by PPh_3, PMe_3, PEt_3, and $AsPh_3$[26] or when the deprotonated sulfhydryl group is replaced by the thioketonic[27,28] group, the complexes tend to be monomeric or at most dimeric. This is presumably due to the lower Lewis acidity of mercury when it is coordinated to the methyl or PR_3 and AsR_3 groups. The present polymeric structure with the ionic ligands fits well into this scheme.

The fact that the steroid remains essentially unchanged by complexation to mercury leads us to suggest that spiroxazone protection against mercury poisoning is effected via direct complexation and removal of mercury rather than via some conformational change of the steroid which in turn triggers some other defence mechanism.

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Registry No. $HgBr(C_{22}H_{31}O_2S)$, 64968-01-0.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Notes

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The Selenotrithionate Dianion: Crystal and Molecular Structure of $K_2SeS_2O_6$

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Trithionate,[2] $S_3O_6^{2-}$, was the first of the polythionates reported (1840) and the first of the polythionates examined crystallographically (1934). Selenotrithionate, $SeS_2O_6^{2-}$, was the first substituted polythionate reported (1865), and it has been followed by an impressive list of Se- and Te-substituted tetra- and pentathionates.

Our interest in the polythionates and our concurrent studies of mono- and diselenotetrathionates prompted us to examine monoselenotrithionate. Earlier studies[3] had shown that $BaSeS_2O_6{\cdot}2H_2O$ probably has the same anion geometry as $K_2S_3O_6{\cdot}2H_2O$ although the space groups are different. Space groups of several salts of $SeS_2O_6^{2-}$ have been reported,[3] and there is no isomorphism with corresponding salts of $S_3O_6^{2-}$.

Selenotrithionate, for which we report structural details, is a fundamental member of the substituted polythionates and a member of the homologous series disulfate, $OS_2O_6^{2-}$, trithionate, $S_3O_6^{2-}$, and selenotrithionate, $SeS_2O_6^{2-}$. The space group of $K_2SeS_2O_6$ has been reported[3] previously.

Experimental Section

Potassium selenotrithionate was prepared as described by Rathke.[4] $K_2SeS_2O_6$ is monoclinic, of space group $P2_1/c$ with a = 9.5032 (12) Å, b = 5.9375 (10) Å, c = 15.3132 (21) Å, β = 110.418 (12)°, V = 809.8 Å^3, mol wt 317.3, D(obsd) = 2.57 g cm^{-3}, D(calcd for Z = 4) = 2.60 g cm^{-3}, and μ = 64.5 cm^{-1} for Mo Kα radiation.

The data crystal was mounted on a glass fiber nearly parallel to [010]. Distances between the parallel bounding faces (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001), and ($00\bar{1}$) were 0.058, 0.446, and 0.172 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 radiation. Lattice parameters were obtained by careful measurement of the θ and ω values of 17 reflections with θ between 21.5 and 25°. Intensity data were collected in two independent octants to a maximum θ of 25° with the "*five-value*" procedure, a scan width of 0.7° θ, and a maximum scan rate of 24 s/deg θ. Three reference reflections were measured after every 50 data reflections and indicated an instability factor of 1.4% and no discernible decay of the crystal during data collection. The data were corrected for Lorentz and polarization effects and assigned weights according to standard formulas.[5] Of the 1401 independent reflections, 136 were less than three standard deviations above background. Calculations were performed on a Univac 1110 computer with the X-ray System[6] and locally written programs. Scattering factors[7] were those of Cromer and Mann and of Stewart et al., with atoms S and heavier corrected for anomalous dispersion.

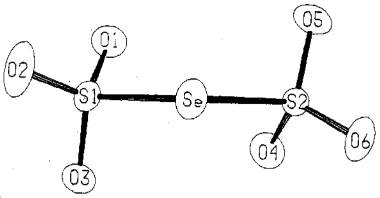

Figure 1. A view of the selenotrithionate down the pseudo-twofold axis. Thermal ellipsoids are at 50% probability.

Solution and Refinement of the Structures

The positions of the K, Se, and S atoms and three O atoms were revealed by direct methods and the remaining O atoms were located in the subsequent electron density map. Full-matrix least-squares refinement with all atoms isotropic lowered the R factor to 11.1%. An absorption correction, where the factors ranged from 1.43 to 3.21, and more isotropic refinement lowered R to 7.8%. Full-matrix least-squares refinement with all atoms anisotropic lowered R to 2.2%, and the refinement of a secondary extinction parameter, clearly warranted by the strong reflections, lowered R to 2.0%.

From the final refinement cycle, the unweighted and weighted R factors were 2.0% and 2.8%, respectively, the standard deviation of an observation of unit weight was 2.6, and all parameter shifts were less than 3% of the associated estimated standard deviation. A final difference electron density calculation showed no peaks over 0.5 e Å^{-3}.

Discussion

The structure consists of essentially discrete ions situated in general positions of the space group. K(1) is coordinated by six oxygen atoms at distances of 2.66–2.86 Å, and K(2) is coordinated by seven oxygens at distances of 2.66–2.96 Å. The selenotrithionate has, in addition to the O···K contacts, a 3.78-Å Se···Se contact propagated by the 2_1 axis.

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

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	0.874 03 (4)	0.168 12 (6)	0.200 90 (2)	228 (2)	456 (3)	279 (2)	78 (2)	78 (1)	0 (2)
S(1)	0.661 32 (9)	0.290 83 (13)	0.090 46 (5)	268 (4)	218 (5)	205 (4)	12 (3)	56 (3)	5 (3)
S(2)	0.808 87 (9)	0.239 82 (15)	0.326 47 (5)	239 (4)	297 (5)	203 (4)	−10 (4)	37 (3)	−8 (3)
O(1)	0.539 71 (25)	0.231 5 (4)	0.122 88 (16)	212 (13)	405 (15)	360 (14)	6 (11)	47 (11)	101 (11)
O(2)	0.664 25 (31)	0.164 2 (5)	0.010 18 (16)	559 (18)	483 (17)	228 (12)	91 (14)	70 (12)	−93 (11)
O(3)	0.676 39 (28)	0.530 1 (4)	0.081 92 (16)	500 (16)	217 (14)	435 (14)	12 (12)	182 (13)	74 (11)
O(4)	0.734 23 (29)	0.455 8 (4)	0.313 00 (15)	508 (15)	241 (13)	342 (13)	9 (12)	199 (12)	−16 (10)
O(5)	0.709 42 (27)	0.057 9 (4)	0.329 70 (16)	430 (14)	260 (13)	322 (12)	−38 (11)	155 (11)	29 (10)
O(6)	0.950 16 (31)	0.234 5 (6)	0.402 21 (18)	332 (16)	991 (24)	260 (13)	10 (16)	−43 (12)	−14 (15)
K(1)	0.220 67 (9)	0.235 20 (13)	0.032 67 (5)	290 (4)	309 (4)	244 (4)	7 (3)	38 (3)	16 (3)
K(2)	0.446 88 (9)	0.278 13 (13)	0.319 12 (5)	323 (4)	254 (4)	379 (4)	7 (3)	91 (3)	17 (3)

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

Table II. Bond Distances (Å) and Angles (Deg) for Selenotrithionate

(a) Bond Distances

Se–S(1)	2.2566 (8)	S(2)–O(4)	1.4448 (26)
Se–S(2)	2.2567 (10)	S(2)–O(5)	1.4474 (27)
S(1)–O(1)	1.4515 (29)	S(2)–O(6)	1.4361 (24)
S(1)–O(2)	1.4495 (29)		
S(1)–O(3)	1.4385 (25)		

(b) Bond Angles

S(1)–Se–S(2)	97.896 (34)	Se–S(2)–O(4)	108.23 (11)
Se–S(1)–O(1)	106.09 (9)	Se–S(2)–O(5)	105.36 (11)
Se–S(1)–O(2)	101.01 (11)	Se–S(2)–O(6)	103.11 (14)
Se–S(1)–O(3)	107.19 (9)	O(4)–S(2)–O(5)	111.91 (16)
O(1)–S(1)–O(2)	114.66 (16)	O(4)–S(2)–O(6)	114.13 (18)
O(1)–S(1)–O(3)	112.79 (17)	O(5)–S(2)–O(6)	113.19 (17)
O(2)–S(1)–O(3)	113.78 (16)		

A symmetric selenotrithionate may be described by a Se–S bond distance, a S–Se–S bond angle, and the rotation of the $-SO_3$ from some arbitrary position. That arbitrary position could be the C_{2v} conformation, wherein Se, the two S atoms, and two O atoms lie in a planar W, or it could be the C_2 conformation, wherein two oxygen atoms are in trans arrangement across the SeS_2 plane and are as far from the plane as possible. The choice of a reference conformation may reflect one's prejudice as to the conformation of "free" trithionate. Since the symmetry of $S_3O_6^{2-}$ in $K_2S_3O_6$[8] is C_s and nearly C_{2v}, it might seem natural to describe the geometry of $SeS_2O_6^{2-}$ as distorted from C_{2v} by approximately equal rotations of the $-SO_3$ groups around the Se–S bonds. However, an examination of the dihedral angles of the known polythionate anions reveals that in many cases the $-SO_3$ orientation conforms most nearly to the "trans C_2" conformation.

Thus, the selenotrithionate dianion appears as a Se atom coordinated by two $-SO_3$ groups at an angle of 97.90 (4)° and distances of 2.257 (1) Å. The dianion contains no crystallographic symmetry elements but displays approximate C_2 geometry. The orientation of the $-SO_3$ groups is distinctly different from that found for $S_3O_6^{2-}$, and the pentachalcogen chain O(3)–S(1)–Se–S(2)–O(5) bears a startling resemblence to the central pentachalcogen chain of the known trans pentathionate structures.

The Se–S bond length, 2.257 (1) Å, is short when compared to the corresponding distances in $Se_2S_2O_6^{2-}$[9] of 2.273 (2), 2.278 (2), 2.282 (4), and 2.295 (3) Å. There are several bond lengths for dibonded Se–dibonded S,[10-12] 2.180 (3), 2.181 (2), 2.178 (2), and 2.153 (4) Å, which should not be compared.

The bond angle at Se, 97.90 (4)°, might be compared to the bond angles at Se in the selenopentathionates,[10-12] 103.06 (11), 104.00 (8), and 104.9 (2)°, or to the average angle at dibonded Se listed by Abrahams,[13] 104°, or to the average angles at Se in the selenotetrathionates[9,14] which are of range 100.36 (11)–103.80 (7)°. With any of these comparisons, the S–Se–S bond angle in the present structure seems unusually small. It is tempting to speculate that the Se orbitals used in bonding to the two relatively electronegative $-SO_3$ groups are relatively high in p character.

The orientation of the $-SO_3$ groups is best illustrated by dihedral angles. The dihedral angle O(3)–S(1)–Se–S(2) is 84.9°, and the dihedral angle O(5)–S(2)–Se–S(1) is 78.2°. We expect these angles to be 90° in the "trans C_2" conformation and 60° or 120° in the C_{2v} conformation. Curiously, in Na^+, K^+, and NH_4^+ salts of the polythionates, the corresponding angles are in the range 79–94° while in Ba^{2+} and $Co(en)_2Cl_2^+$ salts, the corresponding angles are in the range 66–72°.[15] Thus, with current knowledge, there seem to be two reasonably well-delineated groups and the implication that it is the counterion which dictates $-SO_3$ orientation. We would prefer to believe that it is coincidences of packing geometry that dictate the $-SO_3$ orientation in the solid state.

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Registry No. $K_2SeS_2O_6$, 15099-06-6.

Supplementary Material Available: Listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Metal Binding to N(1) of 9-Methyladenine in the 1:1 Complex with Methylmercuric Nitrate

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A large body of structural data is now available concerning metal complexes with DNA bases, and the coordination sites normally used have been identified for all the bases. For N(9)-blocked adenine ligands, imidazolic nitrogen N(7) is considered as the primary target for most metal ions. This statement is supported by a number of crystal structures[1] as

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