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The Selenotetrathionate Dianion: Preparation and X-ray Structures of $K_2SeS_3O_6 \cdot H_2O$ and $[Co(en)_2Cl_2]_2SeS_3O_6$

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Crystal and molecular structures of potassium selenotetrathionate hydrate and *trans*-dichlorobis(ethylenediamine)cobalt(III) selenotetrathionate have been determined from Mo Kα diffractometer data and refined by least squares to R values of 0.034 and 0.055 for 1606 and 3059 observed reflections, respectively. Crystals of $K_2SeS_3O_6 \cdot H_2O$ (I) are monoclinic, of space group $P2_1/c$ with $a = 5.6687$ (13) Å, $b = 18.6704$ (50) Å, $c = 9.5317$ (21) Å, $\beta = 90.783$ (23)°, and $Z = 4$. Crystals of $[Co(en)_2Cl_2]_2SeS_3O_6$ (II) are monoclinic, of space group $P2_1/n$ with $a = 6.5843$ (14) Å, $b = 33.3523$ (55) Å, $c = 12.2291$ (10) Å, $\beta = 106.830$ (9)°, and $Z = 4$. In both cases the anion was found to be disordered. The sulfur–selenium chain of the selenotetrathionate dianion is unbranched and nonplanar. Significant distances and angles for I and II, respectively, are as follows: S(1)–Se = 2.2552 (13) and 2.2495 (26) Å; Se–S(3) = 2.1851 (17) and 2.145 (8) Å; S(3)–S(4) = 2.2027 (11) and 2.171 (8) Å; S(1)–Se–S(3) = 102.11 (4) and 100.36 (20)°; Se–S(3)–S(4) = 103.81 (3) and 102.24 (29)°. The dihedral angles S(1)–Se–S(3)–S(4) are 81.16 and 119.07°, respectively.

Introduction

The first of the polythionate anions reported was the trithionate[2] in 1840, and the tetrathionate[3] was reported a year later. Blomstrand[4] and Mendeleev[5] correctly proposed the polythionate structures to contain unbranched chalcogen chains, but there was a long time lapse before this proposal was proved.

The chemistry[6-9] and structures[10,11] of the tri-,[12] tetra-,[13,14] penta-,[15-18] monosubstituted penta-,[19-25] and hexathionates[26,27] have been elaborated in the past 15–20 years especially. One of the characteristic features[28] of the higher polythionates and of organic noncyclic polysulfide compounds is 70–110° dihedral angles within the polychalcogen chain. The explanation of these approximately 90° dihedral angles is probably the same as for the approximately 90° dihedral angles found in hydrogen peroxide and the S_8 molecule.[29] A very interesting problem now is to document and rationalize the causes and consequences of (large) deviations from the "optimum" 90° dihedral angle.

One outstanding example of adherence to the "90° rule" is the tetrathionate[14] dianion with a 90.4° dihedral angle. An outstanding exception to the "rule" is the peroxydisulfate dianion[30] with a 180° dihedral angle. With tetrathionate and peroxydisulfate related by the exchange of two congener atoms and yet unrelated structurally, it seemed interesting to investigate some of the other members of the series. To this end we report here the preparation and structures of two salts of the selenotetrathionate dianion which show very different dihedral angles.

Experimental Section

Potassium selenotetrathionate hydrate was prepared from $K_2SeS_2O_6$ and $K_2SeS_4O_6 \cdot {}^3/_2H_2O$ according to published procedures.[31] *trans*-Dichlorobis(ethylenediamine)cobalt(III) selenotetrathionate was prepared by metathesis of $K_2SeS_3O_6 \cdot H_2O$ and $[Co(en)_2Cl_2]Cl$. The preparation of high-quality crystals proved to be a challenge, and so we report the details of recrystallization. For $K_2SeS_3O_6 \cdot H_2O$, 2 g of impure $K_2SeS_3O_6 \cdot H_2O$ and 0.15–0.20 g of $K_2SeS_4O_6 \cdot {}^3/_2H_2O$ were dissolved in 7.2 mL of 0.2 N HCl. The solution was warmed gently to 40 °C and then allowed to stand at 0° for several days. Clear colorless crystals formed and were filtered and washed with 50% ethanol, pure ethanol, and ether. For the preparation of $[Co(en)_2Cl_2]_2SeS_3O_6$, 9 g of recrystallized $K_2SeS_3O_6 \cdot H_2O$ and 1 g of $K_2SeS_4O_6 \cdot {}^3/_2H_2O$ were dissolved in 10 mL of 0.2 N HCl, and 15 mL of H_2O which contained 5 g of $[Co(en)_2Cl_2]Cl$ was added. Green needlelike crystals, which form and grow slowly, may be filtered and washed with ethanol and ether.

$K_2SeS_3O_6 \cdot H_2O$ is monoclinic, of space group $P2_1/c$ with $a = 5.6687$ (13) Å, $b = 18.6704$ (50) Å, $c = 9.5317$ (21) Å, $\beta = 90.783$ (23)°, $V = 1008.7$ Å^3, mol wt 367.4, D(obsd) = 2.43 g cm^{-3}, D(calcd for $Z = 4$) = 2.42 g cm^{-3}, and $\mu = 60$ cm^{-1} for Mo Kα radiation.

The data crystal was mounted on a glass fiber nearly parallel to the a axis and 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 0.13, 0.13, and 0.31 mm, respectively. Intensity data and the lattice and orientation parameters were measured with a Siemens off-line automatic quarter-circle single-crystal diffractometer with Nb-filtered Mo Kα radiation. Intensities were measured in two independent octants to a maximum θ of 25° with the "*five-value*" procedure, a scan width of 0.7° in θ and a maximum scan rate of 24 s (deg θ)$^{-1}$. Four standard reflections were measured after every 50 data reflections. The standards indicated an instrument instability of 2% and no significant decay of the crystal during data collection. The data were corrected

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Potassium Selenotetrathionate Hydrate[a]

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.225 31 (18)	0.214 62 (6)	0.368 99 (11)	263 (5)	312 (5)	214 (5)	14 (4)	16 (4)	−33 (4)
Se(2)	0.278 53 (12)	0.103 55 (4)	0.456 86 (7)	350 (4)	380 (4)	423 (4)	41 (3)	119 (3)	88 (3)
S(3)	0.647 83 (27)	0.082 54 (9)	0.408 63 (16)	273 (8)	336 (9)	328 (9)	31 (6)	−10 (6)	−30 (7)
S(4)	0.636 97 (19)	0.048 96 (16)	0.187 06 (12)	306 (6)	252 (5)	372 (6)	8 (4)	33 (4)	−33 (5)
O(1)	0.427 9 (5)	0.257 55 (17)	0.410 08 (34)	300 (17)	441 (19)	409 (18)	−73 (14)	−12 (14)	−41 (15)
O(2)	0.205 1 (6)	0.206 45 (18)	0.218 22 (32)	634 (23)	448 (19)	225 (17)	87 (17)	−8 (15)	−50 (14)
O(3)	0.008 4 (5)	0.236 70 (18)	0.432 28 (34)	286 (16)	445 (19)	417 (19)	52 (14)	81 (14)	−70 (15)
O(4)	0.846 0 (7)	0.005 88 (22)	0.179 8 (4)	551 (24)	635 (24)	617 (25)	332 (20)	−66 (19)	−177 (21)
O(5)	0.652 9 (7)	0.113 38 (17)	0.103 8 (4)	698 (25)	309 (17)	418 (19)	−64 (17)	130 (17)	6 (15)
O(6)	0.415 9 (7)	0.011 95 (21)	0.162 6 (4)	547 (22)	591 (23)	473 (21)	−276 (19)	−47 (17)	−19 (18)
O(7)	0.168 1 (8)	0.610 04 (21)	0.748 8 (5)	712 (28)	451 (22)	927 (32)	49 (20)	−267 (24)	−264 (23)
K(1)	0.147 42 (19)	0.112 32 (6)	0.003 05 (11)	492 (6)	336 (5)	355 (6)	12 (5)	−20 (4)	−45 (4)
K(2)	0.709 78 (17)	0.256 33 (5)	0.160 48 (10)	327 (5)	335 (5)	327 (5)	−28 (4)	44 (4)	−22 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)/100000]$.

for Lorentz and polarization effects and weights assigned according to standard formulas.[32,33] Of the 1771 reflections measured, 165 were less than three standard deviations above background. Finally 20 reasonably intense reflections over 20° θ were carefully centered in θ and ω for the calculation of accurate lattice parameters. Calculations were performed on a Univac 1110 computer with the X-ray System[34] and locally written programs. Scattering factors were those of Cromer and Mann[35] and of Stewart et al.[36] and included anomalous dispersion for elements sulfur and heavier.

The structure was solved by symbolic addition and Fourier synthesis followed by structure factor, difference electron density calculations. Full-matrix least-squares refinement of an isotropic undisordered model converged with an *R* factor of 12.5%, and it was clear from the temperature factors that the selenotetrathionate anion was disordered. At this point the data were corrected for absorption effects, and we introduced a disorder model for the two central dibonded chalcogen atoms of the anion. The model described two atom sites, each with its own temperature factor(s), and one population parameter which gave the partial occupancy for each of the two orientations of the Se–S fragment. To our very great delight it never became necessary to consider separate positions for the sulfonate groups. Refinement continued smoothly until, with all atoms anisotropic, it converged with weighted and unweighted *R* factors of 3.8% and 3.4%. In the final refinement cycle the largest shift was less than 6% of the associated standard deviation, and the standard deviation of an observation of unit weight was 1.03. The largest peak in the subsequent difference electron density map was 0.74 e Å^{-3}.

$[Co(en)_2Cl_2]_2SeS_3O_6$ is monoclinic, of space group $P2_1/n$ with a = 6.5843 (14) Å, b = 33.3523 (55) Å, c = 12.2291 (10) Å, β = 106.830 (9)°, V = 2571 Å^3, mol wt 771.3, D(obsd) = 1.96 g cm^{-3}, D(calcd for Z = 4) = 1.99 g cm^{-3}, and μ = 35.5 cm^{-1} for Mo Kα radiation.

The data crystal was mounted on a glass fiber nearly parallel to the *a* axis and was bounded by the faces (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (031), (0$\bar{3}\bar{1}$), (0$\bar{3}$1), and (03$\bar{1}$) with parallel faces separated by 0.17, 0.062, 0.086, and 0.086 mm, respectively. The data collection and reduction procedures were the same as above except that data were collected to 28° θ, three standard reflections were measured, and 21 reflections over 18° θ were used in the determination of accurate lattice parameters. Of the 6783 reflections measured, 3059 were more than three standard deviations above the background radiation. The standards indicated an instrument instability of 1.4% and no significant decay of the crystal during data collection.

The crystallographic independent unit contains one formula unit, but the pattern of systematic weakness seen in the Weissenberg photographs suggested that at least one of the two independent $Co(en)_2Cl_2$ cations occupies centers of symmetry separated by $c/2$. All atoms heavier than oxygen were readily located with a Patterson map, and all C, N, and O atoms appeared in the subsequent difference electron density maps. Isotropic refinement of an undisordered model converged to an *R* factor of 9.9%, and it was again apparent that the central dibonded chalcogen atoms were disordered. An absorption correction was performed and, with the disorder model of the potassium salt and all atoms anisotropic, the refinement finally converged with weighted and unweighted *R* factors of 4.0% and 5.5%. The anisotropic refinement cycles were performed in two blocks, and the anisotropic temperature factors which were coupled to the population parameter converged slowly. In the final refinement cycle, one shift was 23% of its associated standard deviation, and the rest were much smaller. The standard deviation of an observation of unit weight was 1.70. The largest peak in the subsequent difference electron density map was 0.76 e Å^{-3}.

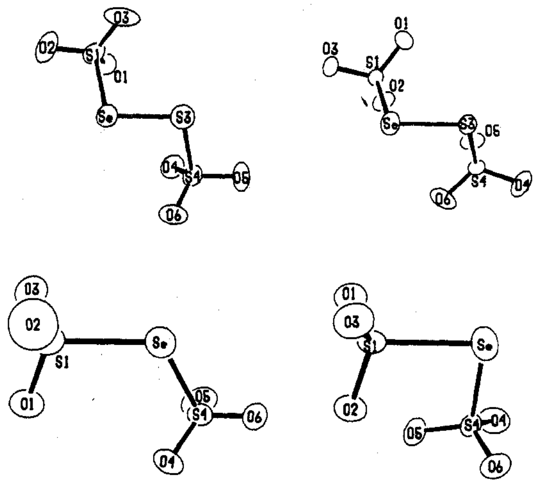

Figure 1. Two views each of the anions in $K_2SeS_3O_6 \cdot H_2O$ (right) and $[Co(en)_2Cl_2]_2SeS_3O_6$ (left). The views at the top are down the pseudo-twofold axes. The views at the bottom are down the Se–S(3) bonds with S(3) hidden and so illustrate the differences in the dihedral angles S(1)–Se–S(3)–S4. Thermal ellipsoids are at 50% probability.

There is no indication in the final results of either structure determination of disorder in the $-SO_3$ groups. The entire $SeS_3O_6^{2-}$ anion must be disordered in both structures, but, since anisotropic refinement shows approximately spherical electron density for the atom sites involved, the addition of more parameters seems pointless.

The population of the major component in the disorder models above were 70.2% and 57.4% for the potassium and cobalt salts, respectively. In both cases the standard deviation of the population was less than 0.2%. A 50% population would have required consideration of a $S_4O_6^{2-}$, $Se_2S_2O_6^{2-}$ disorder.

Tables I and II contain atomic parameters for the two structures, and Tables III and IV contain the bond distances and angles. Figure 1 contains drawings of the anions.

Discussion

At first glance the anion geometries reflect the patterns observed before in chalcogen chain and sulfonate compounds, but a close examination of bond lengths and angles and dihedral angles reveals some startling differences.

The four-membered chalcogen chain may be characterized by three bond lengths, two bond angles, and one dihedral angle.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for *trans*-Dichlorobis(ethylenediamine)cobalt(III) Selenotetrathionate[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	−0.159 19 (34)	0.346 16 (7)	−0.070 99 (18)	393 (12)	515 (5)	373 (12)	45 (11)	120 (10)	−80 (11)
Se(2)	0.034 12 (24)	0.391 76 (5)	0.051 04 (13)	421 (10)	445 (11)	414 (10)	−65 (8)	196 (7)	4 (7)
S(3)	0.059 9 (4)	0.362 72 (7)	0.211 00 (19)	538 (14)	501 (15)	460 (13)	140 (12)	121 (11)	16 (11)
S(4)	−0.094 07 (33)	0.405 37 (7)	0.295 19 (17)	347 (11)	457 (14)	315 (11)	60 (11)	55 (9)	−10 (10)
O(1)	−0.371 3 (8)	0.347 46 (17)	−0.060 4 (5)	332 (32)	508 (40)	502 (36)	28 (29)	153 (27)	7 (30)
O(2)	−0.135 5 (11)	0.361 80 (22)	−0.176 0 (5)	806 (50)	1020 (60)	419 (39)	−114 (46)	295 (36)	−19 (38)
O(3)	−0.056 3 (10)	0.308 27 (18)	−0.035 8 (6)	551 (43)	402 (42)	970 (55)	157 (34)	17 (38)	−228 (36)
O(4)	−0.317 1 (8)	0.407 91 (19)	0.233 6 (5)	309 (32)	700 (47)	514 (38)	47 (32)	22 (28)	−22 (33)
O(5)	−0.048 4 (11)	0.385 67 (20)	0.404 5 (5)	1006 (56)	718 (51)	334 (35)	305 (43)	157 (36)	206 (34)
O(6)	0.015 9 (9)	0.442 80 (17)	0.298 2 (5)	466 (37)	362 (39)	668 (42)	−9 (31)	107 (33)	−106 (30)
N(1)	0.234 8 (10)	0.024 00 (20)	0.115 2 (5)	312 (37)	453 (47)	240 (35)	20 (33)	5 (29)	6 (31)
N(2)	−0.035 7 (10)	0.051 63 (19)	−0.079 6 (5)	350 (38)	384 (44)	309 (37)	101 (33)	70 (31)	49 (31)
N(3)	0.011 2 (10)	0.058 52 (18)	0.495 6 (5)	348 (35)	329 (39)	238 (32)	−25 (33)	21 (27)	14 (30)
N(4)	0.246 3 (9)	−0.002 97 (20)	0.633 1 (5)	281 (33)	378 (42)	247 (32)	6 (33)	2 (26)	−28 (30)
C(1)	0.274 9 (14)	0.065 99 (26)	0.075 9 (7)	442 (53)	386 (57)	532 (56)	−22 (44)	46 (44)	120 (45)
C(2)	0.068 3 (13)	0.082 33 (26)	0.004 0 (7)	454 (54)	435 (62)	421 (51)	3 (44)	84 (44)	20 (42)
C(3)	−0.130 3 (12)	0.072 11 (26)	0.382 9 (6)	318 (46)	481 (57)	319 (45)	−46 (41)	−6 (36)	62 (40)
C(4)	0.326 2 (12)	−0.045 46 (25)	0.648 6 (6)	263 (43)	388 (54)	430 (49)	6 (39)	70 (37)	−8 (40)
Cl(1)	−0.225 99 (31)	0.019 89 (7)	0.096 22 (16)	326 (11)	594 (15)	320 (11)	71 (10)	148 (9)	11 (10)
Cl(3)	1.001 68 (30)	0.251 46 (6)	0.299 02 (17)	278 (10)	491 (14)	408 (12)	−6 (9)	23 (9)	−51 (10)
N(5)	0.793 9 (10)	0.217 28 (21)	0.069 8 (5)	397 (40)	489 (48)	271 (35)	89 (35)	158 (31)	33 (32)
N(6)	0.710 5 (10)	0.179 98 (19)	0.248 6 (5)	382 (38)	306 (40)	279 (35)	54 (31)	107 (30)	21 (29)
N(7)	0.634 7 (10)	0.289 98 (20)	0.129 0 (5)	346 (39)	403 (46)	437 (42)	12 (34)	101 (33)	156 (34)
N(8)	0.552 6 (10)	0.254 77 (19)	0.306 3 (5)	361 (37)	301 (42)	290 (36)	56 (31)	36 (29)	4 (29)
C(5)	0.869 3 (17)	0.174 14 (29)	0.093 0 (8)	826 (77)	444 (64)	771 (75)	58 (58)	506 (64)	17 (55)
C(6)	0.734 2 (15)	0.154 02 (26)	0.154 2 (7)	766 (69)	323 (55)	514 (58)	62 (50)	324 (52)	−62 (44)
C(7)	0.485 7 (14)	0.311 98 (28)	0.176 1 (7)	493 (57)	555 (70)	500 (60)	186 (50)	100 (48)	67 (47)
C(8)	0.540 5 (15)	0.300 01 (28)	0.300 8 (7)	594 (61)	502 (64)	359 (51)	171 (51)	18 (46)	16 (44)
Cl(2)	0.213 41 (30)	−0.003 42 (7)	0.385 47 (15)	342 (11)	582 (15)	309 (10)	−17 (11)	144 (9)	20 (10)
Cl(4)	0.344 85 (31)	0.220 09 (7)	0.079 89 (16)	301 (10)	558 (15)	333 (11)	−58 (10)	31 (9)	−14 (10)
Co(1)	0.000 00	0.000 00	0.000 00	238 (7)	393 (10)	214 (7)	57 (7)	53 (6)	23 (7)
Co(2)	0.000 00	0.000 00	0.500 00	236 (7)	334 (9)	209 (7)	−70 (7)	64 (6)	−28 (7)
Co(3)	0.672 74 (15)	0.235 612 (32)	0.189 14 (8)	238 (5)	353 (6)	235 (5)	−4 (5)	60 (4)	33 (5)

[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 Potassium Selenotetrathionate Hydrate

(a) Bond Distances

S(1)-Se(2)	2.2552 (13)	S(4)-O(4)	1.435 (4)
Se(2)-S(3)	2.1851 (17)	S(4)-O(5)	1.444 (4)
S(3)-S(4)	2.2027 (11)	S(4)-O(6)	1.447 (4)
S(1)-O(1)	1.4499 (32)		
S(1)-O(2)	1.4482 (32)		
S(1)-O(3)	1.4376 (32)		

(b) Bond Angles

S(3)-Se(2)-S(1)	102.11 (4)	O(1)-S(1)-O(2)	112.22 (20)
Se(2)-S(3)-S(4)	103.808 (34)	O(1)-S(1)-O(3)	114.03 (19)
Se(2)-S(1)-O(1)	107.84 (14)	O(2)-S(1)-O(3)	112.95 (20)
Se(2)-S(1)-O(2)	106.27 (15)	O(4)-S(4)-O(5)	112.49 (23)
Se(2)-S(1)-O(3)	102.63 (14)	O(4)-S(4)-O(6)	116.01 (23)
S(3)-S(4)-O(4)	101.18 (17)	O(5)-S(4)-O(6)	111.68 (22)
S(3)-S(4)-O(5)	106.73 (14)		
S(3)-S(4)-O(6)	107.67 (16)		

With the assumption of twofold symmetry, crystallographically required only in $Na_2S_4O_6 \cdot 2H_2O$,[14] the chains may be characterized by two bond lengths, one bond angle, and one dihedral angle.

The two bond lengths of a symmetric tetrathionate are the "internal" and "external" bonds. The internal bond is between two dibonded chalcogen atoms while the external bond is between a dibonded chalcogen and a tetrabonded chalcogen (a sulfonate sulfur atom). Some characteristic lengths for the internal and external bonds, respectively, are as follows: in tetrathionate[14] itself, 2.019 and 2.116 Å; in diselenotetrathionates,[37] 2.295 and 2.279 Å. The selenotrithionate ion,[38] with only an external Se–S bond, shows 2.257 Å, and the selenopentathionate dianion[19–21] displays internal Se–S distances ranging from 2.153 to 2.181 Å. The penta-[15–25] and hexathionates[26,27] have $S-SO_3$ bond lengths rather uniformly near 2.11 Å and internal S–S bond lengths in the range 2.02–2.07 Å.

For the selenotetrathionates the internal Se–S bonds are 2.145 and 2.185 Å, respectively, for the cobalt and potassium salts. One may compare these values with the corresponding lengths in the selenopentathionates[19–21] (2.175-Å average) or with the average of average internal S–S and Se–Se bonds (2.159 Å). An attempt to extrapolate our bond distances to a 100% population parameter gave unrealistic results. The difference between the two independently determined internal Se–S bond lengths is 0.040 (6) Å or 7σ. The usual Gaussian translation to confidence level probably does not apply because of the disorder model used. We conclude that the internal Se–S bond length of selenotetrathionate is not significantly outside the range indicated by related structures or reasonable estimates.

The presence of disorder obfuscates the interpretation of the external bond lengths of selenotetrathionate. A typical $S-SO_3$ distance is 2.11 Å, and the known $Se-SO_3$ distances are 2.257[38]–2.295 Å,[37] which leads us to predict 2.20 Å for the $Se(S)-SO_3$ bond length. The averages found for the cobalt and potassium salts, respectively, are 2.210 and 2.229 Å, which we feel are reasonably near the predicted value.

The previously known $S-S-SO_3$ bond angles[12–27] range from 100 to 105°. The selenotetrathionates have corresponding bond angles from 100 to 104°.

The dihedral angles, S(1)–Se(2)–S(3)–S(4), of the Co and K salts are 81.16 and 119.07°, respectively. The dihedral

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(37) Foust, A. S.; Janickis, V; Marøy, K. *Inorg. Chem.*, companion article in this issue.

(38) Foust, A. S.; Janickis, V. *Inorg. Chem.*, companion note in this issue.

Table IV. Bond Distances (Å) and Angles (Deg) for *trans*-Dichlorobis(ethylenediamine)cobalt(III) Selenotetrathionate

(a) Bond Distances			
S(1)-Se(2)	2.2495 (26)	S(3)-S(4)	2.171 (8)
Se(2)-S(3)	2.145 (8)		
S(1)-O(1)	1.440 (6)	S(1)-O(3)	1.440 (6)
S(1)-O(2)	1.436 (7)		
S(4)-O(4)	1.446 (5)	S(4)-O(6)	1.438 (6)
S(4)-O(5)	1.441 (6)		
N(1)-C(1)	1.528 (11)	Co(1)-N(1)	1.937 (5)
N(2)-C(2)	1.469 (10)	Co(1)-N(2)	1.958 (6)
N(3)-C(3)	1.493 (9)	Co(1)-Cl(1)	2.2478 (22)
N(4)-C(4)	1.504 (10)	Co(2)-N(3)	1.954 (6)
C(1)-C(2)	1.493 (11)	Co(2)-N(4)	1.939 (5)
C(3)-C(4)	1.522 (11)	Co(2)-Cl(2)	2.2558 (22)
N(5)-C(5)	1.522 (12)	Co(3)-N(5)	1.953 (7)
N(6)-C(6)	1.487 (12)	Co(3)-N(6)	1.982 (6)
N(7)-C(7)	1.470 (12)	Co(3)-N(7)	1.945 (7)
N(8)-C(8)	1.512 (11)	Co(3)-N(8)	1.935 (7)
C(5)-C(6)	1.479 (16)	Co(3)-Cl(4)	2.2458 (20)
C(7)-C(8)	1.515 (12)	Co(3)-Cl(3)	2.2562 (20)
(b) Bond Angles			
S(3)-Se(2)-S(1)	100.36 (20)	Se(2)-S(3)-S(4)	102.24 (29)
Se(2)-S(1)-O(1)	107.29 (25)	S(3)-S(4)-O(4)	109.57 (31)
Se(2)-S(1)-O(2)	99.24 (29)	S(3)-S(4)-O(5)	98.1 (4)
Se(2)-S(1)-O(3)	105.56 (25)	S(3)-S(4)-O(6)	106.3 (4)
O(1)-S(1)-O(2)	115.4 (4)	O(4)-S(4)-O(5)	114.7 (4)
O(1)-S(1)-O(3)	112.6 (4)	O(4)-S(4)-O(6)	113.0 (4)
O(2)-S(1)-O(3)	115.0 (5)	O(5)-S(4)-O(6)	113.8 (4)
C(1)-N(1)-Co(1)	108.9 (4)	C(2)-C(1)-N(1)	108.0 (7)
C(2)-N(2)-Co(1)	107.6 (4)	N(2)-C(2)-C(1)	108.5 (7)
C(3)-N(3)-Co(2)	108.1 (4)	N(3)-C(3)-C(4)	108.2 (7)
C(4)-N(4)-Co(2)	109.3 (4)	N(4)-C(4)-C(3)	106.2 (6)
C(5)-N(5)-Co(3)	109.8 (6)	N(5)-C(5)-C(6)	108.2 (9)
C(6)-N(6)-Co(3)	106.9 (5)	N(6)-C(6)-C(5)	110.0 (7)
C(7)-N(7)-Co(3)	110.2 (5)	N(7)-C(7)-C(8)	105.8 (7)
C(8)-N(8)-Co(3)	108.9 (5)	N(8)-C(8)-C(7)	107.6 (7)
N(2)-Co(1)-Cl(1)	89.90 (21)	Cl(1)-Co(1)-N(1)	90.40 (21)
N(2)-Co(1)-N(1)	87.35 (25)		
N(3)-Co(2)-Cl(2)	89.91 (22)	N(3)-Co(2)-N(4)′	87.42 (25)
N(4)-Co(2)-Cl(2)	89.93 (20)		
Cl(3)-Co(3)-N(5)	89.38 (18)	Cl(3)-Co(3)-Cl(4)	179.76 (17)
Cl(3)-Co(3)-N(6)	90.23 (18)	N(5)-Co(3)-N(6)	86.91 (29)
Cl(3)-Co(3)-N(7)	90.17 (19)	N(5)-Co(3)-N(7)	92.57 (30)
Cl(3)-Co(3)-N(8)	90.54 (18)	N(5)-Co(3)-N(8)	178.95 (27)
N(5)-Co(3)-Cl(4)	90.77 (18)	N(6)-Co(3)-N(7)	179.34 (28)
N(6)-Co(3)-Cl(4)	89.96 (18)	N(6)-Co(3)-N(8)	94.14 (27)
N(7)-Co(3)-Cl(4)	89.64 (19)	N(7)-Co(3)-N(8)	86.38 (28)
N(8)-Co(3)-Cl(4)	89.30 (18)		

angles of a chalcogen chain are parameters which can be determined with a standard deviation which is far lower than the observed range for these parameters. One hopes that "dramatic" variations in dihedral angle admit to simple explanations. Among the many attempts to explain variations in S–S bond lengths there has been postulated[28] a correlation between dihedral angle and bond length. Among the factors which might couple dihedral angle and bond length have been named $p\pi$–$p\pi$ repulsion,[29] $p\pi$–$d\pi$ bonding,[39,40] and electronegativity and donor–acceptor properties[41] as they affect the size and energy of the orbitals involved. Multiple determinations of a dihedral angle in different salts of the same polythionate include *cis*-pentathionate,[15-17] 107–110°, *cis*-selenopentathionate,[19,21] 106–107°, and *trans*-telluropentathionate,[22,24,25] 78–99°. In all studied polythionates the range of dihedral angles is from below 72° (found in $S_6O_6^{2-}$ [27]) to above 119° (present study). The present study seems to demonstrate clearly that the dihedral angle, in polythionates at least, is determined to a large extent by packing forces although there is a tendency toward 90° angles probably because of $p\pi$–$p\pi$ repulsion. The deviations seem entirely reasonable since tens of degrees rotation against a barrier of 10 kcal mol^{-1} is energetically approximately equivalent to hundreths of an angstrom motion in a reasonable ionic potential. Wells has made similar observations concerning peroxides.[42]

One might still hope to find a correlation between dihedral angle and bond lengths even though the dihedral angles are largely dictated by the environment. The "rule" has been that large deviations from a 90° dihedral angle correspond to large chalcogen–chalcogen bond lengths. In the two salts reported here, the largest dihedral angle corresponds to the "distinctly" shorter Se–S bond length. Others[43,44] have found more reliable correlations between dihedral angles and bond lengths, but we find that, in the polythionates at least, there must be a variety of factors which contribute to the chalcogen–chalcogen bond lengths.

The potassium salt has the following ionic environment: each oxygen atom has at least one contact to K(1) while O(4) and O(5) have two; K(1) is thus nine-coordinate, and it has contacts to six sulfonate groups and one H_2O oxygen; K(2) has two contacts to each of O(1), O(2), and O(3) and one contact each to O(5) and O(7); K(2) is thus eight-coordinate, and it has contacts to five sulfonate groups and one H_2O oxygen; the water of hydration has contacts to the two potassium ions and to two sulfonate oxygen atoms. The situation in the cobalt salt is even more complex. It seems tendentious to attempt quantitative justification for the dihedral angles observed.

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Supplementary Material Available: Listings of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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