The sulfonate groups of the diselenotetrathionates have trigonal symmetry, but, as in the other polythionates,[24] the trigonal axis of the SO_3 pyramid does not coincide with the direction of the Se–S bond. The tilt of the pyramid is such that one of the Se–S–O angles is significantly smaller than the two others. The unique S–O bond is in each case near the Se–Se–S plane and trans to the Se–Se bond. The weighted mean values of the dimensions of the four independent sulfonate groups are S–O = 1.437 (2) Å, O–S–O = 113.4 (1)°, one Se–S–O = 100.5 (1)°, and two Se–S–O = 107.1 (1)°. The weighted mean values of fourteen sulfonate groups of nine tetra-, penta-, selenopenta-, telluropenta-, and hexathionates are S–O = 1.444 (1) Å, O–S–O = 113.4 (1)°, one S–S–O = 100.7 (1)°, and two S–S–O = 106.9 (1)°.[24]

The *trans*-dichlorobis(ethylenediamine)cobalt(III) ions in the present structures and in the selenotetrathionate[2] have in each case a planar or nearly planar coordination of the four nitrogen atoms to cobalt, and the Cl–Co–N angles are in the range 87.47 (17)–91.41 (25)°. The two carbon atoms of an ethylenediamine group are twisted to different sides of the cobalt–nitrogen plane. The weighted mean values of the dimensions for the coordination to cobalt in the eight independent cations are 2.253 (1) Å for the Co–Cl bond, 1.957 (1) Å for the Co–N bond, 86.8 (1)° for the N–Co–N angle when the N atoms are of the same ethylenediamine group, and 93.2 (1)° for the N–Co–N angle when the N atoms are of different ethylenediamine groups.

Acknowledgment. The authors wish to express gratitude to Professor Olav Foss of this department for stimulating discussions and guidance. V.J. thanks the Royal Norwegian Ministry of Foreign Affairs for a Norwegian Government Scholarship.

Supplementary Material Available: Listings of observed and calculated structure factors and of assumed hydrogen atom positions (55 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of the Bunte Salt *trans*-Dichlorobis(ethylenediamine)cobalt(III) *S*-Hydroxymethyl Thiosulfate, $[Co(en)_2Cl_2]HOCH_2S_2O_3$

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The title compound has been isolated from acidified thiosulfate solutions containing formaldehyde and the complex cation *trans*-dichlorobis(ethylenediamine)cobalt(III). Crystals of $[Co(en)_2Cl_2]HOCH_2S_2O_3$ are orthorhombic, of space group $P2_12_12_1$ with $a = 9.9931$ (5) Å, $b = 22.6950$ (13) Å, $c = 6.3310$ (5) Å, and $Z = 4$. The structure has been solved with Mo Kα diffractometer data and refined to $R = 0.024$ by full-matrix least squares by employing 1857 observed reflections. The bond lengths within the S(1)–S(2)–C–O chain are 2.0779 (15), 1.829 (4), and 1.399 (6) Å, which may be interpreted in terms of a loose complex between formaldehyde and thiosulfate and used to explain the stability of thiosulfate in the presence of acids and formaldehyde. The $HOCH_2S_2O_3^-$ anions are arranged in head-to-tail spirals along 2_1 symmetry elements and with hydroxyl hydrogen to sulfonate oxygen intermolecular hydrogen bonding.

Introduction

S-Alkyl and *S*-aryl thiosulfates are called "Bunte salts"[2] and are classically used to synthesize mercaptans via acid-catalyzed hydrolysis:

$$RS_2O_3^- + H_2O \xrightarrow{H^+} RSH + HSO_4^-$$

For various Bunte salts, electron-withdrawing substituents are associated with decreased rate of hydrolysis, which is consistent with the protonation of bivalent sulfur in the transition state.[3]

Thiosulfate may be titrated iodometrically in the presence of sulfite[4] and is considerably more resistant to acid when formaldehyde is added.[5] The reaction of formaldehyde and thiosulfate in the presence of strong acid has been postulated to give "formaldehyde thiosulfuric acid", the title compound, although neither the acid nor a simple salt has been isolated. There is the claim[6] that reactions 1 and 2 together lead to a trimeric salt (**1**).

$$CH_2O + 2H^+ + S_2O_3^{2-} \rightarrow CH_2(OH)S_2O_3H \qquad (1)$$

$$3C_6H_5(NH)_2(N(CH_3)_2)S_2O_3H + 3CH_2O \rightarrow [C_6H_5(N{=}CH_2)(N(CH_3)_2)SH]_3 + 3H_2SO_4 \qquad (2)$$

$$[CH_2(OH)S_2O_3H \cdot C_6H_5(N{=}CH_2)(N(CH_3)_2)SH]_3$$

1

Our interest in the hydrothiosulfate anion and in "thiosulfuric acid" led us to investigate the "formaldehyde thiosulfuric acid" reaction. We report here the preparation and X-ray structural examination of *trans*-dichlorobis(ethylenediamine)cobalt(III) *S*-hydroxymethyl thiosulfate. To our knowledge this is the first Bunte salt for which structural details are available. The structures of two "aminoalkyl thiosulfate" zwitterions have been reported.[7,8]

Experimental Section

A solution of 2 g of $Co(en)_2Cl_3$ dissolved in 5 mL of water was added to the mixture of 5 mL of 1 N $Na_2S_2O_3$, 5 mL of 1 N H_2SO_4, and 1.2 mL of 40% CH_2O. The resulting solution was allowed to

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for *trans*-Dichlorobis(ethylenediamine)cobalt(III) *S*-Hydroxymethyl Thiosulfate[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.187 38 (9)	0.373 46 (4)	0.840 82 (15)	248 (4)	348 (5)	333 (5)	8 (4)	30 (4)	35 (4)
S(2)	0.151 55 (10)	0.419 75 (5)	0.563 34 (18)	349 (5)	558 (6)	411 (6)	35 (5)	−39 (5)	102 (5)
O(1)	0.055 83 (25)	0.353 55 (13)	0.903 3 (6)	231 (12)	556 (18)	689 (21)	31 (13)	124 (16)	170 (20)
O(2)	0.277 38 (26)	0.325 35 (13)	0.789 5 (5)	299 (14)	484 (17)	579 (19)	112 (13)	89 (14)	111 (16)
O(3)	0.250 31 (35)	0.414 16 (15)	0.986 6 (5)	718 (22)	570 (19)	357 (16)	−150 (19)	−61 (17)	−28 (16)
C(5)	0.322 9 (4)	0.436 07 (20)	0.480 2 (7)	386 (22)	569 (26)	334 (20)	−75 (22)	26 (20)	106 (20)
C(4)	0.389 70 (32)	0.480 13 (14)	0.593 2 (7)	559 (20)	633 (20)	650 (23)	−112 (17)	−72 (21)	181 (21)
Co	0.174 58 (4)	0.153 595 (19)	0.112 51 (7)	184 (2)	238 (2)	165 (2)	−4 (2)	−4 (2)	12 (2)
Cl(1)	0.277 72 (9)	0.111 12 (4)	0.388 70 (15)	362 (5)	430 (5)	219 (4)	100 (4)	−34 (4)	49 (4)
Cl(2)	0.066 95 (10)	0.193 78 (4)	−0.162 72 (13)	329 (4)	379 (5)	223 (4)	89 (4)	−33 (4)	33 (4)
N(1)	0.054 47 (29)	0.193 74 (14)	0.306 9 (4)	219 (14)	310 (16)	222 (14)	8 (13)	15 (12)	13 (13)
N(2)	0.287 94 (27)	0.222 94 (13)	0.138 3 (5)	243 (14)	316 (15)	297 (16)	−58 (12)	24 (13)	−23 (14)
N(3)	0.062 10 (28)	0.083 45 (13)	0.077 8 (5)	252 (14)	301 (15)	328 (17)	−30 (12)	22 (14)	16 (15)
N(4)	0.299 58 (27)	0.114 73 (13)	−0.077 5 (4)	212 (14)	309 (14)	217 (14)	7 (12)	−6 (12)	5 (13)
C(1)	0.089 9 (4)	0.257 70 (17)	0.318 9 (7)	351 (20)	310 (19)	378 (23)	18 (17)	59 (18)	−41 (19)
C(2)	0.243 2 (4)	0.259 63 (18)	0.318 0 (7)	365 (21)	384 (21)	384 (24)	−107 (18)	59 (19)	−131 (19)
C(3)	0.115 2 (4)	0.047 46 (16)	−0.097 1 (8)	374 (19)	308 (18)	405 (22)	−92 (16)	11 (21)	−94 (20)
C(4)	0.265 7 (4)	0.051 17 (15)	−0.091 7 (7)	334 (18)	276 (17)	326 (20)	46 (15)	−20 (19)	−48 (18)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)/10000]$.

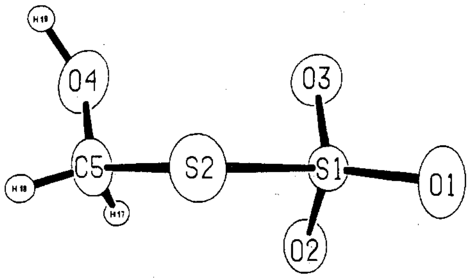

Figure 1. A view of the *S*-hydroxymethyl thiosulfate ion with 50% probability thermal ellipsoids.

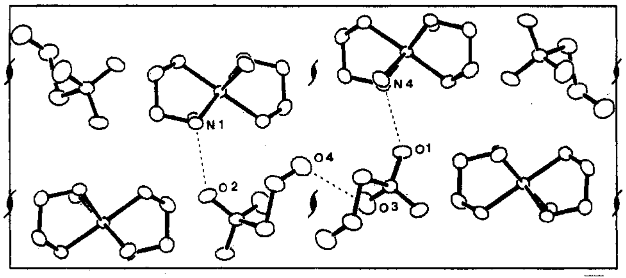

Figure 2. A projection of the cell contents of $[Co(en)_2Cl_2]HOCH_2S_2O_3$ up the c axis. Thermal ellipsoids are at 50% probability. The dashed lines show the hydrogen bonding mentioned in the text.

Table II. Bond Distances (Å) and Angles (Deg) for *trans*-Dichlorobis(ethylenediamine)cobalt(III) *S*-Hydroxymethyl Thiosulfate

(a) Bond Distances			
S(1)–S(2)	2.0779 (15)	C(5)–O(4)	1.399 (6)
S(2)–C(5)	1.829 (4)		
H(17)–C(5)	0.961	H(19)–O(4)	1.018
H(18)–C(5)	0.942		
S(1)–O(1)	1.4454 (28)	S(1)–O(3)	1.4494 (34)
S(1)–O(2)	1.4516 (30)		
Co–Cl(1)	2.2470 (10)	N(1)–C(1)	1.496 (5)
Co–Cl(2)	2.2417 (10)	N(2)–C(2)	1.479 (5)
Co–N(1)	1.9455 (30)	N(3)–C(3)	1.475 (5)
Co–N(2)	1.9459 (29)	N(4)–C(4)	1.484 (5)
Co–N(3)	1.9612 (29)	C(1)–C(2)	1.533 (5)
Co–N(4)	1.9456 (28)	C(3)–C(4)	1.507 (5)
(b) Bond Angles			
S(2)–S(1)–O(1)	103.46 (14)	O(1)–S(1)–O(2)	112.93 (17)
S(2)–S(1)–O(2)	107.33 (15)	O(1)–S(1)–O(3)	114.81 (20)
S(2)–S(1)–O(3)	106.93 (14)	O(2)–S(1)–O(3)	110.68 (19)
S(1)–S(2)–C(5)	100.63 (14)	S(2)–C(5)–O(4)	116.38 (30)
H(19)–O(4)–C(5)	132.2	H(17)–C(5)–O(4)	106.6
H(17)–C(5)–H(18)	109.3	H(18)–C(5)–S(2)	108.4
H(17)–C(5)–S(2)	107.3	H(18)–C(5)–O(4)	108.7
Cl(1)–Co–Cl(2)	178.25 (4)	N(2)–Co–N(3)	178.31 (14)
Cl(1)–Co–N(1)	89.52 (9)	N(2)–Co–N(4)	92.57 (12)
Cl(1)–Co–N(2)	90.84 (9)	N(3)–Co–N(4)	86.02 (12)
Cl(1)–Co–N(3)	90.10 (9)	Co–N(1)–C(1)	109.93 (23)
Cl(1)–Co–N(4)	89.54 (9)	Co–N(2)–C(2)	110.12 (22)
Cl(2)–Co–N(1)	90.30 (9)	Co–N(3)–C(3)	109.12 (22)
Cl(2)–Co–N(2)	90.89 (9)	Co–N(4)–C(4)	109.36 (22)
Cl(2)–Co–N(3)	88.18 (9)	N(1)–C(1)–C(2)	105.29 (30)
Cl(2)–Co–N(4)	90.69 (9)	N(2)–C(2)–C(1)	106.81 (32)
N(1)–Co–N(2)	85.83 (13)	N(3)–C(3)–C(4)	108.10 (33)
N(1)–Co–N(3)	95.59 (13)	N(4)–C(4)–C(3)	106.48 (28)
N(1)–Co–N(4)	178.14 (12)		

stand undisturbed at room temperature. Formation and growth of green needlelike crystals began after 10–15 min. The crystals may be washed with ethanol and ether, and the compound may be analyzed by titration with iodine with the assumption of 1 equiv of iodine/mol of formaldehyde thiosulfate.

$[Co(en)_2Cl_2]O_3S_2CH_2OH$ is orthorhombic, of space group $P2_12_12_1$ with a = 9.9931 (5) Å, b = 22.6950 (13) Å, c = 6.3310 (5) Å, V = 1436 Å^3, mol wt 393.23, D(obsd) = 1.77 g cm^{-3}, D(calcd for Z = 4) = 1.82 g cm^{-3}, and μ = 19 cm^{-1} for Mo Kα radiation.

The data crystal was mounted on a glass fiber nearly parallel to the needle, c, axis. The distances between the bounding faces (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (120), ($\bar{1}\bar{2}$0), (1$\bar{3}$0), and ($\bar{1}$30) were 0.37, 0.13, 0.17, and 0.17 mm, respectively. Intensity data and the lattice and orientation parameters were measured on a Siemens off-line automatic quarter-circle single-crystal diffractometer with Nb-filtered Mo Kα radiation. One octant of data was measured to a maximum θ of 28° with the "*five-value*" procedure, θ–2θ scans of 0.7° θ, and a maximum scan time of 24 s/deg θ. Three standard reflections were measured after every 50 data reflections. The standards indicated an instrument instability of 1.4% and no decay of the crystal during data collection. Calculations were performed on a Univac 1110 computer with the X-ray System[9] and locally written programs. Scattering factors[10] were those of Cromer and Mann and of Stewart et al. with atoms S and heavier corrected for anomalous dispersion.

The data were corrected for Lorentz, polarization, and absorption effects. Factors in the absorption correction ranged from 1.23 to 1.43. Weights were assigned according to standard formulas for counting statistics and instrument instability.[11] Of the 2017 reflections measured, 160 were less than three standard deviations above background. The structure was solved by the use of symbolic addition, the tangent formula, and Fourier synthesis which revealed the positions of the Co, Cl, and S atoms. The remaining nonhydrogen atoms were

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quickly revealed by structure factor, electron density calculations. Hydrogen atoms were located in later electron density maps. Their positions were not refined, and their temperature factors were constrained to $U = 0.076$ Å^2. Since the space group, $P2_12_12_1$, is a polar one, there are two possible enantiomeric forms, and the structure was therefore refined to convergence in each form. The full-matrix least-squares refinement with all nonhydrogen atoms anisotropic converged to weighted and unweighted R factors of 2.8% and 2.4%, respectively, for the enantiomeric form presented in the tables and figures. The corresponding R factors for the other enantiomeric form were as high as 4.1% and 3.7%, and we therefore concluded that the former was the correct one. In the final refinement cycle the largest shift was less than 1% of the associated estimated standard deviation, and the standard deviation of an observation of unit weight was 0.97. The largest peak in the subsequent difference electron density map was 0.32 e Å^{-3}.

Figure 1 shows a view of the *S*-(hydroxymethyl)thiosulfate anion, and Figure 2 is a projection of the cell contents down the *c* axis. Table I gives atomic coordinates, and Table II lists selected bond distances.

Discussion

Anions, $HOCH_2S_2O_3^-$, are arranged in head-to-tail spirals along 2_1 symmetry elements parallel to the (6.331 Å) *c* axis. The spirals are continuous because of intermolecular hydroxyl hydrogen to sulfonate oxygen hydrogen bonding (O(4)–H(19)···O(3)). There is also a continuous bond/hydrogen bond system in the *a* axis direction, involving –O(2)···H(1)–N(1)–Co–N(4)–H(15)···O(1)–S(1)– and repeated by the lattice translation. The shortest intramolecular sulfonate oxygen to hydroxyl oxygen contact is 3.22 Å for O(3)···O(4), which is considerably longer than the 2.86–2.88 Å for the three previously mentioned intermolecular contacts.

The $-S_2O_3$ fragment has the expected deviations from trigonal and mirror symmetries. The bond S(2)–C(5) is nearly trans to S(1)–O(1) and, in projection down the S(2)–S(1) bond, nearly bisects O(2)–S(1)–O(3). The dihedral angle O(1)–S(1)–S(2)–C(5) is 6° with C(5) closest to O(2) and with O(4) closest to O(3), which demonstrates the rotation of the $-SO_3$ group as a result of the position of O(4). O(1) is 0.07 Å closer to S(2) than are O(2) and O(3), which demonstrates the tilt of the O(1)–O(2)–O(3) plane away from C(5). Similar effects have been observed in the polythionates.[12,13]

The tetrabonded to dibonded S(1)–S(2) bond length of 2.078 (2) Å is perhaps short when compared to known polythionate tetrabonded to dibonded distances of range 2.09–2.13 Å.[12,13] The dibonded sulfur to carbon distance, S(2)–C(5), of 1.829 (5) Å is perhaps long when compared to bond lengths in $S_2(CH_3)_2$ (1.81 Å)[14] and $S_2(C_6H_5)_2$ (1.79 Å).[15] The C(5)–O(4) distance of 1.399 (6) Å is perhaps short compared to the corresponding distance in CH_3OH of 1.427 (7) Å.[16]

These distances are in accord with considerable ionic character in the S–C bond or with a loose complex between thiosulfate and protonated formaldehyde. They confirm the existence of "formaldehyde thiosulfate" and offer an explanation for the equilibria seen in solutions of formaldehyde and thiosulfate.

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Registry No. $[Co(en)_2Cl_2]O_3S_2CH_2OH$, 72709-18-3; $Na_2S_2O_3$, 7757-83-7; CH_2O, 50-00-0.

Supplementary Material Available: Listings of observed and calculated structure factors and of hydrogen atom positions (15 pages). Ordering information is given on any current masthead page.

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Structures of Bis(μ-thiourea-*S*)-bis[bis(thiourea-*S*)tellurium(II)] Cations

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The structures of tris(ethylenethiourea-*S*)tellurium(II) perchlorate (I) and of two modifications of tris(trimethylenethiourea-*S*)tellurium(II) perchlorate (II and III) have been solved and refined with Mo Kα diffractometer data to reveal "planar", dimeric $L_2Te(\mu\text{-}L)_2TeL_2$ cations. The dimers are situated on crystallographic centers of symmetry and the Te_2S_6 moieties display approximate C_{2h} geometry with significant distortions from D_{2h} geometry along a B_{1g} vibrational coordinate. Trans pairs of Te–S bonds exhibit lengths in accord with three-center four-electron bonding. Crystals of I are monoclinic, of space group $P2_1/c$ with $a = 11.911$ (2) Å, $b = 11.455$ (2) Å, $c = 16.994$ (3) Å, $\beta = 112.10$ (2)°, and $Z = 2$ dimers. Crystals of II are triclinic, of space group $P\bar{1}$ with $a = 12.597$ (2) Å, $b = 10.018$ (3) Å, $c = 9.997$ (2) Å, $\alpha = 96.15$ (2)°, $\beta = 92.48$ (1)°, $\gamma = 77.89$ (1)°, and $Z = 1$ dimer. Crystals of III are monoclinic, of space group $P2_1/c$ with $a = 12.143$ (2) Å, $b = 14.675$ (3) Å, $c = 14.240$ (3) Å, $\beta = 106.49$ (2)°, and $Z = 2$ dimers. The Te–S distances range from 2.441 (2) to 3.040 (2) Å.

Introduction

Te(II), with four valence electrons and four two-electron-donor ligands, adopts a pseudooctahedral configuration with lone pairs of electrons above and below the coordination plane.[1] The ligands may be considered to contain two orthogonal three-center, four-electron bonding systems. Such systems may be very unsymmetrical when the opposing ligands are different in character. This "trans influence" in Te(II) complexes leads to bond-length variations which are much larger than those observed in the corresponding transition metal complexes.

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(1) Reviews of the chemistry and geometry of related examples of Te(II) and other linear three-center systems of the sixth main group have been presented by Foss, Vikane, and Hauge (see following references).

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