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Crystal and Molecular Structure of a Mercury–Thiosteroid Complex

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Reaction of the steroid 7α-(thioacetyl)-(17*R*)-spiro[androst-4-ene-17,2(3*H*)-furan] (spiroxazone = SXZ) with $HgBr_2$ produced a crystalline solid with composition $HgBr(C_{22}H_{31}O_2S)$, which has been fully characterized by X-ray crystallography. It crystallizes in $P4_1$ with unit cell dimensions $a = 12.953$ (4) Å, $c = 12.727$ (4) Å, $V = 2135.2$ Å^3, $Z = 4$, and $d_{\text{calcd}} = 1.989$ g cm^{-3}. The structure was refined to residuals (R_1, R_2) of 0.025 and 0.031. It is a polymeric structure where both the sulfur and bromine atoms act as bridges between adjacent Hg atoms. The bond distances and angles of the steroid remain essentially unchanged by its coordination to mercury.

Introduction

Recently there has been some interest in thiosteroid–metal interactions because of the increasing utilization in industry of the highly toxic cadmium and mercury metals and the highly publicized "Minamata disease"[1] (poisoning from organic mercury compounds) and the outbreak of the "itai-itai disease".[2] The known antidotes against mercury poisoning have a sulfur-containing group which is believed to complex the mercury and remove it from the tissue. It has been known for some time that some thiosteroids offer considerable protection against mercury poisoning.[3,4] From experiments on rats, it has been found that pretreatment with these thiosteroids prevents renal and kidney damage by mercury. In vitro[5] and in vivo[6] experiments with mercury and two thiosteroids, i.e., 7α-(thioacetyl)-17-hydroxy-3-oxoandrostene-17α-propionic acid γ-lactone (spironolactone, SNL) and SXZ, have yielded satisfactory results. Here we report on the structure of the complex of deacetylated SXZ with Hg.

Experimental Section

Crystal Data. Crystals of the complex[7] suitable for X-ray work were obtained from an ethanol solution. The colorless crystals decompose slowly, turning yellow-orange, to give canrenone[6] and a mixed sulfide–bromide of Hg.[7] The reciprocal lattice symmetry observed from precession photographs showed that the crystals are tetragonal and the systematic absences ($00l$, $l = 2n + 1$) were consistent with space groups $P4_1$ and $P4_3$. The cell parameters were calculated by least-squares refinement of the setting angles of 12 automatically centered reflections (Cu Kα radiation, $\lambda = 1.5418$ Å, $60° < 2\theta < 70°$): $a = 12.953$ (4) Å, $c = 12.727$ (4) Å, $V = 2135.2$ Å^3, and a calculated density of 1.989 g cm^{-3} for $C_{22}H_{31}BrO_2SHg$ with $Z = 4$. The density measured by flotation in dibromomethane/chloroform at 23 °C is 1.97 (2) g cm^{-3}.

Collection and Reduction of Intensity Data. A well-formed crystal of approximate dimensions 0.20 × 0.22 × 0.28 mm was accurately centered on a Picker FACS-1 four-circle automatic diffractometer, and data to $2\theta = 125°$ (graphite monochromated Cu Kα radiation) were collected. The general procedure has been described previously.[8] Three standard reflections were measured at a period of 30 reflections. There was a uniform drop in their intensities of about 12%. The scatter in their intensities was less than 2.0% from their respective means. A total of 1921 intensity measurements were made and reduced to a set of 1847 independent reflections after averaging the duplicate ones and removing the systematic absences. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - 0.5t_T/t_B(B_1+B_2)$ where $I(\text{scan})$ is the number of counts over the scan range, t_T is the scan time, and t_B is the time for each background count B_1 and B_2. The standard deviations $\sigma(I)$ were calculated as in ref 8 by using an "ignorance factor" of $c = 0.035$. Only data for which $I > 2.0\sigma(I)$ were used, which left 1831 reflections to be entered in the least-squares refinement. Absorption correction was applied, and the calculated transmission coefficients, based on a linear absorption coefficient of 173.3 cm^{-1} for Cu Kα radiation, ranged from 0.053 to 0.155. Lorentz and polarization corrections were applied.[9]

Solution and Refinement of the Structure. The structure was solved by the standard heavy-atom method in space group $P4_1$ and refined by full-matrix least squares initially and by block-diagonal least squares in the later stages. The mercury and bromine positions were evident from the three-dimensional Patterson map. A Fourier synthesis phased on these positions revealed the positions of all the nonhydrogen atoms. Refinement proceeded normally using unit weights and the block-diagonal least-squares approximation (in blocks of 9 × 9) and converged initially at an R_1 $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.056, after the positional and individual isotropic temperature factors for all nonhydrogen atoms were varied. At this stage a secondary extinction correction was entered,[10] and refinement was carried out in both space groups $P4_1$ and $P4_3$. Inclusion of anisotropic temperature factors reduced R_1 to 0.034 in $P4_1$ and 0.051 in $P4_3$. Work continued in $P4_1$. A difference map easily revealed the positions of the hydrogen atoms. Inclusion of these positions in the refinement, as well as the weights $w = 1/\sigma^2(F_o)$, led after three cycles to a final R_1 of 0.025 and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0.031. The function $w(|F_o| - |F_c|)^2/N$, where N is the number of reflections in the particular range, showed no significant variation with F_o, h (the slowest varying index during data collection), or $(\sin\theta)/\lambda$. The maximum shifts in the final least-squares refinement are 0.2σ. The scattering factors for all atoms were taken from Cromer and Mann[11] and the anomalous dispersion components from Cromer and Lieberman.[12]

The calculated and observed structure factors are available as supplementary material, and the final positional and thermal parameters are found in Tables I and II for the nonhydrogen and hydrogen atoms, respectively.

Discussion

The molecular structure appears in Figure 1 while the bond distances and angles appear in Figure 2. The C–H bond distances ranged between 0.80 (9) and 1.14 (9) Å, and bond angles involving hydrogen atoms ranged between 110 and 120° with esd's of 4–7°. The esd's for Figure 2, where not reported, are 0.01 Å for bond distances and 0.5–0.7° for bond angles.

The geometry around Hg can be described as a distorted triangle of two sulfur and one bromine atoms. The metal is displaced by 0.30 Å from the plane of this triangle toward the bromine of the next molecule with which it interacts rather

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(1) L. T. Kurland, *World Neurol.*, **1**, 370 (1960).
(2) M. Fleischer, *Environ. Health Perspect.*, **No. 7**, 253 (1974).
(3) H. Selye, *Science*, **169**, 775 (1970).
(4) J. E. Haddow and R. Lester, *Gastroenterology*, **64**, 159 (1973); P. Kourounakis and Y. Romain, *Abstr., Proc. Can. Fed. Biol.*, **20**, 128 (1977).
(5) G. Pouskoulleli, P. Kourounakis, and T. Theophanides, *Inorg. Chim. Acta*, **18**, 5 (1976).
(6) G. Pouskouleli, Master Thesis, University of Montreal, 1976.
(7) G. Pouskouleli, P. Kourounakis, and T. Theophanides, *Inorg. Chim. Acta*, **24**, 45 (1977).
(8) A. Terzis, *Inorg. Chem.*, **15**, 793 (1976).
(9) The computer programs used were those of ref 8.
(10) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).
(11) D. T. Cromer and A. Mann, *Acta* Crystallogr., *Sect. A*, **24**, 321 (1968).
(12) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 1891 (1970).

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Table I. Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters of the Nonhydrogen Atoms[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	217.1 (3)	895.8 (3)	10000.0	54.0 (2)	57.4 (2)	31.6 (2)	−9.2 (1)	17.8 (1)	−6.8 (1)
Br	1160 (1)	682 (1)	11885 (1)	45.6 (4)	50.2 (5)	34.5 (4)	0.2 (2)	−0.8 (2)	2.2 (2)
S	950 (1)	1528 (1)	8341 (1)	34 (1)	33 (1)	25 (1)	−2 (1)	8 (1)	−3 (1)
O(C3)	−106 (5)	4426 (6)	11497 (6)	62 (4)	74 (4)	57 (4)	8 (2)	32 (2)	2 (2)
O(C22)	3435 (4)	2893 (4)	3955 (4)	50 (3)	51 (3)	28 (3)	−5 (1)	10 (1)	4 (1)
C1	1162 (6)	5019 (6)	9063 (6)	44 (4)	40 (4)	26 (4)	7 (2)	7 (2)	−3 (2)
C2	863 (6)	5331 (6)	10179 (6)	51 (4)	40 (4)	35 (4)	4 (2)	8 (2)	−10 (2)
C3	553 (6)	4407 (7)	10813 (6)	41 (4)	55 (5)	26 (4)	3 (2)	−1 (2)	−10 (2)
C4	1127 (6)	3453 (6)	10608 (6)	35 (4)	43 (4)	26 (4)	−3 (2)	6 (2)	−5 (2)
C5	1804 (5)	3339 (5)	9819 (5)	32 (4)	34 (3)	21 (4)	−1 (1)	−3 (1)	0 (1)
C6	2406 (6)	2370 (6)	9707 (6)	29 (4)	35 (4)	34 (4)	3 (1)	5 (1)	3 (2)
C7	2319 (5)	1911 (5)	8610 (5)	28 (3)	26 (3)	20 (4)	1 (1)	4 (1)	4 (1)
C8	2671 (5)	2714 (5)	7800 (5)	26 (3)	25 (3)	25 (4)	3 (1)	0 (1)	−2 (1)
C9	2032 (5)	3721 (5)	7888 (5)	26 (3)	27 (3)	22 (3)	3 (1)	1 (1)	−1 (1)
C10	2019 (5)	4198 (5)	9013 (5)	30 (3)	31 (4)	22 (3)	−7 (1)	0 (1)	−4 (1)
C11	2345 (6)	4522 (6)	7058 (6)	42 (4)	32 (4)	28 (4)	−0 (2)	−0 (2)	1 (2)
C12	2303 (6)	4087 (6)	5926 (6)	37 (4)	36 (4)	22 (4)	8 (2)	1 (1)	6 (2)
C13	2985 (6)	3131 (5)	5839 (6)	35 (4)	30 (4)	25 (4)	1 (1)	10 (2)	2 (1)
C14	2647 (5)	2335 (5)	6659 (5)	32 (3)	25 (3)	23 (4)	−0 (1)	2 (1)	−3 (1)
C15	3280 (6)	1370 (6)	6389 (7)	48 (5)	30 (4)	38 (5)	8 (2)	13 (1)	5 (2)
C16	3377 (7)	1423 (6)	5172 (7)	65 (5)	37 (4)	34 (4)	10 (2)	9 (2)	−9 (2)
C17	2880 (6)	2454 (6)	4830 (6)	41 (4)	36 (4)	21 (3)	−2 (2)	11 (2)	−3 (2)
C18	4126 (6)	3450 (6)	5960 (7)	32 (4)	52 (5)	43 (4)	−6 (2)	4 (2)	5 (2)
C19	3067 (6)	4692 (6)	9314 (7)	37 (4)	40 (4)	40 (4)	−12 (2)	−5 (2)	−9 (2)
C20	1774 (7)	2349 (7)	4429 (7)	51 (5)	62 (5)	27 (4)	−12 (2)	1 (2)	−20 (2)
C21	1686 (7)	3152 (8)	3564 (7)	53 (5)	79 (6)	25 (4)	−1 (2)	−1 (2)	−5 (2)
C22	2770 (7)	3083 (7)	3090 (7)	68 (6)	48 (5)	26 (4)	1 (2)	8 (2)	4 (2)

[a] Thermal parameters are listed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

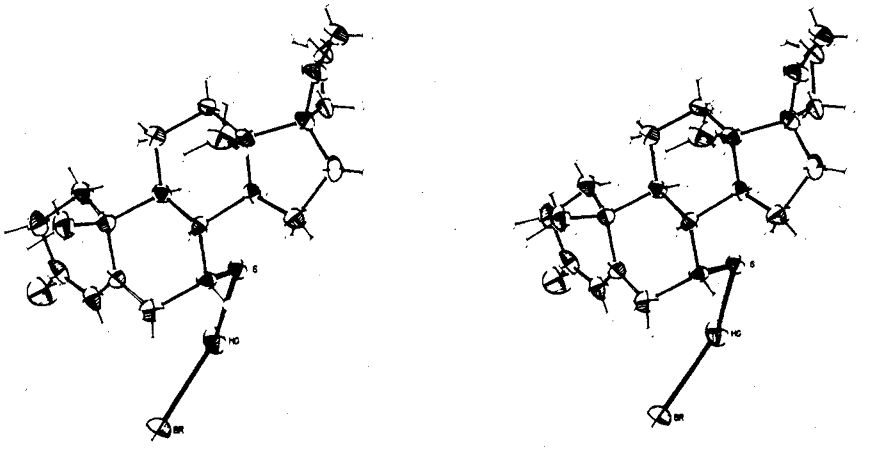

Figure 1. Stereoscopic view of the molecule (hydrogens have arbitrary sizes).

strongly. In this manner both the sulfur and the bromine atoms act as bridges between the mercury atoms, and thus an extended structure results.

The Hg–S distances are 2.455 and 2.50 Å. These compare with 2.38,[13] 2.32,[14] and 2.36 Å[15] for two-coordinate mercury. In compounds where three strong covalent bonds to mercury are present, Hg–S distances are 2.462 and 2.514 Å in $Hg(SCN)_2(AsPh_3)$[16] and 2.42 Å in $[Hg(thiourea)_2Cl]Cl$,[17] where the coordination is trigonal planar. Typical distances reported for tetrahedrally coordinated mercury are 2.51 Å in $HgCl_2(thiourea)_4$,[18] 2.565 and 2.577 Å in $Hg(SCN)_2(PPh_3)_2$,[19] and 2.54 Å in HgS, $K_2Hg(SCN)_4$, and $NiHg(SCN)_4(H_2O)_2$,[20] while for six-coordinate mercury in *cis*-$Hg(SCN)_2(phen)_2$,[21]

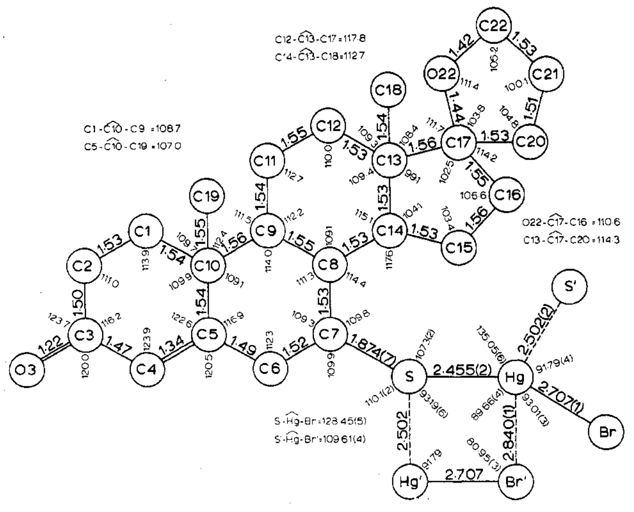

Figure 2. Bond distances and angles.

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(13) A. L. Beauchamp and D. Goutier, *Can. J. Chem.*, **50**, 977 (1972).
(14) Y. S. Wong, P. C. Chieh, and A. J. Carty, *Can. J. Chem.*, **51**, 2597 (1973).
(15) A. J. Carty and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 214 (1976).
(16) J. Habert, A. L. Beauchamp, and R. Rivest, *Can. J. Chem.*, **53**, 3383 (1975).
(17) P. D. Brotherton, P. C. Healy, C. L. Ralston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 334 (1973).
(18) P. D. Brotherton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2696 (1973).
(19) R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Dalton Trans.*, 2447 (1973).

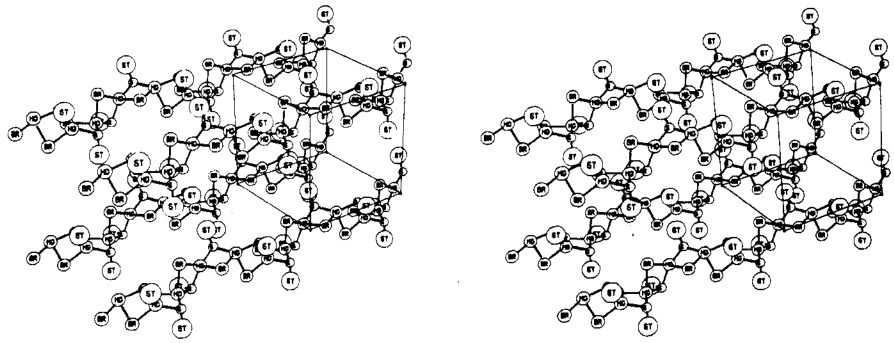

Figure 3. ORTEP drawing showing the polymeric nature of the complex (ST stands for the steroid nucleus).

Table II. Positional (×10^3) and Thermal (×10^2) Parameters of the Hydrogen Atoms

atom	x	y	z	U_{iso}, Å^2
H(1A)	138 (6)	564 (5)	875 (6)	3 (2)
H(1B)	50 (5)	478 (6)	879 (6)	3 (2)
H(2A)	150 (6)	572 (6)	1066 (7)	4 (2)
H(2B)	30 (7)	569 (8)	1029 (9)	8 (4)
H(4)	103 (5)	289 (5)	1098 (5)	2 (2)
H(6A)	298 (5)	251 (5)	980 (6)	2 (2)
H(6B)	227 (6)	193 (6)	1024 (7)	5 (2)
H(7)	274 (5)	127 (6)	861 (6)	3 (2)
H(8)	328 (5)	278 (5)	803 (5)	1 (2)
H(9)	133 (5)	347 (5)	763 (6)	3 (2)
H(11A)	182 (6)	508 (7)	711 (8)	5 (3)
H(11B)	296 (7)	473 (6)	729 (8)	5 (3)
H(12A)	170 (5)	391 (5)	585 (6)	2 (2)
H(12B)	243 (6)	456 (6)	544 (7)	4 (2)
H(14)	189 (6)	219 (6)	661 (6)	3 (2)
H(15A)	396 (6)	120 (6)	669 (6)	3 (2)
H(15B)	299 (5)	75 (5)	655 (5)	2 (2)
H(16A)	401 (6)	147 (6)	505 (8)	5 (2)
H(16B)	307 (6)	81 (6)	483 (8)	5 (2)
H(18A)	423 (7)	380 (7)	533 (8)	6 (3)
H(18B)	420 (6)	380 (6)	676 (7)	4 (2)
H(18C)	461 (6)	295 (6)	588 (7)	4 (2)
H(19A)	354 (6)	429 (6)	921 (8)	4 (2)
H(19B)	313 (6)	494 (6)	1016 (7)	4 (2)
H(19C)	316 (6)	523 (6)	901 (7)	5 (2)
H(20A)	155 (9)	174 (9)	399 (9)	11 (4)
H(20B)	128 (4)	242 (4)	491 (6)	1 (2)
H(21A)	109 (9)	304 (8)	318 (9)	9 (4)
H(21B)	152 (8)	381 (9)	383 (9)	9 (4)
H(22A)	278 (6)	257 (6)	269 (7)	4 (2)
H(22B)	291 (8)	366 (8)	276 (9)	7 (3)

Table III. Torsion Angles[a]

	ϕ_{A-B}, deg			ϕ_{A-B}, deg	
bond	steroid	complex	bond	steroid	complex
Ring A					
C1–C2	−51.0	−55.6	C4–C5	−5.3	−1.7
C2–C3	25.6	36.8	C5–C10	−19.8	−16.0
C3–C4	2.4	−9.3	C10–C1	47.2	44.5
Ring B					
C5–C6	−50.1	−54.1	C8–C9	54.2	53.9
C6–C7	51.8	56.8	C9–C10	−48.2	−46.2
C7–C8	−54.5	−57.1	C10–C5	46.7	47.0
Ring C					
C8–C9	−51.4	−50.6	C12–C13	56.8	56.3
C9–C11	52.2	53.9	C13–C14	−59.6	−57.8
C11–C12	−55.3	−56.4	C14–C8	57.2	55.0
Ring D					
C13–C14	46.1	49.0	C16–C17	24.2	25.0
C14–C15	−31.4	−33.7	C17–C13	−42.8	−44.8
C15–C16	4.0	4.8			
Ring E					
C17–C20	25.8	−25.0	C22–O22	0.5	21.7
C20–C21	−34.8	36.7	O22–C17	−22.9	1.9
C21–C22	22.0	−35.7			

[a] The sign convention for the direction of the torsion angle is that of Klyne and Prelog (W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960)). ϕ_{A-B} is the torsion angle about the A–B bond, in which the other atoms which define the angle are those attached to either end of the bond and are in the ring in question.

they are 2.582 and 2.622 Å. Therefore a gradual progression in bond lengths with increasing coordination number is apparent in these Hg(II) complexes. The Hg–S distances in the present structure fall in the range of three-coordinate mercury. The Hg–Br distances support this view with the one (2.707 Å) being considerably shorter than the other (2.840 Å) although even the long Hg–Br distance represents a strong interaction since it is much shorter than the sum of the van der Waals radii of the mercury (1.50 Å) and bromine (1.95 Å) atoms. The mean Hg–Br distance in $N(CH_3)_4HgBr_3$[22] is 2.52 Å in the plane of the trigonal coordination while there is a close approach of 2.9 Å between the mercury atom of each anion, $HgBr_3^-$, and one bromine of a neighboring anion.

The geometry around mercury can also be viewed as a distorted tetrahedron with adjacent tetrahedra sharing sides and the distortion imparting a twist to the resulting polymeric structure (Figure 3).

The C–S bond (1.874 Å) is slightly longer than in spiroxazone[23] (1.833 Å) while the Hg–S–C angles are normal tetrahedral, 107.3 and 110.1°.

A comparison of the bond distances and angles in the present structure with those of spiroxazone[23] shows that the steroid ligand remains unchanged by its coordination to mercury. Even the torsion angles (Table III) show only small changes upon complexation, and these are probably due to crystal-packing forces, since the differences in the torsion angles[23] between spiroxazone and spironolactone, two very similar molecules, are even greater. Only the furan ring shows large changes in the torsion angles, but these are hardly due to complexation.

Conclusion

We note that a general trend with mercury coordination is that when the ligands are ionic[15,22,24] (halides, thiocyanate, deprotonated sulfhydryl groups), the complexes tend to be polymeric, while when they are in the form of methylmercury[14,25] or when some of the ionic ligands are replaced

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(20) D. Gardenic, *Q. Rev., Chem. Soc.*, **19**, 303 (1965).

(21) A. L. Beauchamp, B. Saperas, and R. Rivest, *Can. J. Chem.*, **52**, 2923 (1974).

(22) J. G. White, *Acta Crystallogr.*, **16**, 397 (1963).

(23) A. Terzis and B. J. Faught, *Cryst. Struct. Commun.*, **7**, 493 (1978).

(24) A. Sakhri and A. L. Beauchamp, *Inorg. Chem.*, **14**, 740 (1975).

(25) N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 438 (1975).

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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(26) N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, *J. Chem. Soc., Chem. Commun.*, 1039 (1976).

(27) P. Lavertune, J. Hubert, and A. L. Beauchamp, *Inorg. Chem.*, **15**, 322 (1976).

(28) W. J. Kozarek and Q. Fernando, *Inorg. Chem.*, **12**, 2129 (1973).

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, $\beta = 110.418$ (12)°, $V = 809.8$ Å^3, mol wt 317.3, $D(\text{obsd}) = 2.57$ g cm^{-3}, $D(\text{calcd for } Z = 4) = 2.60$ g cm^{-3}, and $\mu = 64.5$ 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.

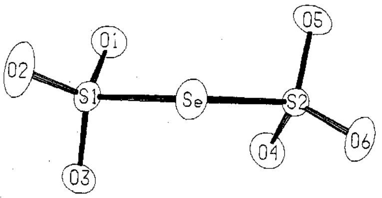

Figure 1. A view of the selenotrithionate down the pseudo-twofold axis. Thermal ellipsoids are at 50% probability.

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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(2) For historical references and reviews see preceding articles and particularly: Foss, O. *Acta Chem. Scand.* **1949**, *3*, 435; Janickis, J. *Acc. Chem. Res.* **1969**, *2*, 316.

(3) Foss, O.; Mørch, O. H. *Acta Chem. Scand.* **1954**, *8*, 1169.

(4) Rathke, B. *J. Prakt. Chem.* **1865**, *95*, 1.

(5) (a) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563. (b) Abrahams, S. C. *Acta Crystallogr., Sect. A* **1969**, *25*, 165.

(6) Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972.

(7) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321. (b) Stewart, R. F.; et al. *J. Chem. Phys.* **1965**, *42*, 3175.

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