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The Diselenotetrathionate Dianion: Preparation and X-ray Structures of Two Crystalline Modifications of $[Co(en)_2Cl_2]_2Se_2S_2O_6 \cdot H_2O$

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trans-Dichlorobis(ethylenediamine)cobalt(III) diselenotetrathionate hydrate has been crystallized in space groups $P2_1/n$ and $C2/c$, and both crystal structures have been solved and refined with Mo Kα diffractometer data to R values of 0.039 and 0.068 with 4085 and 2833 observed reflections, respectively. The prismatic needle form is space group $P2_1/n$ with a = 12.5576 (23) Å, b = 16.6963 (32) Å, c = 13.3334 (17) Å, β = 99.815 (16)°, and Z = 4. The extended plate form is space group $C2/c$ with a = 48.1366 (40) Å, b = 9.8713 (11) Å, c = 12.4315 (10) Å, β = 100.458 (6)°, and Z = 8. The sulfur–selenium chain of the anion is unbranched and nonplanar. Some significant distances and angles for the $P2_1/n$ and $C2/c$ forms, respectively, are as follows: S(1)–Se(2) = 2.2728 (18) and 2.2947 (30) Å; Se(2)–Se(3) = 2.2928(10) and 2.3047 (23) Å; Se(3)–S(4) = 2.2779 (19) and 2.282(4) Å; S(1)–Se(2)—Se(3) = 102.85 (5) and 102.24 (10)°; Se(2)–Se(3)–S(4) = 101.66 (5) and 103.01 (12)°. The dihedral angles S(1)–Se(2)–Se(3)–S(4) are 88.5 and 92.6°, respectively.

Introduction

The polythionate ions, which are sulfur chains terminated in both ends by sulfonate groups, have been known since 1840. The stereochemistry and bonding in the polythionates are investigated through numerous crystal structure determinations of tri-, tetra-, penta-, and hexathionates. The structure determinations also include tri-, tetra-, and pentathionates with one dibonded sulfur atom substituted by selenium and pentathionates with one dibonded sulfur atom substituted by tellurium.[2]

The only known disubstituted polythionate, diselenium tetrathionate, was reported in 1955.[3] As a part of our investigation of polythionates and polyselenium compounds,[4] we have now determined the structures of two crystalline modifications of *trans*-dichlorobis(ethylenediamine)cobalt(III) diselenotetrathionate hydrate, $[Co(en)_2Cl_2]_2Se_2S_2O_6 \cdot H_2O$.

Experimental Section

trans-Dichlorobis(ethylenediamine)cobalt(III) diselenotetrathionate hydrate may be prepared from potassium diselenotetrathionate[5] and *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride or by the interaction of selenous and sulfurous acids[6] in the presence of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride. Two different crystalline modifications result.

One gram of $[Co(en)_2Cl_2]Cl$ dissolved in 5 mL of water was added to a solution of 1 g of $K_2Se_2S_2O_6 \cdot H_2O$ dissolved in 10 mL of 0.1 M H_2SeO_3 and the resulting solution allowed to stand at 0 °C. After 1.5–2 h, the crystals were filtered, washed with ethanol and ether, and air-dried. The green crystals were primarily elongated plates with a very few needlelike prisms (space groups $C2/c$ and $P2_1/n$, respectively; vide infra).

One milliliter of concentrated HCl, then 3 g of $[Co(en)_2Cl_2]Cl$, and then 10 mL of 0.5 M $KHSO_3$ were added to 10 mL of 0.5 M H_2SeO_3. Crystallization began very soon and yielded only the needlelike prism ($P2_1/n$) modification. This is the first time this method has been used to prepare *trans*-dichlorobis(ethylenediamine)cobalt(III) diselenotetrathionate.

The prismatic needle form of $[Co(en)_2Cl_2]_2Se_2S_2O_6 \cdot H_2O$ is monoclinic, of space group $P2_1/n$, with a = 12.5576 (23) Å, b = 16.6963 (32) Å, c = 13.3334 (17) Å, β = 99.815 (16)°, V = 2755 Å^3, mol wt 836.2, D(obsd) = 1.99 g cm^{-3}, D(calcd for Z = 4) = 2.016 g cm^{-3}, and μ = 46.84 cm^{-1} for Mo Kα radiation.

The data crystal, mounted on a glass fiber parallel to [100], was bounded by the faces (011), (0$\bar{1}\bar{1}$), (0$\bar{1}$1), (01$\bar{1}$), (100), and ($\bar{1}$00) with the distances between parallel faces respectively 0.123, 0.123, and 0.508 mm. Intensity data and the lattice and orientation parameters were measured with a Siemens automatic off-line quarter-circle single-crystal diffractometer equipped with Mo X-ray tube and Nb filter. Intensity data were measured on two independent octants to a maximum θ = 29° with the "*five-value*" procedure, a scan width of 0.70° in θ, and a maximum scan time of 24 s/deg θ. Three standard reflections were measured for every 50 data reflections. Analysis of the reference reflection intensities yielded an instability factor of 4.6%. The intensities of the standards had decayed to 92% of their original value by the end of the data collection, and the decay was essentially linear with time. Next, 20 reasonably intense reflections between 20 and 24° in θ were carefully centered in θ and ω for the accurate determination of lattice parameters. The data were corrected for Lorentz, polarization, and decay effects and assigned weights based on counting statistics and instrument instability.[7] Of the 6528 reflections measured, 2443 were less than three standard deviations above background. Calculations were performed on a Univac 1110 computer with the X-ray System[8] and locally written programs. Scattering factors were those of Cromer and Mann[9] and of Stewart et al.[10] Atoms S and heavier were corrected for anomalous dispersion.

With four formula units in the unit cell, all atoms may occupy general positions. Symbolic addition and E-map calculations readily revealed Co, Se, Cl, and S positions, and the remaining nonhydrogen atoms were quickly revealed by structure factor, electron density calculations. Full-matrix, least-squares refinement of an isotropic model converged to an R factor of 11.5%. An absorption correction, where the factors ranged from 1.6 to 1.8, and the introduction of anisotropic thermal parameters and hydrogens in assumed positions led to the final model with weighted and unweighted R factors of 4.6% and 3.9%, respectively. The anisotropic refinement was performed in three blocks. All parameter shifts in the last refinement cycle were less than 1% of the corresponding estimated standard deviation. The standard deviation of an observation of unit weight was 1.58, and the largest peak in the subsequent difference electron density map was 1.2 e Å^{-3}.

The extended-plate form of $[Co(en)_2Cl_2]_2Se_2S_2O_6 \cdot H_2O$ is monoclinic, of space group $C2/c$ with a = 48.1366 (40) Å, b = 9.8713 (11) Å, c = 12.4315 (10) Å, β = 100.458 (6)°, V = 5809 Å^3, mol wt 836.2, D(calcd for Z = 8) = 1.910 g cm^{-3}, and μ = 44.3 cm^{-1} for Mo Kα radiation.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $P2_1/n$ *trans*-Dichlorobis(ethylenediamine)cobalt(III) Diselenotetrathionate Hydrate[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.284 79 (13)	−0.085 62 (9)	0.341 47 (12)	490 (9)	469 (9)	373 (8)	3 (7)	95 (7)	0 (7)
Se(2)	0.226 02 (7)	0.007 42 (4)	0.443 87 (5)	820 (5)	409 (4)	432 (4)	122 (3)	110 (3)	31 (3)
Se(3)	0.350 16 (7)	−0.002 25 (4)	0.590 89 (5)	814 (5)	473 (4)	463 (4)	−242 (4)	58 (4)	−36 (3)
S(4)	0.270 96 (14)	−0.094 39 (10)	0.680 51 (12)	561 (10)	456 (9)	360 (8)	−78 (7)	64 (7)	−45 (7)
O(1)	0.261 5 (4)	−0.163 04 (27)	0.380 4 (4)	735 (34)	445 (26)	735 (34)	94 (24)	252 (26)	18 (23)
O(2)	0.399 5 (4)	−0.075 2 (4)	0.346 6 (4)	626 (35)	1096 (48)	867 (42)	−196 (34)	312 (30)	−29 (35)
O(3)	0.217 3 (5)	−0.066 60 (32)	0.246 9 (4)	1100 (46)	708 (35)	468 (30)	255 (32)	−92 (29)	−41 (25)
O(4)	0.318 2 (5)	−0.076 02 (29)	0.783 86 (35)	1077 (44)	583 (31)	417 (28)	−168 (29)	−153 (28)	−12 (23)
O(5)	0.157 2 (4)	−0.081 5 (4)	0.656 9 (4)	585 (33)	1142 (48)	623 (34)	35 (31)	195 (26)	103 (32)
O(6)	0.301 6 (4)	−0.172 19 (27)	0.647 4 (4)	866 (38)	409 (26)	792 (37)	−151 (25)	358 (29)	−83 (23)
O(7)	0.271 3 (4)	−0.026 62 (30)	0.059 1 (4)	583 (30)	597 (30)	739 (35)	79 (24)	232 (26)	−9 (25)
Co(1)	0.483 82 (6)	0.214 57 (5)	−0.001 11 (5)	288 (4)	415 (4)	250 (4)	34 (3)	69 (3)	49 (3)
Cl(1)	0.377 31 (12)	0.162 84 (10)	0.102 84 (11)	467 (9)	586 (9)	371 (8)	−89 (7)	178 (6)	19 (7)
Cl(2)	0.594 31 (12)	0.261 59 (10)	−0.103 48 (11)	406 (8)	717 (11)	366 (8)	−10 (7)	151 (6)	114 (7)
N(1)	0.439 7 (4)	0.322 87 (29)	0.026 3 (4)	395 (27)	428 (28)	450 (30)	2 (22)	64 (22)	−57 (22)
C(1)	0.525 5 (8)	0.363 7 (5)	0.101 9 (8)	1074 (74)	717 (57)	1061 (79)	−70 (53)	−517 (63)	−242 (53)
C(2)	0.589 0 (7)	0.306 1 (6)	0.164 3 (6)	737 (57)	1108 (72)	633 (56)	93 (50)	−185 (45)	−361 (50)
N(2)	0.600 5 (4)	0.227 98 (32)	0.115 5 (4)	363 (27)	646 (35)	340 (28)	−17 (25)	45 (21)	48 (24)
N(3)	0.523 8 (4)	0.104 40 (31)	−0.029 1 (4)	482 (31)	467 (29)	427 (30)	132 (24)	85 (23)	49 (24)
C(3)	0.468 5 (5)	0.081 6 (4)	−0.136 2 (5)	534 (40)	577 (41)	436 (38)	112 (33)	31 (30)	−99 (30)
C(4)	0.355 4 (5)	0.116 7 (4)	−0.149 2 (5)	514 (39)	507 (37)	447 (38)	20 (31)	57 (30)	−57 (29)
N(4)	0.366 3 (4)	0.202 97 (29)	−0.118 65 (35)	386 (27)	437 (27)	296 (26)	47 (22)	13 (20)	−20 (20)
Co(2)	0.475 70 (6)	0.307 09 (4)	0.532 81 (5)	283 (4)	362 (4)	246 (4)	−39 (3)	46 (3)	43 (3)
Cl(3)	0.372 63 (11)	0.242 21 (9)	0.629 44 (10)	368 (7)	510 (8)	328 (7)	−65 (6)	106 (6)	75 (6)
Cl(4)	0.575 31 (13)	0.373 26 (10)	0.434 19 (11)	527 (9)	634 (10)	374 (8)	−192 (8)	140 (7)	82 (7)
N(5)	0.516 5 (4)	0.204 00 (29)	0.480 86 (34)	374 (27)	444 (27)	335 (28)	−18 (22)	58 (21)	−52 (20)
C(5)	0.432 4 (8)	0.177 7 (5)	0.394 4 (7)	1179 (78)	681 (54)	741 (61)	160 (52)	−566 (58)	−278 (45)
C(6)	0.361 0 (7)	0.237 0 (6)	0.354 5 (6)	650 (50)	1315 (80)	618 (54)	351 (52)	−212 (42)	−575 (54)
N(6)	0.353 6 (4)	0.306 84 (30)	0.418 74 (35)	350 (26)	512 (30)	311 (26)	−48 (22)	9 (20)	53 (22)
N(7)	0.599 0 (4)	0.305 40 (28)	0.645 09 (34)	333 (25)	448 (27)	282 (25)	−39 (21)	8 (19)	27 (20)
C(7)	0.616 5 (6)	0.386 4 (4)	0.688 6 (5)	662 (45)	462 (37)	527 (42)	−75 (34)	−48 (34)	−140 (31)
C(8)	0.510 6 (6)	0.425 0 (5)	0.688 9 (6)	548 (45)	837 (55)	677 (50)	31 (40)	50 (37)	−393 (43)
N(8)	0.434 4 (4)	0.408 82 (29)	0.589 7 (4)	483 (30)	423 (28)	424 (30)	25 (24)	86 (23)	0 (23)

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

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $C2/c$ *trans*-Dichlorobis(ethylenediamine)cobalt(III) Diselenotetrathionate Hydrate[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.072 50 (6)	0.636 61 (29)	0.075 67 (22)	580 (19)	507 (16)	433 (15)	−38 (14)	124 (14)	−2 (13)
Se(2)	0.097 936 (31)	0.484 10 (12)	0.193 68 (11)	779 (9)	519 (7)	623 (8)	−6 (7)	128 (7)	64 (6)
Se(3)	0.140 078 (32)	0.473 92 (14)	0.130 80 (12)	736 (9)	624 (8)	756 (9)	77 (7)	115 (7)	−104 (7)
S(4)	0.167 05 (8)	0.633 3 (4)	0.234 08 (28)	674 (23)	759 (23)	642 (22)	69 (19)	52 (18)	−5 (18)
O(1)	0.044 28 (17)	0.592 0 (9)	0.084 6 (7)	556 (55)	846 (63)	719 (58)	−74 (47)	198 (45)	76 (48)
O(2)	0.080 26 (19)	0.767 4 (8)	0.121 6 (7)	817 (62)	479 (46)	633 (50)	−117 (43)	35 (44)	−62 (41)
O(3)	0.079 86 (19)	0.617 2 (9)	−0.031 1 (6)	794 (64)	927 (66)	501 (50)	17 (52)	168 (45)	−58 (46)
O(4)	0.193 10 (21)	0.611 5 (12)	0.194 1 (10)	573 (67)	1330 (97)	1443 (106)	96 (65)	110 (65)	−242 (82)
O(5)	0.168 28 (26)	0.600 3 (12)	0.348 0 (8)	1320 (98)	1178 (87)	601 (63)	−93 (72)	−87 (62)	130 (59)
O(6)	0.154 26 (20)	0.761 8 (9)	0.205 1 (7)	953 (70)	658 (56)	619 (53)	−6 (52)	173 (48)	−72 (45)
Co(1)	0.121 706 (30)	−0.006 29 (14)	0.418 13 (10)	469 (9)	496 (9)	282 (7)	38 (7)	102 (6)	8 (6)
Cl(1)	0.090 99 (6)	0.070 60 (29)	0.270 59 (19)	527 (17)	636 (17)	305 (13)	34 (14)	85 (12)	43 (12)
Cl(2)	0.152 19 (6)	−0.083 07 (31)	0.563 97 (21)	594 (19)	734 (19)	376 (14)	97 (16)	40 (13)	43 (14)
N(1)	0.114 67 (19)	−0.192 2 (9)	0.367 7 (7)	523 (59)	536 (53)	452 (53)	−10 (46)	149 (45)	−34 (43)
N(2)	0.153 15 (19)	0.016 7 (9)	0.338 9 (7)	472 (56)	606 (59)	470 (53)	−80 (48)	180 (45)	−65 (45)
N(3)	0.128 33 (20)	0.180 6 (9)	0.468 7 (7)	606 (63)	576 (56)	404 (51)	−116 (50)	177 (47)	−9 (44)
N(4)	0.090 88 (20)	−0.027 6 (8)	0.498 5 (7)	572 (59)	522 (53)	302 (43)	−21 (47)	104 (41)	49 (40)
C(1)	0.087 46 (24)	−0.244 1 (13)	0.398 2 (9)	521 (76)	797 (83)	463 (65)	−106 (66)	187 (57)	−73 (63)
C(2)	0.166 3 (4)	0.151 0 (16)	0.362 0 (16)	1192 (140)	914 (116)	1552 (162)	−451 (107)	982 (130)	−582 (114)
C(3)	0.149 9 (4)	0.244 7 (16)	0.409 7 (17)	1064 (132)	782 (102)	1837 (180)	−224 (95)	976 (132)	−487 (115)
C(4)	0.084 41 (27)	−0.173 4 (12)	0.506 5 (10)	629 (80)	607 (73)	573 (74)	−82 (65)	238 (64)	5 (60)
Co(2)	0.000 00	0.094 74 (21)	0.250 00	404 (12)	556 (13)	304 (10)	0	93 (9)	0
Cl(3)	−0.025 23 (6)	0.095 10 (29)	0.078 02 (20)	521 (17)	678 (18)	319 (13)	2 (14)	62 (12)	9 (12)
N(5)	−0.024 79 (19)	0.241 0 (9)	0.286 6 (7)	498 (58)	552 (57)	511 (52)	58 (48)	182 (44)	2 (47)
N(6)	0.023 91 (19)	−0.048 5 (9)	0.208 8 (7)	487 (57)	548 (55)	453 (49)	12 (45)	178 (44)	−7 (43)
C(5)	−0.016 53 (25)	0.369 4 (12)	0.239 9 (10)	652 (77)	562 (71)	568 (72)	76 (62)	169 (66)	10 (61)
C(6)	0.015 59 (24)	−0.179 9 (12)	0.256 7 (10)	488 (69)	614 (72)	714 (80)	−26 (60)	244 (66)	59 (65)
Co(3)	0.250 00	0.250 00	0.000 00	528 (15)	1022 (20)	614 (15)	−32 (15)	118 (12)	−4 (15)
Cl(4)	0.278 41 (9)	0.402 1 (5)	0.098 8 (4)	726 (25)	1210 (33)	963 (29)	−162 (24)	91 (21)	−209 (25)
N(7)	0.246 26 (24)	0.370 4 (14)	−0.127 8 (10)	545 (72)	1440 (121)	852 (89)	8 (76)	136 (64)	404 (83)
N(8)	0.282 95 (25)	0.168 1 (15)	−0.049 7 (10)	690 (79)	1298 (108)	738 (82)	−16 (76)	148 (66)	−103 (75)
C(7)	0.273 5 (5)	0.347 (4)	−0.180 7 (18)	1493 (217)	3263 (392)	1006 (168)	475 (250)	595 (156)	701 (215)
C(8)	0.285 3 (4)	0.216 1 (18)	−0.162 0 (14)	1176 (149)	1001 (130)	863 (119)	147 (110)	297 (106)	99 (97)
O(7)	0.482 47 (20)	0.152 3 (9)	0.016 0 (7)	856 (66)	724 (58)	642 (57)	−34 (51)	167 (49)	−20 (46)

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

Table III. Bond Distances (Å) and Angles (Deg) for the $P2_1/n$ Modification of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Diselenotetrathionate Hydrate

(a) Bond Distances

S(1)–Se(2)	2.2728 (18)	Se(3)–S(4)	2.2779 (19)
Se(2)–Se(3)	2.2928 (10)		
S(1)–O(1)	1.441 (5)	S(1)–O(3)	1.429 (5)
S(1)–O(2)	1.441 (6)		
S(4)–O(4)	1.437 (5)	S(4)–O(6)	1.445 (5)
S(4)–O(5)	1.426 (5)		
Co(1)–Cl(1)	2.2558 (18)	N(1)–C(1)	1.506 (10)
Co(1)–Cl(2)	2.2474 (18)	C(1)–C(2)	1.423 (13)
Co(1)–N(1)	1.944 (5)	C(2)–N(2)	1.477 (11)
Co(1)–N(2)	1.959 (5)	N(3)–C(3)	1.526 (8)
Co(1)–N(3)	1.959 (5)	C(3)–C(4)	1.519 (9)
Co(1)–N(4)	1.970 (4)	C(4)–N(4)	1.497 (8)
Co(2)–Cl(3)	2.2533 (17)	N(5)–C(5)	1.491 (10)
Co(2)–Cl(4)	2.2529 (19)	C(5)–C(6)	1.380 (13)
Co(2)–N(5)	1.956 (5)	C(6)–N(6)	1.459 (11)
Co(2)–N(6)	1.967 (4)	N(7)–C(7)	1.473 (8)
Co(2)–N(7)	1.962 (4)	C(7)–C(8)	1.478 (11)
Co(2)–N(8)	1.966 (5)	C(8)–N(8)	1.519 (9)

(b) Bond Angles

S(1)–Se(2)–Se(3)	102.85 (5)	Se(2)–Se(3)–S(4)	101.66 (5)
Se(3)–S(4)–O(4)	102.29 (23)	Se(2)–S(1)–O(1)	106.86 (23)
Se(3)–S(4)–O(5)	107.05 (25)	Se(2)–S(1)–O(2)	108.29 (26)
Se(3)–S(4)–O(6)	106.49 (24)	Se(2)–S(1)–O(3)	99.99 (24)
O(4)–S(4)–O(5)	114.46 (34)	O(1)–S(1)–O(2)	110.71 (33)
O(4)–S(4)–O(6)	113.39 (30)	O(1)–S(1)–O(3)	112.96 (31)
O(5)–S(4)–O(6)	112.13 (33)	O(2)–S(1)–O(3)	116.9 (4)
Cl(1)–Co(1)–Cl(2)	177.62 (7)	Cl(3)–Co(2)–Cl(4)	178.69 (6)
Cl(1)–Co(1)–N(1)	91.32 (16)	Cl(3)–Co(2)–N(5)	89.45 (15)
Cl(1)–Co(1)–N(2)	89.87 (16)	Cl(3)–Co(2)–N(6)	89.61 (15)
Cl(1)–Co(1)–N(3)	87.45 (17)	Cl(3)–Co(2)–N(7)	90.70 (15)
Cl(1)–Co(1)–N(4)	90.51 (15)	Cl(3)–Co(2)–N(8)	88.82 (16)
Cl(2)–Co(1)–N(1)	90.82 (16)	Cl(4)–Co(2)–N(5)	91.12 (15)
Cl(2)–Co(1)–N(2)	89.22 (16)	Cl(4)–Co(2)–N(6)	89.24 (15)
Cl(2)–Co(1)–N(3)	90.44 (17)	Cl(4)–Co(2)–N(7)	90.46 (15)
Cl(2)–Co(1)–N(4)	90.43 (15)	Cl(4)–Co(2)–N(8)	90.63 (16)
N(1)–Co(1)–N(2)	86.73 (21)	N(5)–Co(2)–N(6)	86.63 (19)
N(1)–Co(1)–N(3)	178.31 (21)	N(5)–Co(2)–N(7)	92.12 (19)
N(1)–Co(1)–N(4)	92.42 (20)	N(5)–Co(2)–N(8)	177.94 (21)
N(2)–Co(1)–N(3)	94.42 (21)	N(6)–Co(2)–N(7)	178.71 (21)
N(2)–Co(1)–N(4)	179.08 (22)	N(6)–Co(2)–N(8)	94.48 (20)
N(3)–Co(1)–N(4)	86.44 (20)	N(7)–Co(2)–N(8)	86.78 (20)
Co(1)–N(1)–C(1)	110.6 (4)	Co(2)–N(5)–C(5)	109.8 (4)
N(1)–C(1)–C(2)	110.6 (7)	N(5)–C(5)–C(6)	114.5 (7)
C(1)–C(2)–N(2)	115.2 (7)	C(5)–C(6)–N(6)	116.7 (7)
Co(1)–N(2)–C(2)	109.6 (4)	Co(2)–N(6)–C(6)	109.7 (4)
Co(1)–N(3)–C(3)	108.8 (4)	Co(2)–N(7)–C(7)	109.4 (4)
N(3)–C(3)–C(4)	106.1 (5)	N(7)–C(7)–C(8)	109.1 (6)
C(3)–C(4)–N(4)	107.4 (5)	C(7)–C(8)–N(8)	110.8 (6)
Co(1)–N(4)–C(4)	109.41 (34)	Co(2)–N(8)–C(8)	108.7 (4)

Table IV. Bond Distances (Å) and Angles (Deg) for the $C2/c$ Modification of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Diselenotetrathionate Hydrate

(a) Bond Distances

S(1)–Se(2)	2.2947 (30)	Se(3)–S(4)	2.282 (4)
Se(2)–Se(3)	2.3047 (23)		
S(1)–O(1)	1.451 (9)	S(4)–O(4)	1.447 (12)
S(1)–O(2)	1.433 (8)	S(4)–O(5)	1.444 (10)
S(1)–O(3)	1.447 (9)	S(4)–O(6)	1.427 (9)
Co(3)–N(7)	1.966 (13)	N(7)–C(7)	1.588 (30)
Co(3)–N(8)	1.977 (13)	C(7)–C(8)	1.41 (4)
Co(3)–Cl(4)	2.241 (4)	C(8)–N(8)	1.499 (23)
Co(2)–N(5)	1.978 (9)	C(5)–C(5)′	1.565 (17)
Co(2)–N(6)	1.949 (9)	N(6)–C(6)	1.512 (15)
Co(2)–Cl(3)	2.2590 (23)	C(6)–C(6)′	1.480 (16)
N(5)–C(5)	1.478 (15)		
Co(1)–N(1)	1.949 (9)	N(1)–C(1)	1.517 (16)
Co(1)–N(2)	1.963 (10)	N(2)–C(2)	1.475 (19)
Co(1)–N(3)	1.957 (9)	N(3)–C(3)	1.513 (22)
Co(1)–N(4)	1.944 (10)	N(4)–C(4)	1.479 (15)
Co(1)–Cl(1)	2.2674 (27)	C(1)–C(4)	1.547 (17)
Co(1)–Cl(2)	2.2469 (29)	C(2)–C(3)	1.415 (26)

(b) Bond Angles

S(1)–Se(2)–Se(3)	102.24 (10)	Se(2)–Se(3)–S(4)	103.01 (12)
Se(2)–S(1)–O(1)	98.7 (4)	O(1)–S(1)–O(2)	115.0 (6)
Se(2)–S(1)–O(2)	105.44 (34)	O(1)–S(1)–O(3)	114.7 (5)
Se(2)–S(1)–O(3)	108.0 (4)	O(2)–S(1)–O(3)	113.2 (5)
Se(3)–S(4)–O(4)	98.3 (5)	O(4)–S(4)–O(5)	114.8 (7)
Se(3)–S(4)–O(5)	108.3 (5)	O(4)–S(4)–O(6)	114.0 (7)
Se(3)–S(4)–O(6)	107.2 (4)	O(5)–S(4)–O(6)	112.8 (6)
N(7)–Co(3)–N(8)	87.5 (5)	C(8)–N(8)–Co(3)	111.3 (10)
N(7)–Co(3)–Cl(4)	89.7 (4)	N(7)–C(7)–C(8)	113.7 (23)
N(8)–Co(3)–Cl(4)	90.1 (4)	C(7)–C(8)–N(8)	110.2 (17)
C(7)–N(7)–Co(3)	106.6 (13)		
Cl(3)–Co(2)–N(5)	88.46 (25)	N(5)–Co(2)–N(6)′	93.4 (4)
Cl(3)–Co(2)–N(6)	89.65 (25)	N(6)–Co(2)–N(6)′	87.0 (4)
Cl(3)–Co(2)–N(5)′	91.41 (25)	Co(2)–N(5)–C(5)	108.6 (7)
Cl(3)–Co(2)–N(6)′	90.48 (25)	Co(2)–N(6)–C(6)	107.9 (7)
Cl(3)–Co(2)–Cl(3)′	179.82 (17)	N(5)–C(5)–C(5)′	106.0 (9)
N(5)–Co(2)–N(6)	178.1 (4)	N(6)–C(6)–C(6)′	106.9 (9)
N(5)–Co(2)–N(5)′	86.2 (4)		
Cl(1)–Co(1)–Cl(2)	179.79 (19)	N(2)–Co(1)–N(3)	87.5 (4)
Cl(1)–Co(1)–N(1)	90.31 (25)	N(2)–Co(1)–N(4)	179.2 (3)
Cl(1)–Co(1)–N(2)	90.25 (26)	N(3)–Co(1)–N(4)	91.8 (4)
Cl(1)–Co(1)–N(3)	89.34 (26)	Co(1)–N(1)–C(1)	110.2 (7)
Cl(1)–Co(1)–N(4)	90.31 (25)	Co(1)–N(2)–C(2)	110.4 (10)
Cl(2)–Co(1)–N(1)	89.53 (25)	Co(1)–N(3)–C(3)	108.9 (8)
Cl(2)–Co(1)–N(2)	89.64 (27)	Co(1)–N(4)–C(4)	109.2 (7)
Cl(2)–Co(1)–N(3)	90.82 (26)	N(1)–C(1)–C(4)	106.7 (9)
Cl(2)–Co(1)–N(4)	89.81 (25)	N(2)–C(2)–C(3)	114.7 (15)
N(1)–Co(1)–N(2)	93.0 (4)	N(3)–C(3)–C(2)	114.4 (13)
N(1)–Co(1)–N(3)	179.4 (4)	N(4)–C(4)–C(1)	109.0 (10)
N(1)–Co(1)–N(4)	87.7 (4)		

The data crystal, mounted on a glass fiber nearly parallel to [100], was bounded by faces (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001), and ($01\bar{2}$) with the distances between parallel faces 0.042 and 0.190 mm. The remaining faces were 0.184 and 0.215 mm, respectively, from a common origin within the crystal. Data were collected as before to a maximum $\theta = 25°$ and yielded 2833 observed reflections in the 5334 measured reflections. The instability factor was 9% because the lowest and highest θ standard reflections decreased by 10% in intensity while the middle θ standard reflection increased by 15%. Data were collected in six approximately equal-volume shells in θ so any effects of anisotropic decay should be minimized. The data were corrected for Lorentz and polarization effects and assigned weights as before.[7]

With 8 formula units in the unit cell, all atoms may occupy general positions. Symbolic addition eventually led to the correct positions for Co, Se, Cl, and S, and the remaining nonhydrogen atoms were located by structure factor, difference Fourier calculations. One Co is in a center of symmetry and another on a twofold axis while the third Co and all other atoms occupy general positions. Isotropic refinement converged to an unweighted R factor of 11%. An absorption correction where the factors varied from 1.2 to 2.4 and the introduction of anisotropic thermal parameters for Co, Se, Cl, and S lowered this R to 7.5% while the final unweighted and weighted R's for the completely anisotropic refinement, including hydrogen in assumed positions, were 6.8% and 9.2%, respectively. The final refinement cycles were performed in two blocks. All parameter shifts in the last cycle were less than 12% of the associated estimated standard deviations. The standard deviation of an observation of unit weight was 1.62, and the largest peak in the subsequent difference electron density map was 1.3 e Å^{-3}.

Tables I and II contain atomic parameters for the two structures, and Tables III and IV contain the bond distances and angles.

Discussion

The tetrathionate ion consists of two dibonded sulfur atoms and two sulfonate groups, $^{-}O_3S–S–S–SO_3^{-}$. In the diselenotetrathionate ion the two dibonded atoms are substituted by selenium. The geometries of the ions in the two crystalline modifications of the $[Co(en)_2Cl_2]$ salt are illustrated in Figure 1. No symmetry is crystallographically required for the ions, but the bond lengths, bond angles, and orientations of the sulfonate groups are nearly the same in the two halves, and

Table V. Bond Lengths (Å) and Angles (Deg) in Pairs of Acyclic X–S–S–X and X–Se–Se–X Compounds

compd	S–S or Se–Se	av angle at S or Se	dihedral angle	Δ	ref
$S_2(SO_3)_2^{2-}$	2.007 (4)	103.7 (2)	90–102	0.288 (4)	11–13
$Se_2(SO_3)_2^{2-}$	2.295 (1)	102.4 (1)	90.6		
$S_2(CH_3)_2$	2.022 (3)	104.1 (3)	83.9	0.304 (5)	14
$Se_2(CH_3)_2$	2.326 (4)	98.9 (2)	87.5		15
$S_2(C_6H_5)_2$	2.023 (1)	105.9 (1)	96.2	0.267 (10)	16
$Se_2(C_6H_5)_2$	2.29 (1)	106.1 (2.0)	82.0		17
$S_2(C_6H_4Cl\text{-}p)_2$	2.039 (1)	106.5 (1)	76.4	0.294 (15)	18
$Se_2(C_6H_4Cl\text{-}p)_2$	2.333 (15)	101.1	74.5		19
$S_2(C_6F_5)_2$	2.059 (4)	101.3 (3)	76.5	0.260 (6)	20
$Se_2(C_6F_5)_2$	2.319 (4)	98.9 (6)	75.3		20
$S_2(NC_4H_8O)_2$	2.069 (1)	111.9 (1)	95.8	0.277 (2)	21
$Se_2(NC_4H_8O)_2$	2.346 (1)	109.1 (1)	94.7		4

so the ions possess a pseudo-twofold symmetry axis.

With the assumption of twofold symmetry, the four-membered S–Se–Se–S chain may be characterized by two bond lengths, one bond angle, and one dihedral angle. These dimensions are nearly the same in the two crystalline modifications of the salt, and the weighted mean values are 2.295 (1) Å for the Se–Se bond, 2.279 (1) Å for the Se–S bond, 102.4 (1)° for the Se–Se–S bond angle, and 90.6° for the S–Se–Se–S dihedral angle.

It has long been noted that a 90° dihedral angle for a polysulfur chain would be a conformation of minimum repulsion between lone pairs of electrons on adjacent sulfur atoms and that this conformation would also be an optimum for lone pair → dπ bonding.[2] The dihedral angles, S–Se–Se–S, are 88.5 and 92.6° for the $P2_1/n$ and $C2/c$ salts, respectively. The corresponding dihedral angles, S–S–S–S, in $BaS_4O_6{\cdot}2H_2O$,[11] $Na_2S_4O_6{\cdot}2H_2O$,[12] and $[Cu(2,2'\text{-bpy})_2]_2S_4O_6$[13] are 90, 90.4, and 102.0°. There is no significant difference in the central S–S bond lengths of these tetrathionates.

Bonds between dibonded Se atoms, while not very common, are documented for $-Se_2-$, $-Se_3-$, $-Se_4-$, and Se_8 compounds.[4] With reference to the great number of known acyclic X–S–S–X compounds, one must expect to find that the bond lengths of corresponding Se compounds are influenced by such factors as the electronegativity of the terminal groups, great deviations from 90° of the dihedral angle, and, in the case of aromatic terminal groups, the orientation of the aromatic plane.[2] In Table V are listed dimensions of pairs of acyclic X–S–S–X and X–Se–Se–X compounds in order to compare –S–S– and –Se–Se– bond lengths. Here the factors mentioned above are eliminated as in each pair the terminal groups are the same, they have nearly the same orientation, and the deviations of the dihedral angles from 90° are small or nearly the same. The weighted mean value of the differences in the –Se–Se– and –S–S– bond lengths of these pairs of compounds is 0.280 (2) Å. This is very close to the difference between the overall average of three different forms of *cyclo*-octaselenium[4,22] and three different forms of *cyclo*-octasulfur,[23] 2.334 Å − 2.045 Å = 0.289 Å.

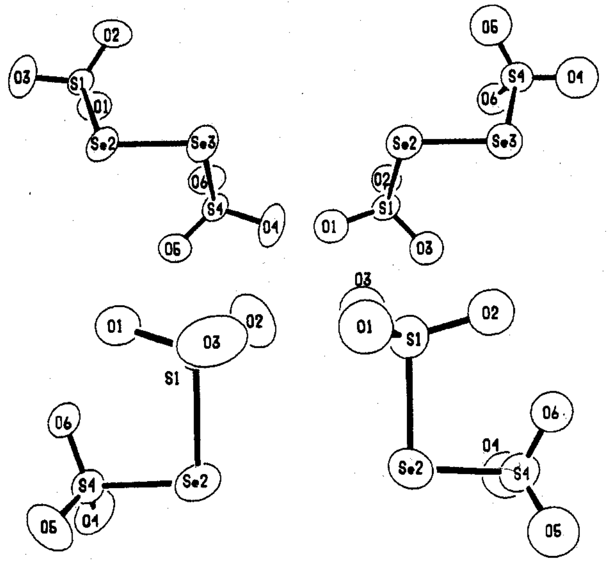

Figure 1. Two views each of the anions in the $P2_1/n$ modification (left) and $C2/c$ modification (right) of $[Co(en)_2Cl_2]_2Se_2S_2O_6{\cdot}H_2O$. The views at the top are down the pseudo-twofold axes. The views at the bottom are down the Se(2)–Se(3) bonds with Se(3) hidden and so show the dihedral angles S(1)–Se(2)–Se(3)–S(4). Thermal ellipsoids are at 50% probability.

The weighted mean value of the four independent $-Se-SO_3$ bonds in the two forms of diselenotetrathionate is 2.279 (1) Å. This might be compared to the $-S-SO_3$ bonds in tetra-, penta-, selenopenta-, telluropenta-, and hexathionates, which have a weighted mean value of 2.110 (1) Å.[24] These bonds are significantly longer than the bonds between the corresponding dibonded atoms, which are 2.153 (4)–2.181 (3) Å for the –Se–S– bond in selenopentathionate and 2.005 (4)–2.069 (3) Å for the –S–S– bond in tetra-, penta-, and hexathionates.[13,24] The difference between the $-Se-SO_3$ and $-S-SO_3$ bond lengths is 0.169 Å, which is significantly more than half the differences between –Se–Se– and –S–S– bonds cited above, 0.280–0.289 Å.

The bond angles at Se determined in the present study, 101.66 (5)–103.01 (12)°, are smaller than those found in the selenopentathionates,[2] 103.06 (11)–104.9 (2)°, smaller than the average value cited by Abrahams,[25] 104°, but distinctly larger than the angle at Se in selenotrithionate,[26] 97.90 (4)°. It is tempting to speculate that the attachment of the relatively electronegative $-SO_3$ group to Se causes the use of more nearly pure p orbitals of the Se atom.

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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.

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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**).

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

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

$$\underset{\mathbf{1}}{[CH_2(OH)S_2O_3H \cdot C_6H_5(N{=}CH_2)(N(CH_3)_2)SH]_3}$$

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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