin and a perchlorate oxygen atom. Mössbauer evidence establishes that the dianion contains Sn(II). The infrared spectrum shows the results of bonding the perchlorate to tin. The compound decomposes over several days at room temperature to give Sn(IV) and ClO_3^- among other products. Mössbauer and IR evidence are adduced to show that this redox process may involve oxygen atom transfer between perchlorate and Sn(II). The implications of this mechanism for solution reduction of perchlorate are discussed.

Introduction

We are currently investigating structural and kinetic trans effects in cobalt (III) complexes with sulfur-bound ligands[1-10] and are especially interested in complexes of the pentaamminecobalt(III) series.[7,10] To increase the number of complexes available in this series we attempted to prepare $[(NH_3)_5CoSC_6H_5]^{2+}$ and $[(NH_3)_5CoS(O)C_6H_5]^{2+}$ from $[(NH_3)_5CoS(O)_2C_6H_5]^{2+}$[7] using the two equivalent reducing agent Sn(II). While this approach did not yield the desired complexes containing reduced sulfur ligands, it did lead to the formation of a crystalline material containing the unreduced (benzenesulfinato-*S*)pentaamminecobalt(III) cation and the novel trichloro(perchlorato)stannate(II) anion. Coordination of the strong oxidant perchlorate to the strong reductant tin(II) within this anion bears directly upon proposed mechanisms for the metal ion reduction of perchlorate in solution. In this paper we report the preparation of the title compound and its characterization by means of infrared and Mössbauer spectrophotometry as well as a single-crystal x-ray structure determination. A brief investigation of the solid-state decomposition of this material is also detailed.

Experimental Section

General Procedure. Common laboratory chemicals were of reagent grade. Infrared spectra were recorded as mineral oil mulls on NaCl plates using a Beckman IR12 spectrophotometer. Computer calculations were performed on an IBM 370/168 located at the University of Cincinnati. Elemental analyses were performed by Galbraith Laboratories, Inc. The tin Mössbauer measurements were carried out using conventional techniques.[11] The various Sn samples were used as resonant absorbers for the 23.88-keV γ ray resulting from the decay of the metastable (250 day) level in ^{119}Sn. The source used in these measurements was ^{119m}Sn in vanadium (New England Nuclear). The spectrometer was run in the constant acceleration mode utilizing transmission geometry.

Preparation. (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)stannate(II) monohydrate, $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$, may be precipitated from an aqueous solution of $[(NH_3)_5CoS(O)_2C_6H_5](ClO_4)_2$ by addition of $SnCl_2$ in hydrochloric acid. Typically, 0.6 g of the $[(NH_3)_5CoS(O)_2C_6H_5](ClO_4)_2$[7] is dissolved in 1 M HCl (15 mL) with stirring and filtered to remove any undissolved solid. The stannous solution is prepared by dilution of 0.5 mL of a stock solution of $SnCl_2$ ($SnCl_2$, 20 g, in concentrated HCl, 40 mL, stored over Sn metal) with 1 M HCl, 5 mL. This stannous solution is added dropwise to the unstirred cobalt(III) solution until precipitation begins. The amount of stannous solution which must be added is variable. Yellow fibrous solid forms over 1–2 h. The solid is filtered, washed with ethanol and ether, and then air-dried rapidly. Moist solid appears to undergo more rapid decomposition than dry material. The dry solid is somewhat light and heat sensitive but can be stored for months if refrigerated in the dark.

Large crystals, suitable for the x-ray structure determination, were grown from similar solutions which were placed in a refrigerator approximately 1 h after the stannous solution was added. If no appreciable solid had formed after 1 day, the solution was swirled and returned to the refrigerator. Generally, after several days these solutions decompose, changing from brown to clear red, and then must be discarded. In some cases the yellow, fibrous material, which often formed first, transmuted into a few well-formed brown crystals. Anal. (crystalline material) Calcd for $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$: C, 11.5; H, 3.5; Cl, 22.6; Co, 9.4; N, 11.2; S, 5.1; Sn, 18.9. Found: C, 11.5; H, 3.8; Cl, 21.9; Co, 9.8; N, 11.8; S, 4.8; Sn, 17.3.

Decomposition. Initial decomposition of the solid material is accompanied by a color change from yellow-brown to a bright green. The rate at which decomposition occurs seems to depend on crystal size, exposure to air and/or light, and storage temperature. Typically, heating a crystalline sample at 100 °C yields a bright green product in 10 min. Prolonged heating leads to a further change in color to light blue and finally pink. *While we have never had an explosion with these materials heated to 100 °C, they regularly explode when heated in an open-ended melting point capillary to temperatures near 150 °C. This material should be handled with extreme caution and only in very small quantities.* Mössbauer and IR spectra were measured for brown $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$ and for a sample of green product prepared via heating at 100 °C for 10 min. A sample of green product prepared via standing at room temperature for several days gave negative results when tested[12] for perchlorate, whereas a sample of brown $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]$ gave a positive perchlorate test.

X-Ray Characterization. A brown, rectangular prism of $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$ with approximate dimensions 0.1 × 0.25 × 0.5 mm was mounted on a glass fiber. The long dimension of the crystal was nearly parallel with the fiber axis. Cu Kα radiation was used to obtain $0kl$, $1kl$, and hkk precession photographs with the crystal oriented to rotate about $b^* + c^*$. From these photographs, the cell constants were calculated to be $a = 14.23$ Å, $b = 6.93$ Å, $c = 21.45$ Å, and $\beta = 105.0°$ for the monoclinic cell.

This crystal was then optically centered on a Syntex $P\bar{1}$ diffractometer equipped with a molybdenum target tube (λ 0.710 69 Å) and graphite monochromator. Fifteen intense reflections were precisely centered. Least-squares analysis of their 2θ values yielded the monoclinic cell constants $a = 14.278$ (1) Å, $b = 6.965$ (7) Å, $c = 21.484$ (1) Å, and $\beta = 105.29$ (1)°. Indexing and crystal quality were checked by partial rotation photographs taken about each of the three axes selected. Although at this point the empirical formula was not known, a formula weight of approximately 600 daltons per cobalt atom

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Table I. Fractional Atomic Positional Parameters[a,b]

Atom	*x*	*y*	*z*
Sn	0.40075 (2)	0.63421 (5)	0.15055 (1)
Co	−0.20964 (4)	0.71418 (8)	0.10002 (2)
S	−0.14492 (9)	0.4579 (1)	0.15854 (5)
N(1)	−0.0947 (3)	0.8781 (5)	0.1311 (1)
N(2)	−0.2606 (3)	0.8067 (5)	0.1706 (1)
N(3)	−0.1588 (3)	0.6256 (5)	0.0289 (1)
N(4)	−0.2785 (2)	0.9347 (5)	0.0457 (1)
N(5)	−0.3265 (3)	0.5574 (5)	0.0674 (1)
O(1)	−0.1690 (2)	0.2859 (4)	0.1166 (1)
O(2)	−0.1751 (2)	0.4565 (5)	0.2180 (1)
C(1)	−0.0152 (3)	0.4617 (5)	0.1833 (1)
C(2)	0.0323 (4)	0.5523 (6)	0.2397 (2)
C(3)	0.1320 (4)	0.5488 (7)	0.2599 (2)
C(4)	0.1840 (4)	0.4523 (8)	0.2245 (2)
C(5)	0.1374 (4)	0.3626 (7)	0.1672 (2)
C(6)	0.0370 (3)	0.3674 (6)	0.1460 (2)
Cl(1)	0.4615 (1)	0.7794 (2)	0.06262 (7)
Cl(2)	0.3691 (1)	0.3165 (1)	0.09256 (5)
Cl(3)	0.5706 (1)	0.5139 (1)	0.21039 (5)
Cl(4)	0.1322 (1)	0.8331 (1)	0.06064 (6)
O(41)	0.1245 (4)	1.0029 (7)	0.0254 (2)
O(42)	0.0519 (3)	0.7126 (7)	0.0348 (2)
O(43)	0.1309 (4)	0.8751 (7)	0.1240 (2)
O(44)	0.2193 (2)	0.7368 (6)	0.0581 (2)
O(00)	−0.3934 (3)	0.1524 (5)	0.1221 (1)

[a] The numbering scheme is shown in the figures. O(00) is the oxygen atom of the water molecule. [b] The estimated errors in the last digit are given in parentheses. This form is used throughout.

Table II. Rms Displacements (Å)

Atom	Min	Med	Max
Co	0.145	0.156	0.173
S	0.159	0.180	0.224
N(1)	0.15	0.19	0.22
N(2)	0.17	0.19	0.20
N(3)	0.17	0.18	0.21
N(4)	0.16	0.16	0.20
N(5)	0.17	0.18	0.20
O(1)	0.14	0.18	0.31
O(2)	0.21	0.23	0.31
C(1)	0.11	0.19	0.21
C(2)	0.17	0.19	0.24
C(3)	0.18	0.21	0.24
C(4)	0.17	0.23	0.26
C(5)	0.20	0.22	0.26
C(6)	0.18	0.19	0.20
Sn	0.191	0.203	0.233
Cl(1)	0.213	0.241	0.286
Cl(2)	0.186	0.221	0.257
Cl(3)	0.186	0.219	0.247
Cl(4)	0.187	0.207	0.237
O(41)	0.25	0.32	0.45
O(42)	0.19	0.29	0.38
O(43)	0.28	0.34	0.43
O(44)	0.18	0.27	0.31

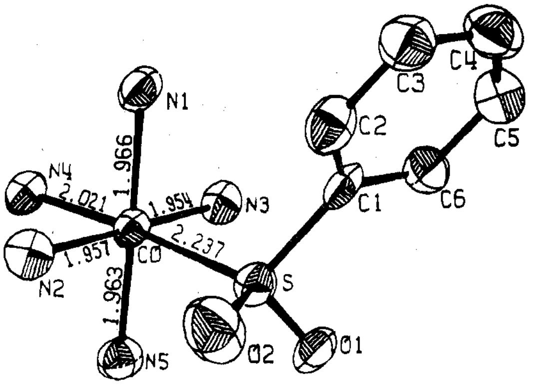

Figure 1. A perspective view of the cation $[(NH_3)_5CoS(O)_2C_6H_5]^{2+}$ with 50% probability ellipsoids. Hydrogen atoms are omitted.

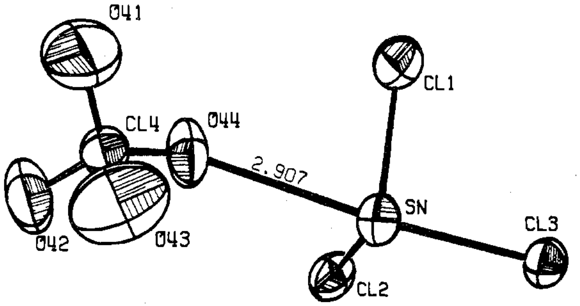

Figure 2. A perspective view of the trichloro(perchlorato)stannate(II) dianion, $[Cl_3SnOClO_3]^{2-}$.

was indicated by a preliminary analysis for % Co. From this and the measured density (1.98 (3) g cm^{-3}) it was anticipated there would be four cobalt atoms per unit cell. Using the subsequently determined formula, the calculated density is 2.02 g cm^{-3}.

A sample data set showed systematic absences for $0k0$, k odd, and for $h0l$, $h + l$ odd, indicating[13] the space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14). Within the sphere $2\theta < 47°$, 3351 reflections were measured as previously described.[1] The $\theta/2\theta$ scan ranged in 2θ values from 1.2° below Kα_1 to 1.3° above Kα_2. The scan rates were varied from 2.0 to 6.0°/min depending on the intensity of the reflection.

Four standard reflections were monitored to check crystal stability. The average of these four intensities decreased in a roughly linear fashion with time to 92.6% of the starting value by the end of data collection. We have corrected the measured intensities by assuming that this decay results from isotropic decomposition. The linear absorption coefficient for this compound is 26.7 cm^{-1} and for this crystal the maximum relative error in F_o would be less than 8%. No corrections for absorption were applied.

A set of 3054 unique, integrated intensities was obtained by averaging equivalent reflections. Of these, 2624 had $I > 2\sigma(I)$ where p, the ignorance factor,[1] was set equal to 0.04. All reflections were used in the subsequent refinement.

Structure Solution and Refinement. A Patterson map was computed[14] which indicated two heavy atoms in the asymmetric unit in contrast to the single cobalt atom expected (vide supra). Assuming both of these atoms to be cobalt, an electron density map was calculated from which coordinates for all nonhydrogen atoms were determined. This model strongly suggested the presence of tin in the crystal and the formulation determined from this electron density map was subsequently confirmed by elemental analysis. The atoms were properly identified (one tin and one cobalt atom, not the original two cobalt atoms) and all atomic positional and isotropic thermal parameters refined to give $R_1 = 0.077$ and $R_2 = 0.099$.[15] The hydrogen atoms of the benzene ring were located at their calculated positions (C–H, 0.95 Å, trigonal-planar geometry) and the ammonia hydrogen atoms were positioned with idealized geometry (N–H, 0.85 Å, tetrahedral angles). The value of the rotation angle about the Co–N bond was chosen to minimize the discrepancy between the calculated[14] hydrogen atom positions and the peak positions found in a difference electron density map. All hydrogen atoms were arbitrarily assigned an isotropic temperature[16] parameter, B, of 4.0 Å^2. Continued refinement of nonhydrogen positional and anisotropic thermal parameters with fixed hydrogen atoms led to convergence with $R_1 = 0.038$ and $R_2 = 0.045$. In the final cycle of refinement the maximum shift/error was 0.099 and the average shift/error was 0.016. The highest peaks on a final difference electron density map were near the tin and cobalt atoms and corresponded to ~0.1 the height of a carbon atom peak on the same scale. The "goodness of fit" parameter was 0.997. Scattering curves were taken from Cromer.[17] Those for H were from Stewart.[18] Anomalous dispersion corrections[19] were Sn, −0.6, 1.9; Co, 0.4, 1.1; S and Cl, 0.1, 0.2 for $\Delta f'$ and $\Delta f''$, respectively. Table A[20] lists $|F_o|$ and F_c.

Results

Final fractional atomic coordinates and their estimated standard deviations are listed in Table I. Anisotropic thermal parameters are collected in Table B and the associated root-mean-square displacements are presented in Table II. The cation and anion are shown in Figures 1 and 2, respec-

Table III. Bond Lengths (Å)

	Cation		
Co–S	2.237 (2)	S–O(2)	1.453 (4)
Co–N(1)	1.966 (4)	S–C(1)	1.787 (5)
Co–N(2)	1.957 (4)	C(1)–C(2)	1.377 (6)
Co–N(3)	1.954 (4)	C(1)–C(6)	1.395 (7)
Co–N(4)	2.020 (4)	C(2)–C(3)	1.373 (8)
Co–N(5)	1.962 (4)	C(3)–C(4)	1.371 (9)
S–O(1)	1.484 (4)	C(4)–C(5)	1.384 (7)
		C(5)–C(6)	1.386 (8)
	Anion		
Sn–Cl(1)	2.492 (2)	Cl(4)–O(41)	1.392 (5)
Sn–Cl(2)	2.521 (2)	Cl(4)–O(42)	1.410 (5)
Sn–Cl(3)	2.568 (1)	Cl(4)–O(43)	1.399 (5)
Sn–O(44)	2.907 (4)	Cl(4)–O(44)	1.426 (5)

Table IV. Bond Angles (deg)

	Metal Coordination Angles		
S–Co–N(1)	95.0 (1)	N(1)–Co–N(5)	178.1 (5)
S–Co–N(2)	90.6 (1)	N(2)–Co–N(3)	179.1 (2)
S–Co–N(3)	90.2 (1)	N(2)–Co–N(4)	88.4 (1)
S–Co–N(4)	175.3 (2)	N(2)–Co–N(5)	90.2 (1)
S–Co–N(5)	86.7 (1)	N(3)–Co–N(4)	90.8 (1)
N(1)–Co–N(2)	89.6 (1)	N(3)–Co–N(5)	90.1 (1)
N(1)–Co–N(3)	90.0 (1)	N(4)–Co–N(5)	88.7 (1)
N(1)–Co–N(4)	89.4 (1)		
	Ligand Angles		
Co–S–C(1)	113.4 (1)	S–C(1)–C(2)	120.0 (4)
Co–S–O(1)	107.9 (1)	S–C(1)–C(6)	119.4 (3)
Co–S–O(2)	108.9 (1)	C(1)–C(2)–C(3)	119.9 (5)
O(1)–S–C(1)	104.4 (2)	C(2)–C(3)–C(4)	120.0 (4)
O(2)–S–C(1)	105.2 (2)	C(3)–C(4)–C(5)	120.7 (5)
O(1)–S–O(2)	116.9 (2)	C(4)–C(5)–C(6)	119.6 (5)
		C(5)–C(6)–C(1)	119.0 (4)
	Anion Angles		
Cl(1)–Sn–Cl(2)	91.96 (7)	O(41)–Cl(4)–O(42)	110.6 (3)
Cl(1)–Sn–Cl(3)	92.29 (5)	O(41)–Cl(4)–O(43)	109.3 (3)
Cl(1)–Sn–O(44)	78.9 (1)	O(41)–Cl(4)–O(44)	108.8 (3)
Cl(2)–Sn–Cl(3)	89.05 (6)	O(42)–Cl(4)–O(43)	106.8 (3)
Cl(2)–Sn–O(44)	82.3 (1)	O(42)–Cl(4)–O(44)	109.3 (2)
Cl(3)–Sn–O(44)	167.4 (1)	O(43)–Cl(4)–O(44)	111.7 (3)
Sn–O(44)–Cl(4)	135.9 (3)		

tively. Bond lengths and angles are given in Tables III and IV. The calculated hydrogen atom positions are listed in Table C.

Description of Structure. The structure is formed by octahedral $[(NH_3)_5CoS(O)_2C_6H_5]^{2+}$ cations, discrete $[Cl_3SnOClO_3]^{2-}$ anions and water molecules linked together by rather weak hydrogen bonds (Table V). The cation geometry is very similar to that observed previously[7] for $[(NH_3)_5CoS(O_2)C_6H_4CH_3]^{2+}$. The five ammonia ligands are at nearly ideal octahedral positions. The benzenesulfinato ligand is displaced toward N(5), $\angle$S–Co–N(5) = 86.7°, and away from N(1), $\angle$S–Co–N(1) = 95.0°, in order to relieve the internal contact between N(1) and the aromatic ring.

This structure confirms that S-bonded sulfinic acids induce a structural trans effect when coordinated to cobalt(III). The average Co–N bond length cis to sulfur is 1.960 (5) Å. The trans Co–N bond length is 2.020 (4) Å, yielding a difference between trans and cis bond lengths of 0.060 (6) Å. This agrees reasonably well with the structural trans effects of 0.054 (12) Å observed[7] for $[(NH_3)_5CoS(O)_2C_6H_4CH_3]^{2+}$ and 0.049 (5) Å found[3] for $[(en)_2CoS(O)_2CH_2CH_2NH_2]^{2+}$. Thus, the best current estimate of the cobalt(III)–sulfinic acid structural trans effect for ammine ligands is 0.054 (6) Å.

The dianion $[Cl_3SnOClO_3]^{2-}$ is formed from pyamidal $SnCl_3^-$ and tetrahedral ClO_4 joined by a long bond (2.91 Å) between tin and a perchlorate oxygen atom. The average Sn–Cl bond length is 2.53 (4) Å and the average Cl–Sn–Cl angle is 91 (2)°. These values may be compared with those determined for $KSnCl_3$[21] and $CsSnCl_3$[22] where the bond lengths average 2.57 (5) and 2.52 (3) Å and the bond angles average 89 (2) and 90 (3)°. The perchlorate moiety is also quite regular with an average Cl–O distance of 1.400 (9) Å for the three terminal oxygen atoms and a marginally longer bond, 1.426 (5) Å, between chlorine and the bridging oxygen atom. The overall coordination geometry about the tin atom may be described as square pyramidal where the equational plane is formed by two chlorine atoms, the perchlorate oxygen atom and, presumably, the unshared pair of electrons on tin.

In terms of the decomposition of this material (vide infra) it is noteworthy that the two reducible sites in the cation, Co(III) and S(II), seem relatively insulated from the reducing agent, Sn(II).

Table V. Possible Hydrogen Bonds

Atoms Co–N–H···A–B	Dist, Å N···A	Angles, deg Co– N···A	 N··· A–B
N(1), H(11), O(42), Cl(4)	3.50	100	97
N(1), H(12), Cl(3),[a] Sn[a]	3.45	112	117
N(2), H(22), O(00),[b] H(01)[b]	3.07	108	112
N(2), H(23), Cl(3),[c] Sn[c]	3.43	115	108
N(3), H(31), Cl(2),[d] Sn[d]	3.45	97	106
N(3), H(32), O(44),[d] Cl(4)[d]	3.13	128	107
N(4), H(41), O(41),[e] Cl(4)[e]	3.03	95	116
N(4), H(43), O(00),[b] H(01)[b]	3.01	109	126
N(5), H(51), Cl(1),[c] Sn[c]	3.37	115	106
N(5), H(52), Cl(2),[d] Sn[d]	3.45	97	103

[a] Transformed to $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$. [b] $x, y + 1, z$. [c] $x - 1, y, z$. [d] $x, -y + 1, -z$. [e] $-x, -y + 2, -z$.

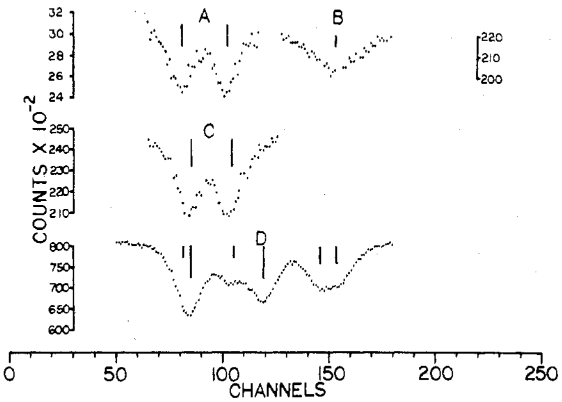

Figure 3. Mössbauer spectra of tin compounds recorded for this study: (A) $SnCl_2{\cdot}2H_2O$; (B) $BaSnO_3$; (C) $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]{\cdot}H_2O$, freshly prepared, crystalline sample; (D) green product material obtained via heating C for 10 min at 100 °C. Vertical lines give approximate peak positions. The calibrated channel spacing was 0.0591 mm s^{-1} channel^{-1}.

Discussion

$[Cl_3SnOClO_3]^{2-}$. This species is shown by its Mössbauer spectrum, presented in Figure 3, to be a well-defined tin(II) complex. The isomer shift, δ = 3.52 (2) mm/s (relative to $BaSnO_3$), and the quadrupole splitting, Δ = 1.14 (1) mm/s, are very close to those found for $SnCl_2{\cdot}H_2O$ (δ = 3.66 (2) and Δ = 1.32 (1) mm/s) which is known[23] to have a pyramidal structure with two chlorine atoms and one water molecule bound to tin. In addition, tin(II) compounds generally[24] have isomer shifts of 2.3–4.1 mm/s more positive than $BaSnO_3$. The Sn–Cl bond lengths (2.53 Å) confirm the assignment as Sn(II), since Sn(II)–Cl lengths fall in the range 2.5–2.6 Å, whereas Sn(IV)–Cl lengths are found[25] in the range 2.3–2.4 Å. The comparatively large value of Δ observed in $[Cl_3SnOClO_3]^{2-}$ indicates a large asymmetry in the electric field gradient produced by the particular arrangement of ligands about the tin atom, consistent with the structure established by x-ray methods.

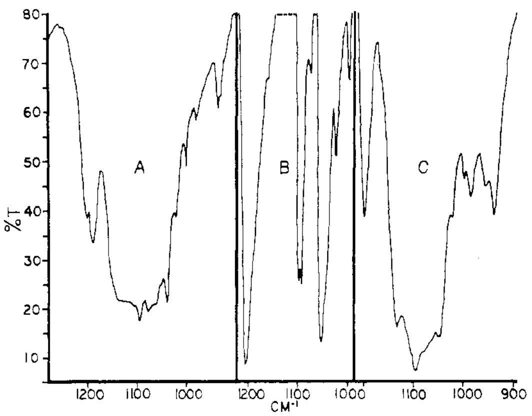

Figure 4. Infrared spectra recorded in the region 900–1250 cm^{-1}: (A) $[(NH_3)_5CoS(O)_2C_6H_5](ClO_4)_2$ showing free perchlorate; (B) $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]$, showing bound perchlorate; (C) green product material obtained via heating for 10 min at 100 °C, showing free perchlorate plus bands at 938 and 984 cm^{-1} assigned to chlorate.

Perchlorate binding to Co(III),[26] Co(II),[27,28] Ni(II),[28,29] Zn(II),[30] and Sn(IV)[31] is well established. As far as we can determine, this is the first example of perchlorate bound to Sn(II) and also the first anionic complex containing bound perchlorate. Evidence for a bonding interaction between tin and the perchlorate oxygen atom arises from both spectroscopic and structural data. The infrared spectra of $[(NH_3)_5CoS(O)_2C_6H_5](ClO_4)_2$ and $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]$ in the region 900–1250 cm^{-1} are illustrated in Figure 4. The former shows the broad band, ν_3, centered at 1100 cm^{-1} characteristic of the free perchlorate ion with T_d symmetry. The latter shows the splitting of ν_3 on coordination giving rise to a sharp band at 1053 cm^{-1} and a sharp doublet centered at 1095 cm^{-1}. Similar changes in infrared spectra on coordination of perchlorate have been discussed.[32]

The tin–oxygen distance of 2.91 Å indicates a rather weak bond between the pyramidal $SnCl_3^-$ and the perchlorate moieties in $[Cl_3SnOClO_3]^{2-}$. However, the Sn–O distance of 2.91 Å is much less than the sum (3.70 Å) of the van der Waals radii[33] of tin and oxygen. Also the tendency of Sn(II) to increase its coordination number above three by the formation of additional rather long bonds is well documented.[25] For example, in $SnCl_2$ the tin atom is surrounded by five chlorine atoms at 2.66, 2.78, 2.78, 3.06, and 3.06 Å, and in several $MF–SnF_2H_2O$ systems the tin atom is bound to four fluorine atoms. In distannous ethylenediaminetetraacetate dihydrate,[34] one tin atom is enclosed by the hexadentate ligand with the four tin–oxygen bonds ranging in length from 2.29 to 2.70 Å. The second tin atom serves to link four tin units of the first type. The tin–oxygen distances in this eight-coordinate species span from 2.15 to 3.18 Å.

Solid-State Decomposition. The decomposition of $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]$ appears complicated and probably occurs through several different paths. The products are noncrystalline and difficult to characterize. During decomposition we observe a series of color changes in the material, at least two new absorptions arising in the Mössbauer spectrum, and significant changes in the infrared spectrum.

Inspection of the crystal structure of the title compound shows one possible decomposition pathway which requires very little rearrangement. Perchlorate is a strong, though kinetically inert, oxidizing agent and Sn(II) is a relatively good reducing agent. If the perchlorate oxygen atom bridging between tin and chlorine is transferred from chlorine to tin, then the species present would be $OSn^{IV}Cl_3^-$ and $Cl^VO_3^-$. Some of the experimental results indicate that such an atom transfer may be occurring. The Mössbauer spectrum of the green product material shows a broad absorption with an isomer shift (δ = 0.15 (2) mm/s relative to $BaSnO_3$) characteristic of Sn(IV). This band seems to show a relatively small quadrupole coupling (Δ = 0.56 (2) mm/s) which is indicative of a rather small electric field gradient in the Sn(IV) product, as would be expected for an approximately tetrahedral $OSnCl_3^-$ species. The infrared spectrum of the decomposed material shows free perchlorate but also exhibits two new bands at 938 and 984 cm^{-1}. Since $KClO_3$ is known[35] to have two bands in this region at 910 and 960 cm^{-1}, it appears reasonable to conclude that some of the perchlorate is being reduced to chlorate. Such reasoning is also supported by the negative results of perchlorate tests on some decomposed samples.

Clearly other reactions must be occurring as well. The infrared spectrum of the decomposed material shows free perchlorate; the Mössbauer spectrum appears to show a new Sn(II) species with a very large quadrupole coupling[36] (δ = 3.00 (2), Δ = 2.00 (1) mm/s); and the observed color changes indicate that the cobalt complex is also involved.

Perchlorate Reduction in Solution. The existence of the $[Cl_3SnOClO_3]^{2-}$ anion and the above evidence for its decomposition to tin(IV) and chlorate are relevant to proposed mechanisms for the metal ion reduction of perchlorate in solution. Rothmund[37] first noted that the rate at which metal ions reduce perchlorate is not related to the reduction potential of the reductant. Zatko and Kratochvil[38] correlated the effectiveness of a metal ion in perchlorate reduction with the tendency of the oxidized metal to form stable metal–oxygen bonds and suggested a general mechanism involving oxygen atom transfer from perchlorate to the metal. This mechanism has received support from recent studies[39,40] showing that perchlorate must coordinate to Ru(II) before it is reduced. In the case of tin(II), it has been well established that this ion does *not* reduce perchlorate in aqueous solution unless a transition metal catalyst is present,[41,42] a lack of reactivity presumably resulting from the low stability of pechlorate–tin complexes. However, in $[Cl_3SnOClO_3]^{2-}$ facile reduction of perchlorate apparently takes place. We presume this arises from the intimate association of perchlorate and tin(II) within the complex dianion.

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Registry No. $[(NH_3)_5CoS(O)_2C_6H_5][Cl_3SnOClO_3]\cdot H_2O$, 64825-48-5; $[(NH_3)_5CoS(O)_2C_6H_5](ClO_4)_2$, 64715-10-2; $SnCl_2$, 7772-99-8; $BaSnO_3$, 12009-18-6.

Supplementary Material Available: Tables A–C giving F_o and F_c, anisotropic thermal parameters, and hydrogen positional parameters (22 pages). Ordering information is given on any current masthead page.

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Trans Effect in Octahedral Complexes. 3. Comparison of Kinetic and Structural Trans Effects Induced by Coordinated Sulfur in Sulfito- and Sulfinatopentaamminecobalt(III) Complexes[1,2]

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The synthesis and characterization of arylsulfinatopentaamminecobalt(III) complexes are described. Single-crystal x-ray structure analyses of (*p*-toluenesulfinato-*S*)pentaamminecobalt(III) perchlorate monohydrate and (sulfito-*S*)pentaamminecobalt(III) chloride monohydrate, refined to conventional *R* factors of 0.039 and 0.028, respectively, are reported. Both cobalt(III) centers are ligated by one sulfur and five nitrogen atoms in a configuration that closely approximates octahedral. The salient structural feature of both complexes is that the Co–N bond trans to sulfur is significantly longer than the average of the cis Co–N bonds in the same complex. In the sulfito complex, this sulfur-induced structural trans effect (STE) is 0.089 (3) Å. In $[(NH_3)_5CoS(O)_2C_6H_4CH_3]^{2+}$, the STE is 0.054 (12) Å. Two other sulfinato complexes have STE's of 0.049 (5) and 0.060 (6) Å, yielding 0.054 (6) Å as the best estimate of the sulfinato STE. Thus the sulfito STE is significantly larger than the sulfinato STE, Δ(STE) = 0.035 (7) Å. The rates of ligation of $[(NH_3)_5CoSO_3]^+$, $[(NH_3)_5CoS(O)_2C_6H_4CH_3]^{2+}$, and $[(NH_3)_5CoS(O)_2C_6H_5]^{2+}$ by thiocyanate, under identical conditions, as a function of $[NH_3]$, $[SCN^-]$, and temperature (*p*-toluene complex at 25 °C only) are reported. With NH_3 and SCN^- present in pseudo-first-order excess, all reactions are first-order in cobalt complex and the observed first-order rate constant k_{obsd} has the form $k_{obsd} = (a + bc[SCN^-]/[NH_3])/(1 + c[SCN^-]/[NH_3])$. This and other evidence are interpreted in terms of a limiting S_N1 mechanism governing labilized ligation at the coordination site trans to sulfur. The salient kinetic features of these reactions are that all complexes exhibit a significant kinetic trans effect (KTE); the KTE exerted by SO_3^{2-} is more than 2 orders of magnitude greater than that exerted by RSO_2^-, and this difference in KTE's resides in a significantly lower ΔH^* for the sulfito reaction (the effect of which is partially offset by a less positive ΔS^*). The lower ΔH^* for dissociation of the NH_3 trans to SO_3^{2-} is qualitatively correlated with the greater STE exerted by SO_3^{2-}. Treatment of this correlation within a simple harmonic oscillator model leads to 3.2 Å as an estimate of the distance to which a cobalt(III)–ligand bond must be stretched in order to achieve a dissociative transition state; this value is in good agreement with an independent estimate obtained from volume of activation measurements. Other interrelations between sulfur-induced KTE's and STE's are discussed.

Introduction

Experiments on a wide variety of complexes have shown that when the S-bonded sulfito ligand (SO_3^{2-}) is coordinated to cobalt(III), it exerts a marked kinetic trans effect (KTE); i.e., it labilizes the ligand situated trans to it.[1-8] Halpern and co-workers[4,5] first detailed the kinetics of ligand substitution trans to SO_3^{2-} in the $[(NH_3)_5CoSO_3]^+$ system, showing that the process occurs via a limiting S_N1 mechanism and that only one ammonia ligand is labilized. In a preliminary communication,[9] two of us have reported that the trans Co–N bond length in $[(NH_3)_5CoSO_3]^+$ is significantly greater than the average of the cis Co–N bond lengths, and thus SO_3^{2-} also induces a significant ground-state structural trans effect (STE) in this system. This observation argues strongly for the hypothesis that the KTE documented by Halpern[4] results at least partially from a ground-state weakening of the trans cobalt–ligand bond. Two recent observations have indicated that in cobalt(III) complexes the *extent* of the sulfur-induced KTE may be qualitatively correlated with the *extent* of the concomitant STE: (1) S-bonded sulfinic acids (RSO_2^-) exert a KTE in bis(dimethylglyoximato)cobalt(III) complexes which is smaller than that exerted by SO_3^{2-} in the same complexes;[1,2] (2) the S-bonded sulfinic acid in $[(en)_2Co(S(O)_2CH_2CH_2NH_2]^{2+}$ exerts an STE which is smaller than that exerted by SO_3^{2-} in $[(NH_3)_5CoSO_3]^+$.[10] In order to quantitatively correlate the STE and KTE exerted by RSO_2^- and SO_3^{2-} we have undertaken an evaluation of these effects within analogous complexes and for a variety of reasons have chosen the pentaamminecobalt(III) system for study. In this paper we report the synthesis of arylsulfinatopentaamminecobalt(III) complexes, the detailed x-ray characterization of one of these sulfinato complexes as well as of the sulfito complex which hitherto has only been briefly described,[9] a detailed comparison (including temperature dependencies) of the rates of ligation