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Synthesis of a S-Bonded Sulfinic Acid Complex of Cobalt(III) by an Oxidative Route. A Structural Trans Effect in (2-Sulfinatoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate Nitrate

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Received June 2, 1976 AIC604097

Treatment of (2-mercaptoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) with excess hydrogen peroxide provides (2-sulfinatoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) in good yield. The mixed nitrate perchlorate salt of this sulfinato product crystallizes in the acentric space group $P2_1$ with $Z = 2$ and unit cell constants $a = 8.638$ (7) Å, $b = 9.165$ (4) Å, $c = 11.128$ (5) Å, and $\beta = 110.53$ (5)°. A single-crystal x-ray structure analysis, refined to an unweighted R factor of 0.042, (1) confirms that the sulfur atom of the title complex is oxidized 4 equiv beyond the sulfur atom of the starting thiolato complex, (2) shows that the primary coordination sphere (octahedral, one sulfur and five nitrogen atoms) of the cobalt atom remains intact throughout the oxidation process, and (3) shows that the RSO_2^- group induces a ground-state trans effect of 0.049 (5) Å (average cis Co–N bond length 1.978 (3) Å; trans Co–N bond length 2.027 (4) Å). Comparisons are made between the cobalt(III) ground-state trans effect of RSO_2^-, RS^-, and SO_3^{2-}, the cobalt(III) kinetic trans effect of RSO_2^- and SO_3^{2-}, the geometries of free and coordinated RSO_2^-, and the uv-visible spectra of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$.

Introduction

Recent studies[1,2] have shown that the coordinated sulfur atoms in the cobalt(III) complexes $[(NH_3)_5CoSO_3]^+$, $[(en)_2Co(SCH_2COO)]^+$, and $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ exert a significant structural trans effect. This ground-state trans effect seems to manifest itself in rather remarkable chemical and kinetic properties.[1,3,4] To date, only ligands containing sulfur in a –II formal oxidation state (thiolato sulfur) and a +IV formal oxidation state (sulfito sulfur) have been studied with respect to determining their cobalt(III) structural trans effect. However, our interest in the various routes available for the oxidation of coordinated thiols[5-8] has led to the synthesis of cobalt(III) complexes which, on the basis of indirect evidence, we and others[9-13] have formulated as containing S-bond sulfinato and sulfenato ligands. The sulfur atoms in these complexes may be assigned formal oxidation states of +II and 0, respectively, and it is therefore of interest to determine the extent of the cobalt(III) ground-state trans effect exerted by these sulfur atoms. This paper then describes the synthesis and detailed x-ray structural characterization of the title sulfinatocobalt(III) complex.

Experimental Section

General Data. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer at ambient temperature. Infrared spectra were recorded on a Beckman Model 18A spectrophotometer. Computer calculations were performed on an IBM 370/168 located at the University of Cincinnati. Elemental analyses were performed by Galbraith Laboratories, Inc. All common laboratory chemicals were of reagent grade.

(2-Sulfinatoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) Salts, $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]X_2$, $X^- = NO_3^-$, ClO_4^-, I^-. In a typical preparation, $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ (5 g), prepared as previously described,[14,15] was slurried in distilled water (20 ml) and 6 M $HClO_4$ (50 ml) was added to the slurry. This reaction mixture was heated to 50 °C and 30% H_2O_2 (10 ml) was added slowly, the color of the solution going from brown to dark red with the addition. Upon cooling of the solution, red-brown crystals formed which were removed by filtration and air-dried. This crude product was dissolved in a minimum amount of warm (50 °C) water and then saturated aqueous $NaClO_4$ solution was added until incipient precipitation. The solution was then cooled to yield crystals which were collected, successively washed with cold water and ethanol, and then air-dried; yield of recrystallized product 60–80%. This perchlorate salt can be converted to the iodide salt by simple metathesis with sodium iodide. Anal. Calcd for $CoC_6H_{22}N_5SO_2I_2$: C, 13.32; H, 4.10; N, 12.94; S, 5.93; Co, 10.89; I, 46.90. Found: C, 13.08; H, 4.20; N, 12.83; S, 5.73; Co, 10.85; I, 46.79. Attempts to prepare the nitrate salt for x-ray analysis by analogous metathesis with ammonium nitrate led to the mixed nitrate perchlorate salt. This fact became apparent during the course of the x-ray structure determination and was confirmed by elemental analysis. Anal. Calcd for $CoC_6H_{22}N_5SO_2(NO_3)(ClO_4)$: C, 16.06; H, 4.94; N, 18.73; S, 7.15; Co, 13.13. Found: C, 16.20; H, 5.04; N, 18.61; S, 6.73; Co, 13.21.

X-Ray Characterization. The unit cell dimensions and crystal class of a crystal of the formula $[Co(en)_2(S(O)_2CH_2CH_2NH_2)](NO_3)(ClO_4)$ were determined using a Syntex $P\bar{1}$ diffractometer. Crystal quality and correctness of indexing were checked by taking oscillation photographs (±14°) about each of the crystal axes. The effective use of precession photographs was precluded by the small size of the crystal. Systematic absences were determined by collecting a limited data set of four octants (hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$) based on the previously determined unit cell constants. The only absences apparent were for $0k0$, k odd, indicating two possible space groups, $P2_1$ or $P2_1/m$.[16] Intensity statistics and an optical acentricity test[17,18] indicated the noncentrosymmetric space group $P2_1$. This choice of space group was subsequently substantiated by a successful refinement.

A rectangular prismatic crystal of the compound with dimensions 0.10 mm × 0.05 mm × 0.20 mm was mounted with its long dimension coincident with the axis of a glass fiber. This crystal was placed on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator and molybdenum target tube (Mo Kα, λ 0.71069 Å). Ten reflections were precisely centered and cell constants determined by least-squares analysis of the measured 2θ values. They are $a = 8.638$ (7) Å, $b = 9.165$ (4), Å, $c = 11.128$ (5) Å, and $\beta = 110.53$ (5)°. All measurements were made at 21 ± 3 °C. Density measurements made by neutral buoyancy in CCl_4/CH_2Br_2 ($d_{measd} = 1.82$ (3) g cm^{-3}, $d_{calcd} = 1.84$ g cm^{-3}) indicated $Z = 2$ and thus there is no required crystallographic symmetry in either the cation or the anions.

Intensity measurements for 2857 reflections in the sphere $2\theta < 59°$ were made as previously described.[2] The asymmetric θ–2θ scan was from 0.8° below to 0.9° above the reflection in 2θ. Scan rates varied from 0.5 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 0.996 to 1.046. Absorption corrections were not applied since μ, the linear absorption coefficient, is only 14.33 cm^{-1}, and the maximum relative error in the measured intensities was estimated to be less than 4%. The set of 2442 unique, normalized structure factors, of which 2092 were considered observed ($I > 2\sigma(I)$), were calculated using a value of 0.05 for p, the Ibers ignorance factor.[19]

Solution and Refinement of Structure. A Patterson map[20] was computed and the positions of the sulfur and cobalt atoms were determined. An electron density map computed using phase angles based on these two atom positions revealed the positions of the 22 remaining nonhydrogen atoms. Six cycles of least-squares refinement of the scale factor, atom positions, and isotropic thermal parameters gave $R_1 = 0.077$.[21] Three additional cycles with anisotropic thermal

Table I. Absorption Spectra of Thiolato- and Sulfinatocobalt(III) Complexes[a]

Complex	$\lambda_{max}(\epsilon)$
$[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ [b]	482 (140), 282 (14 000), 600 sh (44)
$[Co(en)_2(S(O)_2CH_2CH_2NH_2)]^{2+}$	432 (220), 288 (14,200), *c*

[a] Table entries are peak position in nm; values inside parentheses are molar extinction coefficients in M^{-1} cm^{-1}. Spectra recorded in aqueous $HClO_4$. [b] See ref 8. [c] No apparent shoulder at 600 nm; ϵ_{600} ~3 M^{-1} cm^{-1}.

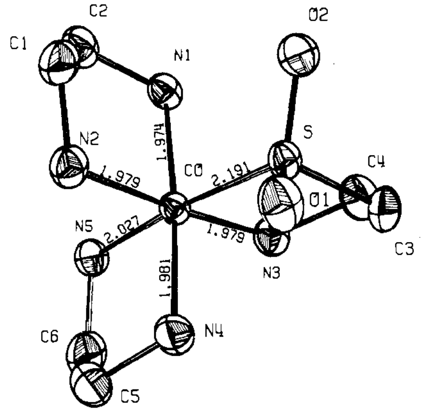

Figure 1. Structure of the complex cation of (2-sulfinatoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III), shown looking down the psuedo-threefold axis. The Δ(λλλ) isomer shown represents the absolute configuration and associated conformations found in the particular crystal studied. Hydrogen atoms have been omitted for clarity. The ellipsoids represent 50% probability. Selected bond lengths are given in Å.

parameters and fixed hydrogen atoms at their calculated positions (C–H = 0.97 Å, N–H = 0.87 Å) yielded R_1 = 0.056. However, the refined model contained widely varying Co–N bond distances, along with poor C–N and C–C distances. Based on the possibility that the incorrect optical isomer had been selected from the initial electron density maps, the coordinates of the alternate enantiomer were entered. Three cycles of least-squares full-matrix refinement using the new coordinates with anisotropic thermal parameters and fixed hydrogen atoms at calculated positions converged to R_1 = 0.042 and R_2 = 0.042. Unlike the previous case, this refined model contained highly consistent Co–N distances, and the C–C and C–N distances were well within the expected ranges. The 2442 values of F_o were used to refine 217 variables. In the last cycle of refinement the maximum shift per error was 0.03 and the average shift per error was 0.008. A final difference map was essentially featureless, the largest peak being less than 0.05 the height of a carbon peak on the same scale. Examination of groups of reflections ordered on $|F_o|$ and on $(\sin\theta)/\lambda$ revealed no significant trends in disagreement with the model. The scattering curves used were those for S, Co, O, N, C,[22] and H.[23] Corrections for anomalous dispersion[24] were made using $\Delta f'$ = 0.4 and $\Delta f''$ = 1.1 for cobalt, 0.2 and 0.2 for sulfur, and 0.1 and 0.2 for chlorine. The values of $|F_o|$ and F_c are listed in Table A.[25]

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

Atom	*x*	*y*	*z*
Co	0.120 07 (7)	−0.250 00[c]	−0.241 16 (5)
S	−0.092 9 (1)	−0.221 6 (1)	0.063 8 (1)
O(1)	−0.149 4 (5)	−0.358 1 (4)	−0.004 4 (3)
O(2)	−0.071 5 (4)	−0.099 6 (4)	−0.015 5 (3)
N(1)	0.222 8 (5)	−0.068 1 (5)	0.210 5 (4)
N(2)	0.248 6 (5)	−0.344 9 (5)	0.146 6 (4)
N(3)	−0.010 4 (5)	−0.142 9 (5)	0.327 4 (3)
N(4)	0.031 2 (6)	−0.442 5 (5)	0.265 9 (4)
N(5)	0.301 8 (5)	−0.285 2 (5)	0.412 6 (4)
C(1)	0.080 6 (6)	−0.232 4 (8)	0.080 6 (4)
C(2)	0.364 8 (6)	−0.103 7 (6)	0.169 0 (5)
C(3)	−0.245 3 (6)	−0.160 2 (6)	0.129 2 (4)
C(4)	−0.157 5 (7)	−0.060 3 (6)	0.239 4 (5)
C(5)	0.164 4 (7)	−0.522 8 (6)	0.367 5 (6)
C(6)	0.255 8 (7)	−0.415 4 (8)	0.474 5 (6)
Cl	0.389 8 (2)	−0.147 0 (2)	0.764 1 (1)
N(11)	0.737 5 (6)	−0.357 0 (5)	0.475 0 (4)
O(11)	0.659 9 (6)	−0.275 2 (5)	0.385 4 (4)
O(12)	0.664 2 (6)	−0.423 5 (6)	0.537 0 (4)
O(13)	0.889 7 (5)	−0.374 5 (5)	0.503 8 (4)
O(21)	0.231 5 (6)	−0.142 1 (8)	0.671 3 (5)
O(22)	−0.405 2 (10)	−0.033 9 (6)	0.854 1 (5)
O(23)	0.420 9 (8)	−0.284 1 (6)	0.826 8 (5)
O(24)	0.502 8 (7)	−0.121 0 (10)	0.703 5 (5)

[a] The estimated errors in the last digit are given in parentheses; this form is used throughout. [b] The numbering scheme for the cation is shown in Figure 1. The nitrate ion is composed of N(11), O(11), O(12), O(13), and the perchlorate ion of Cl, O(21), O(22), O(23), O(24). [c] The *y* value of the cobalt atom coordinate was used to define the origin along the polar axis and thus has no error associated with it.

Table III. Rms Displacements (Å)

Atom	Min	Mean	Max
Co	0.128	0.140	0.162
S	0.128	0.157	0.170
O(1)	0.156	0.189	0.241
O(2)	0.147	0.189	0.231
N(1)	0.146	0.155	0.193
N(2)	0.155	0.178	0.191
N(3)	0.151	0.187	0.192
N(4)	0.153	0.165	0.218
N(5)	0.144	0.182	0.196
C(1)	0.160	0.192	0.235
C(2)	0.150	0.173	0.244
C(3)	0.139	0.198	0.203
C(4)	0.178	0.196	0.221
C(5)	0.169	0.193	0.273
C(6)	0.165	0.211	0.273
Cl	0.180	0.212	0.218
N(11)	0.163	0.177	0.212
O(11)	0.193	0.252	0.280
O(12)	0.211	0.244	0.281
O(13)	0.161	0.237	0.307
O(21)	0.184	0.319	0.346
O(22)	0.230	0.282	0.393
O(23)	0.214	0.279	0.365
O(24)	0.272	0:319	0.413

Results

Characterization of Title Complex. The $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ ion is characterized by (1) elemental analyses of the isolated salts which give empirical compositions in agreement with those predicted from the proposed formulation (see Experimental Section), (2) its cation-exchange elution characteristics which are consistent with the assigned formal charge, (3) its visible–uv absorption spectrum (see Table I) which exhibits d–d bands characteristic of cobalt(III) complexes as well as an intense ligand-to-metal charge transfer (LTMCT) band characteristically arising from coordination of sulfur to a potentially oxidizing center,[26] and (4) its infrared spectrum which exhibits bands characteristic of coordinated sulfinic acids.[27] In regard to this final point, bands at 1220 and 1080 cm^{-1} in the infrared spectrum of $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ salts are not present in the parent thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and, following Vitzthum and Lindner,[27] are assigned as $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, respectively.

Description of Crystal Structure

Atomic positional parameters and their estimated standard deviations for the nonhydrogen atoms as obtained in the last cycle of least-squares refinement are given in Table II, the root-mean-square displacements for these atoms are presented in Table III, and the associated ellipsoids for the cationic complex are shown in Figure 1. Nonhydrogen atom bond lengths and bond angles are given in Tables IV and V, while

Table IV. Bond Lengths (Å)

Co–S	2.191 (2)	Co–N(3)	1.979 (5)
Co–N(1)	1.974 (5)	Co–N(4)	1.981 (5)
Co–N(2)	1.979 (5)	Co–N(5)	2.027 (4)
S–O(1)	1.456 (4)	N(1)–C(2)	1.490 (8)
S–O(2)	1.476 (4)	N(2)–C(1)	1.479 (8)
S–C(3)	1.803 (6)	N(3)–C(4)	1.509 (6)
		N(4)–C(5)	1.494 (7)
C(1)–C(2)	1.501 (8)	N(5)–C(6)	1.499 (9)
C(3)–C(4)	1.505 (7)		
C(5)–C(6)	1.534 (8)	Cl–O(21)	1.396 (5)
		Cl–O(22)	1.416 (6)
N(11)–O(11)	1.241 (6)	Cl–O(23)	1.417 (5)
N(11)–O(12)	1.246 (7)	Cl–O(24)	1.388 (7)
N(11)–O(13)	1.250 (6)		

Table V. Bond Angles (deg)

	Metal Coordination Angles		
S–Co–N(1)	91.8 (1)	N(1)–Co–N(3)	91.8 (2)
S–Co–N(2)	91.4 (1)	N(1)–Co–N(5)	92.9 (2)
S–Co–N(3)	86.4 (1)	N(2)–Co–N(4)	89.9 (2)
S–Co–N(4)	89.3 (1)	N(2)–Co–N(5)	92.1 (2)
S–Co–N(5)	174.4 (2)	N(3)–Co–N(4)	93.5 (2)
N(1)–Co–N(4)	174.7 (2)	N(3)–Co–N(5)	90.4 (2)
N(2)–Co–N(3)	175.9 (2)	N(4)–Co–N(5)	86.4 (2)
N(1)–Co–N(2)	84.8 (2)		
	Intraligand Angles		
Co–S–O(1)	112.9 (2)	Co–N(1)–C(2)	109.7 (3)
Co–S–O(2)	112.8 (2)	N(1)–C(2)–C(1)	106.3 (4)
Co–S–C(3)	100.1 (2)	C(2)–C(1)–N(2)	107.7 (4)
O(1)–S–O(2)	115.4 (2)	C(1)–N(2)–Co	109.4 (4)
S–C(3)–C(4)	106.7 (4)	Co–N(4)–C(5)	108.1 (3)
C(3)–C(4)–N(3)	107.1 (4)	N(4)–C(5)–C(6)	108.8 (5)
C(4)–N(3)–Co	115.3 (3)	C(5)–C(6)–N(5)	107.6 (5)
		C(6)–N(5)–Co	108.4 (3)
	Perchlorate Angles		
O(21)–Cl–O(22)	108.9 (4)	O(22)–Cl–O(23)	110.3 (3)
O(21)–Cl–O(23)	111.1 (4)	O(22)–Cl–O(24)	108.1 (5)
O(21)–Cl–O(24)	108.0 (3)	O(23)–Cl–O(24)	110.3 (5)
	Nitrate Angles		
O(11)–N(11)–O(12)	120.3 (5)	O(12)–N(11)–O(13)	119.2 (4)
O(11)–N(11)–O(13)	120.5 (5)		

hydrogen bond angles and distances are listed in Table VI. Anisotropic thermal parameters for nonhydrogen atoms are given in Table B.[25]

In this structure the cationic species is an octahedrally coordinated cobalt(III) ion; four of the coordination sites are occupied by nitrogen atoms of the two ethylenediamine chelates and the remaining two sites are occupied by the nitrogen and sulfur atoms of the 2-sulfinatoethylamine ligand. The primary cobalt(III) coordination sphere therefore remains intact during oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to the title complex. A ground-state structural trans effect is clearly apparent upon comparing the trans Co–N bond distance of 2.027 (4) Å (N(5), trans to S) with the average cis Co–N bond distance of 1.978 (3) Å;[28] the difference between cis and trans distances is 0.049 (5) Å. The nitrate anion forms hydrogen bonds with the amine hydrogen atoms of two adjacent complex cations. The perchlorate anion is held in position primarily by van der Waals interactions. Additional hydrogen bonding is found between one of the sulfinato oxygens (O(2)) and the amine hydrogens of an adjacent cation.

The particular acentric crystal subjected to x-ray analysis contained only one of the possible enantiomers, i.e., the cation of the Δ(λλλ) configuration. The selection of this crystal was arbitrary and presumably there are equal amounts of both enantiomers in the total product mixture.

Discussion

Preparation and Properties of the Title Complex. The oxidation of a coordinated thiol to an S-bonded sulfinic acid was first realized by Schubert,[11] who treated tris(cysteine)cobaltate(III) with H_2O_2 to give the S-bonded tris(cysteinesulfinato)cobaltate(III) complex which has been used extensively by Gillard[12,13] in the resolution of optical isomers. In an analogous manner, Sloan and Krueger[9] have used H_2O_2 to oxidize coordinated cysteine to the corresponding coordinated sulfinic acid, and we have oxidized $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ (see Experimental Section). This reaction involves a net 4-equiv oxidation of the coordinated sulfur. By careful regulation of the reaction conditions it is also possible to limit the oxidation process to 2 equiv thereby forming a coordinated sulfenic acid.[9,10] We are currently investigating the course, and product, of this 2-equiv oxidation. It appears that oxidation of coordinated thiols provides a feasible and general synthetic route to complexes containing coordinated sulfur in higher formal oxidation states.[7,8]

The visible–uv spectral parameters for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)_2CH_2CH_2NH_2]^{2+}$ are presented in Table I. The nearly identical positions of the uv LTMCT bands indicate that in this system RSO_2^- is as effective a reductant as RS^-, which in turn implies that for both complexes the electron being transferred is one involved in the Co–S σ bond (i.e., a $\sigma_L \rightarrow \sigma_M^*(e_g)$ LTMCT process[29]). The relative positions of the visible d–d absorption bands indicate that in this system coordinated RSO_2^- provides a stronger ligand field than coordinated RS^-. This interpretation is supported by the fact that the 600-nm shoulder of the RS^- complex is not present in the RSO_2^- analogue. Presumably the asymmetric field provided by the five nitrogen atoms and the weak-field thiolato sulfur atom causes splitting of the $^1T_{1g}$ excited state and two transitions are observed; the five nitrogen atoms and the stronger ligand field sulfinato sulfur atom provide a more symmetric field and thus the splitting of the $^1T_{1g}$ state is less and only one band is observed.[30]

The presence of two additional bands at 1220 and 1080 cm^{-1} in the infrared spectrum of $[(en)_2Co(S(O)_2(CH_2CH_2NH_2)]I_2$ relative to that of $[(en)_2Co(SCH_2CH_2NH_2)]I_2$ indicates that they arise from sulfur–oxygen vibrations. These bands are assigned as $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ respectively.[27] The shift of these bands to higher frequencies, relative to their positions in the unbound sulfinate anion, confirms that sulfur–oxygen band positions may be used to indicate whether a coordinated sulfinic acid is S bound or O bound.[27] It has been claimed

Table VI. Possible Hydrogen Bonds

	Distances, Å		Angles, deg		Distances out of NO_3 plane, Å	
N-H···O-X (X = S, N)	N···O	H···O	O···H-N	X-O···H	H	N
N(2)[a]-H(24)[a]-O(2)-S(1)	2.89	2.05	162	139		
N(4)[a]-H(44)[a]-O(2)-S(1)	3.26	2.48	150	154		
N(5)-H(54)-O(11)-N(11)	3.21	2.38	161	98	0.04	0.30
N(1)-H(13)-O(12)[b]-N(11)[b]	2.95	2.08	171	134	1.29	0.47
N(3)-H(33)-O(13)[c]-N(11)[c]	3.21	2.33	175	103	0.75	0.87
N(3)-H(34)-O(13)[b]-N(11)[b]	3.21	2.24	153	104	1.64	0.87

[a] Transformed to $-x, 1/2 + y, 1 - z$. [b] Transformed to $1 - x, 1/2 + y, 1 - z$. [c] Transformed to $-1 + x, y, z$.

that the difference between the two sulfur–oxygen bands, $\Delta\nu = \nu_{as} - \nu_s$, depends on the O–S–O bond angle.[27] However, $\Delta\nu$ for the unbound sulfinate anion, wherein the O–S–O angle is assumed to be 120°, is 223 cm^{-1}, and in the title complex, where the O–S–O angle is only 5° less, $\Delta\nu$ is 140 cm^{-1}. Thus it appears that the correlation proposed by Vizthum and Lindner[27] between $\Delta\nu$ and the O–S–O angle does not hold.

The title complex is expected to exist in both Δ and Λ enantiomeric forms and therefore we did not anticipate the isolation of crystals containing only one form. The intensity statistics for the x-ray data indicate, and the optical acentricity test[17,18] conclusively demonstrates, the presence of an acentric space group containing only one enantiomer. Interestingly, a test for piezoelectricity failed to show any effect.

Structural Characteristics. In $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ the Co–N distances cis to the sulfur atom are normal, averaging 1.978 (5) Å which is in the range of Co–N distances previously tabulated[2] where N is part of an ethylenediamine ligand. The Co–N distance for the group trans to the sulfur atom is 2.027 (4) Å, yielding a ground-state trans lengthening of 0.049 (5) Å. The Co–S bond length of 2.191 (2) Å is noticeably shorter than that found[2] in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (2.226 (2) Å), in accord with the previously noted greater ligand field strength of RSO_2^- over RS^-, and comes closest to that found[1] in $[(NH_3)_5CoSO_3]^+$ (2.218 (2) Å). The S–C distance of 1.803 (6) Å is essentially the same as that found[2] in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (1.818 (8) Å).

Kierkegaard[31] has studied the effect of metal–sulfur bonding on the S–O distances and O–S–O angles in SO_3^- and we find analogous effects induced upon coordination of RSO_2^-. According to Kierkegaard, as based on arguments of Cruickshank,[32] bonding of the SO_3^{2-} sulfur lone pair will serve to strengthen and shorten the S–O bond by increasing the π-bond order. Typically, in going from free Na_2SO_3[33] to coordinated sulfite in compounds such as $[(en)_2Co(NCS)(SO_3)]\cdot 2H_2O$[34] and $[(NH_3)_5CoSO_3]Cl\cdot H_2O$,[1] the S–O distance decreases from an average value of 1.504 (3) Å to average values of 1.485 (13) and 1.483 (7) Å, respectively. At the same time the average O–S–O angle opens from 105.7 (2) to 110.3 (8) and 109.8 (1)°, respectively. If anything, this behavior appears to be even more pronounced for RSO_2^-. The average S–O distance in free sodium hydroxymethanesulfinate dihydrate[35] is 1.513 (6) Å while that found in the title compound is 1.466 (14) Å. Likewise, the O–S–O angle opens from 108.7 (5) to 115.4 (2)°.

The remaining ligand bond lengths and angles, reported in Tables IV and V, are as expected. The perchlorate anion is well behaved in that none of the thermal parameters are excessively large.

Hydrogen Bonding. The possible hydrogen bonds which are formed between coordinated amine hydrogen atoms and the oxygen atoms of the nitrate anions may be examined to see if they satisfy various[36] criteria: (1) short N···O distance (less than 3.1 Å), (2) short H···O distance (less than 2.6 Å), (3) linear N–H···O array, (4) coplanarity of the N–H fragment with the nitrate ion, (5) H···O–N angle near 120°. In examining Table VI it is clear that there is a paucity of strong hydrogen bonds in this structure. Each of the nitrate oxygens (O(11), O(12), O(13)) is involved in hydrogen bonding, but none satisfy all of the criteria above. One of the sulfinato oxygens (O(2)) forms a hydrogen bond with an amine hydrogen atom on an adjacent cation, which may be reflected in the fact that the S–O(2) distance (1.476 (4) Å) is longer than the S–O(1) distance (1.456 (4) Å).

In this complex the gauche conformation of each of the three ligands makes possible eight different isomers, $\Delta(\lambda\lambda\lambda)$, $\Delta(\lambda\lambda\delta)$, $\Delta(\lambda\delta\delta)$, $\Delta(\delta\delta\delta)$, and their four enantiomers. The $\Delta(\lambda\lambda\lambda)$ configuration of $[(en)_2Co(SO_2CH_2CH_2NH_2)]^{2+}$ is the same as that calculated for the most stable structure[37] of $[Co(en)_3]^{3+}$ and has been found[2] in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The small amount of hydrogen bonding and the different packing considerations resulting from the presence of the sulfinato group and the mixed anions are evidently not sufficient to warrant the existence of a different conformation.

Trans Effect. The sulfinato ligand of the title complex exerts a significant structural trans effect (0.049 (5) Å). This lengthening is only marginally greater than that found[2] in the analogous thiolato complex (0.040 (6) Å) and is much less than that associated with the sulfito ligand in $[(NH_3)_5CoSO_3]^+$ (0.089 (4) Å). The change in the formal oxidation state of sulfur from –II in the thiolato ligand to +II in the sulfinato ligand appears to have little influence on the magnitude of the trans effects exerted by these ligands, and therefore it is unlikely that the larger trans effect exerted by SO_3^{2-} is due to the +IV oxidation state of the coordinated sulfur. It may be that a more important factor is the increase in the net formal negative charge of the ligand on going from RS^- and RSO_2^- to SO_3^{2-}. The increased formal negative charge on SO_3^{2-} should enhance its σ-donating properties and it is generally accepted[38] that in d^6 octahedral complexes the σ-donating ability of ligands is a principal factor controlling the extent of the associated ground-state trans effect.

It is interesting to note that just as S-bonded SO_3^{2-} and RSO_2^- exert ground-state trans effects in cobalt(III) complexes, they also exert kinetic trans effects (i.e., labilization of the trans-situated ligand) in cobalt(III) complexes.[38,39] Also, just as in the ground-state trans effect, the kinetic effect exerted by SO_3^{2-} is larger than that exerted by RSO_2.[39,40] Thus, it appears, from the limited data currently available, that kinetic trans effects are related to ground-state trans effects, and it is not unreasonable to hypothesize that the ground-state weakening of the trans ligand–metal bond is in part responsible for the increased rate of trans ligand–metal bond fission.[1,39] Further experiments designed to probe the relationship between ground-state and kinetic trans effects are currently in progress.

Acknowledgment. Financial support by the National Science Foundation, Grant No. MPS74-01540-A01, and the Research Council of the University of Cincinnati is gratefully acknowledged. We thank J.G.B. for performing the acentricity tests.

Registry No. $[(en)_2Co(S(O)_2CH_2CH_2NH_2)](NO_3)(ClO_4)$, 60562-82-5; $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]I_2$, 60537-76-0; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5.

Supplementary Material Available: Tables A and B listing structure factor amplitudes and anisotropic thermal parameters for nonhydrogen atoms (18 pages). Ordering information is given on any current masthead page.

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Structural Chemistry of the {CoNO}^{8} Group. Structure of *trans*-Perchloratonitrosylbis(ethylenediamine)cobalt Perchlorate, $[Co(NO)(C_2N_2H_8)_2(OClO_3)][ClO_4]$.[1]

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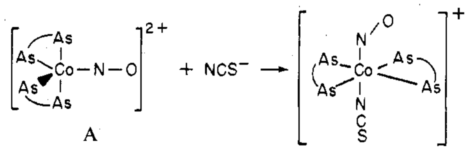
Received June 10, 1975 AIC50408Z

The crystal and molecular structure of $Co(NO)(en)_2(ClO_4)_2$ (en is ethylenediamine) has been determined by single-crystal x-ray diffraction. The compound crystallizes in space group C_{2h}^5-$P2_1/c$ with 4 molecules in a cell of dimensions $a = 7.831$ (3) Å, $b = 15.996$ (6) Å, $c = 12.429$ (4) Å, and $\cos\beta = -0.3949$ (3). The observed and calculated densities are 1.91 and 1.89 g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure using the 1437 data with $F_o^2 \geq 3\sigma(F_o^2)$ gave $R_1 = 3.2\%$. The structure consists of *trans*-$[Co(NO)(en)_2(OClO_3)]^+$ cations and perchlorate anions. The Co–NO distance is 1.806 (6) Å. The CoNO group is strongly bent and the oxygen atom is disordered between two positions above the en rings. The refined Co–N–O angles are 135 (1) and 141 (2)°. An alternative description of the disorder with N–O distances fixed at 1.15 Å gave Co–N–O angles of 122 and 123°. The Co–O distance of the coordinated perchlorate ion is 2.360 (4) Å. Both perchlorate ions in the structure are ordered and involved in an extensive hydrogen-bonding network.

Introduction

In recent years there has been considerable interest in the structural, chemical, and electronic properties of complexes of the {CoNO}^{8} group.[2] This interest stems in part from the ability of this group to form five-coordinate complexes with a range of Co–N–O angles and coordination geometries as well as six-coordinate complexes with a strongly bent Co–N–O moiety.[3] In spite of the demonstrated existence of two different coordination numbers for {CoNO}^{8} complexes there is to our knowledge only one well-characterized example[5] of the conversion of a five-coordinate complex containing the {CoNO}^{8} group into a six-coordinate complex by the addition of a unidentate ligand. We have previously demonstrated that reaction 1 results in the conversion of the trigonal-bipyramidal five-coordinate $[Co(NO)(das)_2]^{2+}$ cation[6] A which has a linearly coordinated NO group in the equatorial position into the six-coordinate complex B with a strongly bent CoNO group. The transformation of A into B results in a large decrease in the NO stretching frequency and in the N 1s binding energy as shown. The chemical reactivities of the coordinated NO group of A and B differ dramatically.



(1)

A

ν_{NO} 1852 cm^{-1}
Co–N–O = 178°
$E_B(N_{1s})$ = 402.3 eV

B

ν_{NO} 1567 cm^{-1}
Co–N–O = 132°
$E_B(N_{1s})$ = 399.1 eV

In order to better understand the scope of reaction 1 and to further explore the behavior of the {CoNO}^{8} group other examples of five- and six-coordinate {CoNO}^{8} complexes related by a simple ligand addition reaction have been sought. Another potential pair of five- and six-coordinate {CoNO}^{8} complexes[7] are $Co(NO)(en)_2(ClO_4)_2$ (C) and $[Co(NO)(en)_2Cl][ClO_4]$ (D). A structure determination of D[8] has already shown it to contain the six-coordinate $[Co(NO)(en)_2Cl]^+$ cation with Co–N–O = 124°. From the similarity of the NO stretching frequencies of C and D (1668 and 1611 cm^{-1}, respectively), it seemed likely that their {CoNO}^{8} groups were similar. On the other hand, the difference in their colors suggested that their overall structures might differ significantly. In view of the weak coordinating ability of the ClO_4^- ion it seemed plausible that C might possess five-coordinate tetragonal-pyramidal coordination geometry with a strongly bent CoNO group. The stereochemistry of C is of further interest because it is an intermediate in a convenient synthesis[9] of