

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

Characterization of (Thiooxalato-*O,S*)bis(ethylenediamine)cobalt(III) and Comparison to the Oxalato-*O,O* and Dithiooxalato-*S,S* Analogues. Single-Crystal Structural Analysis of $[(en)_2Co(SC(O)COO)]_2(S_2O_6) \cdot 2H_2O$

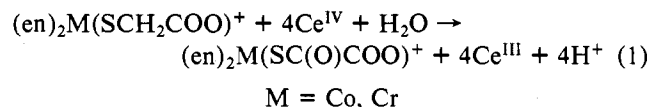
J. D. LYDON, KEVIN J. MULLIGAN, R. C. ELDER, and EDWARD DEUTSCH*

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The title complex, $[(en)_2Co(SC(O)COO)]^+$, is prepared both by oxidation of $[(en)_2Co(SCH_2COO)]^+$ and by substitution of monothiooxalate onto $[(en)_2CoCl_2]^+$. The (oxalato-*O,O*)-, (thiooxalato-*O,S*)- and (dithiooxalato-*S,S*)bis(ethylenediamine)cobalt(III) series is examined, and their visible-UV, IR, and NMR spectral parameters are compared. Single-crystal X-ray structural analysis of $[(en)_2Co(SC(O)COO)]_2(S_2O_6) \cdot 2H_2O$, refined to a conventional *R* factor of 0.048 is reported. The complex is shown to be octahedral, oxidation of the parent thiolato complex occurring at the α -carbon without loss of Co-S coordination. The sulfur-induced trans effect is smaller for the thiooxalato complex than for the precursor thiolato complex (0.005 (8) vs. 0.043 (5) Å); this difference is discussed in terms of a qualitative structural trans-effect series.

Introduction

Several years ago^{1,2} we reported that oxidation of $[(en)_2M(SCH_2COO)]^+$, *M* = Co and Cr, by 1-equiv oxidants led to net oxidation at the carbon atom adjacent to sulfur, rather than to the expected net oxidation at sulfur itself. On the basis of indirect evidence, the oxidation product was identified as a complex containing *O,S*-chelated thiooxalate: e.g.



Since that time we have observed that this complex (*M* = Co) is a major product of many reactions involving oxidation of $[(en)_2Co(SCH_2COO)]^+$ and therefore thought it worthwhile to definitely establish its identity by single-crystal X-ray structural analysis. Moreover, the results of this analysis would allow us to determine the position of the *S*-bonded thio acid moiety in the structural trans-effect series that has been established for sulfur ligands coordinated to cobalt(III).^{3,4}

In this paper we report the preparation and characterization of $[(en)_2Co(SC(O)COO)]^+$ and discuss the properties of this thiooxalato complex in relation to those of the analogous oxalato and dithiooxalato complexes, $[(en)_2Co(OOCCOO)]^+$ and $[(en)_2Co(SC(O)C(O)S)]^+$.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. Dowex 50W-X2 (200-400 mesh) cation-exchange resin was cleaned as previously described;⁵ Sephadex SP-C25 (sodium form) cation exchanger was generated and stored as recommended by the manufacturer (Pharmacia). (Mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate was prepared by a literature procedure;⁶ the chloride salt of this complex was available from a previous study.³ *cis*-Dichlorobis(ethylenediamine)cobalt(III) chloride,⁷ (oxalato)bis(ethylenediamine)cobalt(III) chloride,⁸ (glycolato)bis(ethylenediamine)cobalt(III) chloride,⁹ and (dithiooxalato-*S,S*)bis(ethylenediamine)cobalt(III) chloride¹⁰ were prepared by literature methods. Potassium dithiooxalate (Eastman) was recrystallized from water before use. Potassium thiooxalate and *N*-(phenylthio)phthalimide

were prepared by literature procedures.^{11,12}

(Thiooxalato-*O,S*)bis(ethylenediamine)cobalt(III) Salts. $[(en)_2Co(SC(O)COO)]X$, *X* = ClO₄, Cl, (S₂O₆)_{1/2}. This complex can be prepared by both redox and substitution routes. The most efficacious redox procedure is oxidation of (mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate by *N*-chlorosuccinimide in *N,N*-dimethylformamide. In a typical preparation 0.5 g of $[(en)_2Co(SCH_2COO)]ClO_4$ was dissolved in 250 mL of DMF; 0.20 mL of glacial acetic acid and then 0.362 g of *N*-chlorosuccinimide were added with stirring (mole ratio of oxidant/cobalt = 2.0). After ca. 5 min, enough excess diethyl ether was added with vigorous stirring to cause the product to separate as an oil. The resulting mixture was cooled at ca. 0 °C, and the desired product layer was separated by decantation and then redissolved in 0.01 M aqueous HCl. This solution was sorbed onto a column (2.5 cm i.d. × 20.0 cm) of Sephadex SP-C25 cation exchanger and 0.10 M aqueous NH₄Cl (pH ca. 2) passed through the column until a clear separation of products was obtained. The product with the smallest *R_f* value is the desired material. This product was removed from the column by eluting with 0.20 M aqueous NH₄Cl (pH ca. 2); the eluant was then reduced in volume by rotoevaporation and cooled to yield crystals of the product chloride salt. The yield was ca. 30%. The substitution procedure is similar to that used for the preparation of (dithiooxalato-*S,S*)bis(ethylenediamine)cobalt(III) chloride.¹⁰ In a typical preparation 5.4 g of *cis*- $[(en)_2CoCl_2]Cl$ was dissolved in 35 mL of water at ca. 60 °C and then 3.3 g of potassium thiooxalate added. The resulting mixture was stirred at ca. 60 °C for 10 min, acidified with concentrated HCl to ca. pH 2, and then filtered through a medium-porosity glass frit while still warm. Subsequent cooling to ca. 5 °C yielded small red crystals of the chloride salt which was then recrystallized from warm water at pH ca. 2. The homogeneity of this product was confirmed by ion-exchange chromatography on Sephadex SP-C25; this procedure readily separates the oxalato, thiooxalato, and dithiooxalato complexes. Anal. Calcd for $[(en)_2Co(SC(O)COO)]Cl \cdot H_2O$: C, 21.41; H, 5.35; N, 16.64; S, 9.53; Cl, 10.53; Co, 17.51. Found: C, 21.40; H, 5.65; N, 16.58; S, 8.95; Cl, 10.48; Co, 17.17. Visible-UV and IR spectrophotometric parameters are reported in Tables I and II, respectively. The perchlorate and dithionate salts are much less soluble than the chloride salt and may be prepared in high purity from the chloride salt by simple metathesis by using aqueous NaClO₄ or Na₂S₂O₆ solutions at pH ca. 2. Crystals of the dithionate salt suitable for single-crystal X-ray diffraction were grown by slowly cooling a solution of the chloride salt and Na₂S₂O₆ from 25 to ca. 5 °C at pH ca. 2.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Total cobalt analyses were performed by using a modified Kitson procedure.^{13,14}

Equipment. Visible-UV and infrared spectra were recorded respectively on Cary 14 and Beckman IR-18A spectrophotometers at ambient temperature. X-ray data were collected with a Syntex P1 diffractometer, equipped with a graphite monochromator and mo-

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Table I. Visible-UV Spectrophotometric Parameters for $[(en)_2Co(SC(O)COO)]^+$, $[(en)_2Co(SC(O)C(O)S)]^+$, $[(en)_2Co(OOCCOO)]^+$, and Related Complexes^a

complex	λ_{max} (ϵ)		
$[(en)_2Co(OOCCOO)-O,O]^+$	500 (112)	356 (144)	
$[(en)_2Co(SC(O)COO)-O,S]^+$	512 (156)		273 (15 600) 215 (16 100)
$[(en)_2Co(SC(O)C(O)S)-S,S]^+$	508 (224)	373 (1340)	278 (16 400) 250 (18 500)
$[(en)_2Co(SCH_2COO)-O,S]^+ b$	518 (152)		282 (10 900)
$[(en)_2Co(SCH(CH_3)COO)-O,S]^+ b$	515 (149)		280 (12 600)
$[(en)_2Co(SC(CH_3)_2COO)-O,S]^+ b$	514 (153)		282 (10 900)
$[(en)_2Co(S(O)CH_2COO)-O,S]^+ b$	493 (350)	360 (6000)	285 (3100)
$[(en)_2Co(S(O)_2CH_2COO)-O,S]^+ b$	448 (435)		294 (10 200)

^a Wavelengths, λ , are in nm. Molar extinction coefficients, ϵ , given in parentheses, are in $M^{-1} cm^{-1}$. Spectra are recorded in dilute aqueous perchloric acid. ^b Data from ref 26.

Table II. Infrared Carbonyl Stretching Frequencies (cm^{-1}) for $[(en)_2Co(OOCCOO)]^+$, $[(en)_2Co(SC(O)COO)]^+$, $[(en)_2Co(SC(O)C(O)S)]^+$, and Related Complexesⁱ

Thioglycolato- <i>O,S</i> Complexes				
	ν_{asCO}	ν_{sCO}		
$[(en)_2Co(SCH_2COO)]Cl^a$	1590	1340		
$[(en)_2Cr(SCH_2COO)]Cl^{b,h}$	1560	1340		
Oxalato- <i>O,O</i> Complexes				
	ν_{asCO}		$\nu_{CC} + \nu_{sCO}$	$\delta_{COO} + \nu_{sCO}$
$[(en)_2Co(OOCCOO)]Cl^a$	1694	1676	1405	1270
$[(NH_3)_4Co(OOCCOO)]Cl^c$	1705	1663	1395	1260
$[(NH_3)_4Cr(OOCCOO)]Cl^e$	1704	1668	1398	1258
$[(trien)Co(OOCCOO)]I^d$	1700	1678/58	1400	1262
$K_3[Co(OOCCOO)_3]^e$	1707	1670	1398	1254
$K_3[Cr(OOCCOO)_3]^e$	1708	1684/60	1387	1253
Thiooxalato- <i>O,S</i> Complexes				
	ν_{asCO}		$\nu_{CC} + \nu_{sCO}$	ν_{CS}
$[(en)_2Co(SC(O)COO)Cl]^a$	1660	1625	1340	1015
$[(en)_2Cr(SC(O)COO)Cl]^b$	1670	1630	1340	1020
$(BzPh_3P)_3[Co(SC(O)COO)_3]^f$	1632	1578	1332	1011
$(BzPh_3P)_3[Cr(SC(O)COO)_3]^f$	1640	1583	1320	1005
Dithiooxalato- <i>S,S</i> Complexes				
	ν_{asCO}	$\nu_{CC} + \nu_{CS}$		
$[(en)_2Co(SC(O)C(O)S)]Cl^a$	1569	(1055)		
$[(PPH_3)_4Ag_3][Co(SC(O)C(O)S)_3]^g$	1583/27	1045		
$K(Me_3PhN)_2[Cr(SC(O)C(O)S)_3]^g$	1570	1050		

^a This work. ^b References 2 and 36. ^c Reference 27. ^d Reference 28. ^e Reference 29. ^f Reference 11. ^g Reference 30. ^h Assignments were made without the aid of deuterated complexes. ⁱ ν_s = symmetric; ν_{as} = asymmetric.

lybdenum target tube (Mo $K\alpha$, $\lambda = 0.71069 \text{ \AA}$), at ambient temperature. Computer calculations were performed on an AMDAHL 470/V6 located at the University of Cincinnati. ¹H NMR spectra were obtained on a Varian T-60 instrument.

Procedures. Formal charges on complexes were inferred from elution characteristics on Dowex 50W-X2 (200–400 mesh, H^+ or Na^+ form) and Sephadex SP-C25 (Na^+ form) ion-exchange columns. IR spectra were recorded in KBr pellets. Partial deuteration of the thiooxalato and dithiooxalato complexes was achieved by repeated recrystallization from neutral D_2O . The purity of the deuterated products was confirmed by visible-UV spectrophotometry.

X-ray Characterization of $[(en)_2Co(SC(O)COO)]_2(S_2O_8) \cdot 2H_2O$. Preliminary precession photographs of the $hk0$, hkl , $0kl$, and $1kl$ layers using Cu $K\alpha$ radiation indicated no symmetry higher than triclinic. A crimson crystal in the form of a parallelepiped, of approximate dimensions $0.29 \times 0.29 \times 0.10 \text{ mm}$, was mounted on the diffractometer, and our usual procedures³ were followed to check the crystal quality (three axial-rotation photographs and mosaic-scan measurements), determine unit cell constants (12 pairs of reflections), and measure intensities. The crystal is of the primitive triclinic class with the reduced cell parameters $a = 7.244(4) \text{ \AA}$, $b = 8.321(5) \text{ \AA}$,

Table III. ¹H NMR Spectral Parameters for (Oxalato-*O,O*), (Thiooxalato-*O,S*), (Dithiooxalato-*S,S*), and (Thioglycolato-*O,S*)bis(ethylenediamine)cobalt(III) Complexes^a

complex	δ	character
$[(en)_2Co(OOCCOO)]Cl$	2.77	sym mult
$[(en)_2Co(SC(O)COO)]Cl$	2.65 + 2.95	asym mult ^b
$[(en)_2Co(SC(O)C(O)S)]Cl$	2.73	sym mult
$[(en)_2Co(SCH_2COO)]Cl$	2.60 + 2.93	asym mult ^b

^a Spectra determined in D_2O (pD ca. 2) with DSS as internal standard. Values of δ are in ppm. Only en CH_2 proton signals are reported. ^b These protons are split into two multiplets of approximate relative intensity 1:3, the high-field resonance being the largest.

$c = 12.856(5) \text{ \AA}$, $\alpha = 72.51(6)^\circ$, $\beta = 73.77(3)^\circ$, and $\gamma = 78.62(2)^\circ$. With $Z = 2$, $d_{calcd} = 1.80 \text{ g cm}^{-3}$ and $d_{measd} = 1.79(2) \text{ g cm}^{-3}$ (neutral buoyancy in CCl_4/CBr_4). The rate for the $\theta/2\theta$ scan varied between 1.0 and $4.0^\circ/\text{min}$, depending on the intensity of the reflection being measured. The scan ranged from 0.9° in 2θ below the calculated $K\alpha_1$ peak position to 1.1° above that calculated for $K\alpha_2$. Four standard reflections were monitored to check crystal stability and to account for long-term drift; the drift correction varied randomly from 0.997 to 1.010. The linear absorption coefficient (μ) was 18.09 cm^{-1} , and therefore absorption corrections were applied. The transmission coefficients varied from 0.6389 to 0.8280. Within the sphere $2\theta < 46^\circ$, 2324 reflections were measured; from these, 1897 unique reflections were obtained by averaging.¹⁵ Of these, 1799 had $I > 2\sigma(I)$, where p , the ignorance factor used to calculate³ $\sigma(I)$, was set equal to 0.01.

Structure Solution and Refinement of $[(en)_2Co(SC(O)COO)]_2(S_2O_8) \cdot 2H_2O$. This structure was solved by using normal Patterson techniques. A disorder problem in the water of hydration was successfully treated by using two half-population oxygen atoms. Hydrogen atoms were assigned isotropic temperature parameters¹⁶ of $B = 4.0 \text{ \AA}^2$. Refinement was done by using anisotropic thermal parameters for all nonhydrogen atoms and fixed hydrogen atom positions ($N-H = 0.87 \text{ \AA}$, $C-H = 0.97 \text{ \AA}$, tetrahedral geometry). In the final cycles of least-squares refinement, 191 parameters were varied, including two independent scale factors,¹⁷ the positional parameters, and anisotropic thermal parameters for all nonhydrogen atoms. Convergence was achieved with $R_1 = 0.048$ and $R_2 = 0.045$.¹⁸ In the last cycle of refinement, the maximum shift per error was 0.063 and the average shift per error was 0.013. A final difference map showed four small peaks, the largest of which was less than 0.75 e \AA^{-3} . Two of these were very near the apparently disordered carbon atoms C(1) and C(2) (vide infra). Mean values of $\omega\Delta^2$ did not vary significantly with $(\sin \theta)/\lambda$ or $|F_o|$. Neutral-atom scattering curves as given by Cromer¹⁹ were used for Co, S, N, C, and O; those of Stewart²⁰ were used for

- (15) All computations were performed by using a local version of XRAY 67: J. M. Stewart, University of Maryland, crystallographic computer system.
- (16) Isotropic thermal parameters were of the form $\exp(-B(\sin^2 \theta)/\lambda^2)$.
- (17) Due to experimental difficulties the data were collected in two sets; therefore, two separate scale factors were used.
- (18) $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.
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Table IV. Fractional Atomic Positional Parameters^{a,b} of [(en)₂Co(SC(O)COO)]₂(S₂O₆)·2H₂O

atom	x	y	z
Co	0.0902 (1)	0.37837 (9)	0.22613 (5)
S(1)	0.2379 (2)	0.5846 (2)	0.2345 (1)
S(2)	0.3606 (2)	0.0539 (2)	0.5363 (1)
N(1)	0.3258 (7)	0.2165 (6)	0.2328 (4)
N(2)	-0.0148 (8)	0.1904 (6)	0.2079 (4)
N(3)	-0.1576 (7)	0.5250 (6)	0.2222 (4)
N(4)	-0.0086 (7)	0.3185 (5)	0.3891 (3)
O(1)	0.1744 (6)	0.4470 (5)	0.0669 (3)
O(2)	0.3233 (6)	0.6265 (5)	-0.0846 (3)
O(3)	0.4032 (8)	0.7900 (5)	0.0501 (4)
O(4)	0.2305 (6)	-0.0296 (6)	0.5077 (4)
O(5)	0.3540 (7)	0.0103 (6)	0.6528 (3)
O(6)	0.3538 (6)	0.2327 (5)	0.4795 (3)
O(7) ^c	0.8775 (23)	0.8907 (15)	0.0398 (9)
O(8) ^c	0.7937 (18)	0.9047 (13)	0.1211 (9)
C(1)	0.3032 (12)	0.0561 (9)	0.2152 (6)
C(2)	0.1178 (13)	0.0342 (10)	0.2355 (9)
C(3)	-0.2902 (10)	0.4918 (8)	0.3391 (5)
C(4)	-0.1723 (10)	0.4460 (8)	0.4207 (4)
C(5)	0.2666 (9)	0.5744 (7)	0.0175 (5)
C(6)	0.3140 (9)	0.6677 (7)	0.0938 (5)

^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 1. ^c This atom has a population parameter of 0.5.

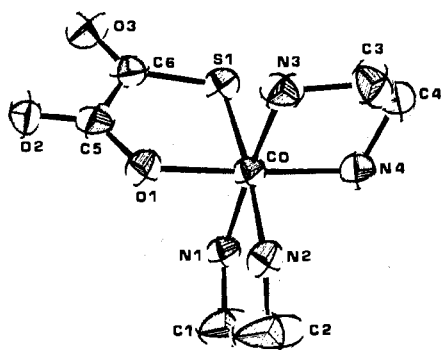


Figure 1. Perspective view of $\Delta\lambda-[(en)_2Co(SC(O)COO)]^+$. The ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

H. Anomalous dispersion corrections²¹ were made for Co and S. The values of $|F_o|$ and F_c are listed in Table A.²²

Results

In addition to the X-ray structure analysis described below, the (thiooxalato-*O,S*)bis(ethylenediamine)cobalt(III) complex is characterized by (1) synthesis by two independent methods (redox and substitution), (2) the visible-UV, IR, and ¹H NMR spectral parameters given in Tables I-III, (3) analyses of the elemental composition of an isolated salt, the results of which are in agreement with the proposed formulation, (4) cation-exchange elution characteristics which are consistent with the assigned formal charge, (5) the generation of H₂S and oxalate upon hydrolysis (vide infra), and (6) the resistance of this complex toward further oxidation. The visible-UV spectrophotometric parameters listed in Table I establish the expected low-energy d-d transition characteristic of the *cis*-CoN₄OS chromophore, as well as the intense ligand-to-metal charge-transfer (LTMCT) band at 273 nm characteristic of sulfur coordinated to cobalt(III).²³ In Table II the IR bands within the carbonyl region are compared to those observed for related

Table V. Root-Mean-Square Displacements (Å) of [(en)₂Co(SC(O)COO)]₂(S₂O₆)·2H₂O

atom	min	med	max
Co	0.175	0.181	0.216
S(1)	0.193	0.207	0.240
S(2)	0.191	0.200	0.268
N(1)	0.182	0.189	0.240
N(2)	0.195	0.226	0.249
N(3)	0.190	0.230	0.261
N(4)	0.190	0.200	0.234
O(1)	0.193	0.208	0.241
O(2)	0.180	0.228	0.274
O(3)	0.205	0.267	0.357
O(4)	0.208	0.246	0.329
O(5)	0.193	0.228	0.362
O(6)	0.195	0.235	0.303
O(7)	0.247	0.309	0.454
O(8)	0.249	0.280	0.373
C(1)	0.207	0.301	0.322
C(2)	0.220	0.255	0.537
C(3)	0.189	0.251	0.314
C(4)	0.191	0.231	0.286
C(5)	0.175	0.206	0.249
C(6)	0.163	0.215	0.272

Table VI. Bond Lengths (Å) of [(en)₂Co(SC(O)COO)]₂(S₂O₆)·2H₂O

Co-N(1)	1.960 (5)	N(1)-C(1)	1.465 (10)
Co-N(2)	1.967 (6)	C(1)-C(2)	1.334 (13)
Co-N(3)	1.965 (5)	C(2)-N(2)	1.469 (9)
Co-N(4)	1.955 (4)	N(3)-C(3)	1.519 (7)
Co-O(1)	1.904 (4)	C(3)-C(4)	1.451 (11)
Co-S(1)	2.237 (2)	C(4)-N(4)	1.480 (8)
C(5)-O(1)	1.269 (7)	S(2)-O(4)	1.453 (6)
C(5)-O(2)	1.228 (7)	S(2)-O(5)	1.421 (4)
C(6)-S(1)	1.702 (6)	S(2)-O(6)	1.445 (4)
C(6)-O(3)	1.217 (8)	S(2)-S(2')	2.118 (2)
C(5)-C(6)	1.560 (11)		

Table VII. Bond Angles (Deg) of [(en)₂Co(SC(O)COO)]₂(S₂O₆)·2H₂O

Metal Coordination Sphere			
S(1)-Co-O(1)	88.5 (2)	S(1)-Co-N(3)	93.1 (2)
S(1)-Co-N(1)	91.4 (2)	S(1)-Co-N(4)	91.0 (2)
S(1)-Co-N(2)	174.0 (1)		
Ligands			
C(5)-O(1)-Co	121.5 (4)	O(2)-C(5)-O(1)	124.9 (7)
C(6)-S(1)-Co	97.2 (3)	S(1)-C(6)-C(5)	115.9 (4)
O(1)-C(5)-C(6)	116.7 (5)	O(3)-C(6)-C(5)	119.0 (5)
O(2)-C(5)-C(6)	118.4 (6)	O(3)-C(6)-S(1)	125.1 (6)
Co-N(1)-C(1)	111.2 (5)	C(1)-C(2)-N(2)	115.2 (7)
N(1)-C(1)-C(2)	112.4 (7)	C(2)-N(2)-Co	108.2 (6)
Co-N(3)-C(3)	109.4 (4)	C(3)-C(4)-N(4)	108.6 (5)
N(3)-C(3)-C(4)	108.7 (5)	C(4)-N(4)-Co	109.6 (3)
Anion			
O(4)-S(2)-O(5)	114.0 (3)	O(5)-S(2)-O(6)	116.1 (3)
O(4)-S(2)-O(6)	112.5 (3)	O(5)-S(2)-S(2')	104.4 (2)
O(4)-S(2)-S(2')	103.5 (2)	O(6)-S(2)-S(2')	104.6 (2)

complexes. Band assignments, facilitated by examining both normal and partially deuterated complexes, are based on published data for similar complexes. The IR spectrum of [(en)₂Co(SC(O)COO)]⁺ in the carbonyl region is clearly more complex than that of the precursor complex [(en)₂Co(SCH₂COO)]⁺. The ¹H NMR data presented in Table III show that the pattern of ethylenediamine CH₂ resonances observed for the thiooxalato-*O,S* complex is more similar to that observed for the thioglycolato-*O,S* complex than to those observed for either of the more symmetric oxalato-*O,O* or dithiooxalato-*S,S* complexes.

Crystal Structure. Final fractional atomic positional parameters, and their estimated standard deviations, for non-

(21) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(22) Supplementary material. This includes all tables designated by alphabetic characters.

(23) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* 1973, 12, 2682.

hydrogen atoms are given in Table IV. The corresponding anisotropic thermal parameters may be found in Table B,²² the root-mean-square displacements calculated therefrom are collected in Table V, and the associated ellipsoids for the complex cation are shown in Figure 1. Bond lengths and bond angles involving nonhydrogen atoms are found in Tables VI and VII, respectively. The calculated hydrogen atomic positional parameters have been collected in Table C.²²

The structure consists of discrete cationic complexes, anions, and waters of hydration weakly hydrogen bonded together. A center of symmetry lies at the midpoint of the S-S bond in the dithionate anion and relates the two enantiomers of the cobalt complex. As shown by Figure 1, the structure is octahedral with two bidentate ethylenediamine ligands and the thiooxalate-*O,S* ligand. This shows conclusively that the oxidation of the precursor thioglycolato complex occurs at the α -carbon with no net reaction of the coordinated sulfur atom. There is disorder both in the water of hydration and in the conformation of one of the ethylenediamine rings (Figure 1). The latter is exhibited in the large anisotropic thermal parameters of C(1) and C(2) and in their unusually short apparent bond length (1.334 Å). As expected, the cobalt-bound thiooxalate ring is very nearly planar, the ligand atoms all lying within 0.015 Å of the ligand plane. The cobalt atom is 0.06 Å from this plane. The crystal contains molecules of the $\Delta\lambda$ and $\Lambda\delta$ configurations with the conformation of the second ethylenediamine unassignable because of the disorder at C(1) and C(2) described above. Any ground-state structural trans effect is slight or nil. The Co-N bond trans to S is 1.967 (6) Å as compared to 1.962 (5) Å for the average of the Co-N bonds cis to S,²⁴ giving a difference of 0.005 (8) Å.

Discussion

Synthesis. In previous studies we had noted that oxidation of $[(en)_2M(SCH_2COO)]^+$ complexes ($M = Co, Cr$) with 1-equiv oxidations such as Np(VI) and Ce(IV) led to the corresponding thiooxalato complex (eq 1).^{1,2} More recently, we attempted to prepare the coordinated unsymmetrical disulfide $[(en)_2Co(S(SC_6H_5)CH_2COO)]^{2+}$ by reaction of $[(en)_2Co(SCH_2COO)]^+$ with *N*-(phenylthio)phthalimide³¹ and isolated the thiooxalato complex as one of the three major products. In this reaction the *N*-(phenylthio)phthalimide presumably functions as a 2-equiv oxidant through the intermediacy of the sulfenium ion $C_6H_4S^+$. To test this hypothesis, we examined the reaction of other X^+ donors with $[(en)_2Co(SCH_2COO)]^+$ and found that *N*-chlorosuccinimide and *N*-bromosuccinimide give substantial yields of the monothiooxalato product. Other oxidants which give this product, but in smaller yields, are $KBrO_3$, $Na_2Cr_2O_7$, and *N*-iodosuccinimide. In addition, Gainsford, Jackson, and Sargeson³² have recently found that oxidation of $[(en)_2Co(SCH_2COO)]^+$ with excess acetic anhydride in dimethyl sulfoxide also yields a significant amount of the thiooxalato complex. It thus appears that $[(en)_2Co(SC(O)COO)]^+$ is a prevalent product of oxidation of $[(en)_2Co(SCH_2COO)]^+$ by a variety of 1- and 2-equiv agents. In marked contrast, oxidation of the oxygen-containing glycolato analogue $[(en)_2Co(OCH_2COO)]^+$

under similar conditions does *not* readily yield the oxalato product $[(en)_2Co(OOCCOO)]^+$. It is thus clear that the coordinated sulfur atom of $[(en)_2Co(SCH_2COO)]^+$ plays an important role in the mechanism of oxidation of this complex, even though net oxidation occurs at the carbon atom rather than at the sulfur atom. From the general reactivity pattern that we have observed, we infer that the initial step in oxidation of $[(en)_2Co(SCH_2COO)]^+$ involves interaction between the electrophilic oxidant, e.g., X^+ , and the nucleophilic^{33,34} sulfur atom of $[(en)_2Co(SCH_2COO)]^+$. At some later stage in the reaction scheme, net oxidation must be transferred from the coordinated sulfur atom to the adjacent carbon atom. We have previously proposed a possible mechanism for this transfer.³⁵

During the characterization of $[(en)_2Co(SC(O)COO)]^+$ we showed that the identical complex could be prepared by direct substitution of monothiooxalato on $[(en)_2CoCl_2]^+$ by using standard procedures employed in the synthesis of the oxalato and dithiooxalato analogues.^{8,10} It is noteworthy that thiooxalato substitution leads to the *O,S* isomer rather than to the *O,O* isomer, presumably because of the greater nucleophilicity of sulfur.

Characterization. The data of Table I show that there is very little change in the visible-UV spectrum when $[(en)_2Co(SCH_2COO)]^+$ is oxidized to $[(en)_2Co(SC(O)COO)]^+$, both complexes having spectra characteristic of the *cis*- CoN_4OS chromophore. This is as expected for a reaction in which none of the atoms coordinated to cobalt are altered, and only the ligand backbone is modified. The thiooxalate-*O,S* and thioglycolate-*O,S* ligands provide approximately equal ligand fields; they also give rise to LTMCT bands, characteristic of low-valent sulfur bonded to cobalt(III),²³ at approximately the same energy. The presence of this LTMCT band in the thiooxalato product establishes that oxidation of the ligand backbone occurs without cobalt-sulfur bond fission. Also, the ordering observed in the position of the low-energy d-d band in the mono(ligand) compounds agrees with that reported by Coucouvanis¹¹ for the tris(ligand) complexes (where the ligands are oxalato-*O,O*, thiooxalato-*O,S*, and dithiooxalato-*S,S*). The change in the IR spectrum upon oxidation of $[(en)_2Co(SCH_2COO)]^+$ to $[(en)_2Co(SC(O)COO)]^+$ is similar to that observed for the analogous chromium complexes.² Most notable is the appearance of a new band in the asymmetric carbonyl stretching region (ca. 1660 cm^{-1}) which is assigned as arising from the COO carbonyl. The thiooxalato-*S,O* ligand is expected to exhibit two high-energy and one low-energy carbonyl bands; the thiooxalato-*O,O* ligand should exhibit one high-energy and two low-energy bands.¹¹ The data of Table II show that $[(en)_2Co(SC(O)COO)]^+$ has bands at 1660, 1625, and 1340 cm^{-1} , the pattern expected for the *S,O* isomer. The data of Table II also show that bands for mono(ligand) and tris(ligand) complexes occur at approximately the same frequency for a given ligand; this correlation holds for all three ligands of the oxalato-*O,O*, thiooxalato-*O,S*, and dithiooxalato-*S,S* series. The data of Table III show that the pattern of ethylenediamine CH_2 resonances in the 1H NMR spectra of $[(en)_2Co(SCH_2COO)]^+$ and $[(en)_2Co(SC(O)COO)]^+$ are similar to each other but dissimilar to the pattern exhibited by $[(en)_2Co(OOCCOO)]^+$ and $[(en)_2Co(SC(O)C(O)S)]^+$. Again, this is as expected since oxidation of the thioglycolate backbone should not significantly affect the ethylenediamine environment. Of course, the sharp singlet arising from the thioglycolate methylene

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protons is lost upon oxidation.

The title complex is further characterized by the reactivity patterns which it displays. For example, both $[(en)_2Co(SC(O)COO)]^+$ and $[(en)_2Co(SC(O)C(O)S)]^+$ undergo rapid base hydrolysis to yield H_2S , cobalt(II), and free oxalate. Both complexes also undergo acid hydrolysis and yield H_2S and oxalic acid on heating in ca. 6 M acid. In addition, $[(en)_2Co(SC(O)COO)]^+$ is much more resistant to oxidation than $[(en)_2Co(SCH_2COO)]^+$, but it can be oxidized under stringent conditions (e.g., by using silver-catalyzed persulfate).

Crystal Structure. Structural parameters observed for $[(en)_2Co(SC(O)COO)]_2(S_2O_6)$ (Tables VI and VII) are in reasonable agreement with those obtained by Gainsford, Jackson, and Sargeson³² in a study of the analogous chloride salt. In general, the structure of the $[(en)_2Co(SC(O)COO)]^+$ cation is as expected from the known structure of the parent thiolato complex $[(en)_2Co(SCH_2COO)]^+$.³ However, the structural trans effect (STE) induced by the coordinated sulfur atom is significantly smaller³⁷ for the thiooxalato complex than for the thiolato complex (0.005 (8) vs. 0.043 (5) Å). This

result is in harmony with the hypothesis that charge donation from sulfur to cobalt(III) is the underlying cause of the STE.³⁴ The electron-withdrawing effect of the adjacent carbonyl in thiooxalato reduces the tendency of the sulfur atom of this ligand to donate electron density (relative to the sulfur atom of the parent thiolato ligand). This result allows us to extend the previously noted³⁴ STE series for cobalt(III): $SO_3^{2-} > RSO^- > RSO_2^- > RS^- > S_2O_3^{2-} \approx RSR \approx RC(O)S^-$.

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Registry No. $[(en)_2Co(SC(O)COO)]_2(S_2O_6) \cdot 2H_2O$, 73612-11-0; $[(en)_2Co(SC(O)COO)]Cl$, 73612-12-1; $[(en)_2Co(SC(O)COO)]ClO_4$, 73612-13-2; $[(en)_2Co(OOCCOO)]^+$, 17835-71-1; $[(en)_2Co(SC(O)COO)]^+$, 73612-09-6; $[(en)_2Co(SC(O)C(O)S)]^+$, 73650-78-9; $[(en)_2Co(SCH_2COO)]Cl$, 54453-35-9; $[(en)_2Co(OOCCOO)]Cl$, 17439-00-8; $[(en)_2Co(SC(O)C(O)S)]Cl$, 14267-12-0; $[(en)_2Co(SCH_2COO)]ClO_4$, 26743-67-9; *cis*- $[(en)_2CoCl_2]Cl$, 14040-32-5.

Supplementary Material Available: Tables A-C giving $|F_o|$ and F_c , anisotropic thermal parameters, and positional parameters of hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

(37) Sargeson³² also finds the shortest Co-N bond to be that trans to O. The sulfur STE computed from his data for the chloride salt is 0.018 (3) Å.

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Tetracarbon Metallacarboranes. 9.¹ New Types of Nido Cage Geometry. Crystal and Molecular Structures of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ (Isomer 1) and $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ (Isomer 2)

RUSSELL N. GRIMES,* EKK SINN, and J. ROBERT PIPAL

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The structures of the title compounds have been determined by single-crystal X-ray diffraction and consist, respectively, of a 13-vertex nido NiC_4B_8 and a 12-vertex nido CoC_4B_7 cage framework. The NiC_4B_8 cluster resembles a 14-vertex closo polyhedron (bicapped hexagonal antiprism) from which one vertex has been removed and is the first example of a 13-vertex nido cage. The CoC_4B_7 geometry is also unprecedented and consists of an irregular basket-shaped framework with one carbon atom bridging three framework atoms across the open top of the basket. The two compounds are structurally related, since one can formally convert a CoC_4B_8 cage (analogous to the NiC_4B_8) to the observed CoC_4B_7 species by removal of one BH unit and linkage of two carbon atoms. Such a mechanism is proposed to account for the structure of the CoC_4B_7 cage. Both species are $(2n + 4)$ -electron frameworks and are formally nido, in agreement with their gross geometries. Crystal data for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$: mol wt 659.9, space group *Pbca*, $Z = 8$; $a = 16.666$ (2), $b = 17.666$ (1), $c = 24.00$ (2) Å; $V = 7066$ Å³; $R = 0.042$ for 3144 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $(\eta^5-C_5H_5)Co(NH_3)_4C_4B_7H_7$: mol wt 314.9, space group *P2₁/b* (unique axis a), $Z = 4$; $a = 7.930$ (3), $b = 14.151$ (6), $c = 14.809$ (5) Å; $\alpha = 101.2^\circ$; $V = 1631$ Å³; $R = 0.047$ for 1542 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Previous papers in this series have demonstrated that large carboranes and metallacarboranes containing four carbon atoms rather than the usual two in the polyhedral framework tend to adopt irregular, unorthodox open-cage structures.¹⁻⁸

That such species are of the open type is not surprising, since the presence of four carbons usually produces an electron-rich condition (relative to the requirement⁹⁻¹¹ of $2n + 2$ skeletal electrons for n -vertex closo, or fully triangulated, clusters); this in turn normally leads to cage opening to produce a nido ($2n + 4$) or arachno ($2n + 6$) system. This paradigm, while very useful as a general rule for classifying clusters, has proved

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