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The Crystal Structure of Monoclinic Barium Telluropentathionate Dihydrate

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The monoclinic dimorph of the salt, $BaTe(S_2O_3)_2 \cdot 2H_2O$, crystallizes in a four-molecule unit cell based on the space group, C_{2h}^3-A2/m, with $a = 4.99$ Å, $b = 10.59$ Å, $c = 23.61$ Å, $\beta = 98°$. The structure has been determined by two-dimensional X-ray methods. With mirror plane symmetry crystallographically required, the telluropentathionate ion occurs in the *cis* form in this salt. The S—S—Te—S—S chain has the dimensions, S—S = 2.10 ± 0.02 Å, S—Te = 2.34 ± 0.02 Å, ∠S—S—Te = 106 ± 1°, ∠S—Te—S = 101 ± 1°. These values are within the experimental errors the same as found earlier for the *trans* form in the ammonium salt. The dihedral angle, SSTe/STeS = 103°.

The crystals have a layer structure and differ from the triclinic and orthorhombic barium pentathionate dihydrates and the acetone and tetrahydrofuran solvates only in the way of packing of the parallel layers.

Solvates of barium pentathionates with dioxane are described, containing one mole of water and half a mole of dioxane per mole of salt. The barium selenopentathionate solvate, $BaSe(S_2O_3)_2 \cdot H_2O \cdot \frac{1}{2}C_4H_8O_2$, crystallizes in the space group, C_{2h}^3-A2/m with $Z = 4$, and $a = 5.02$ Å, $b = 10.59$ Å, $c = 22.72$ Å, $\beta = 102°$, and is isostructural with monoclinic barium telluropentathionate dihydrate.

A recent study of the crystal chemistry of barium salts of telluropentathionic acid [1] led to the characterization of a trihydrate and of a triclinic and a monoclinic dihydrate. Unit cell and space group data indicated that the triclinic dihydrate is isomorphous with triclinic barium pentathionate dihydrate [2], and that the *a*-axis projection of the monoclinic dihydrate has the same symmetry as the *a*-axis projections of orthorhombic barium pentathionate [3] and selenopentathionate [4] dihydrates. A solvate of barium telluropentathionate with tetrahydrofuran furthermore exists [5], isomorphous with the solvates of barium pentathionate and selenopentathionate with tetrahydrofuran and acetone [5,6]. In the barium salts the telluropentathionate ion thus occurs in the *cis* form, with mirror-plane symmetry, like the pentathionate and selenopentathionate ions in the barium salts. This is different from the conditions in the ammonium salt, where the telluropentathionate ion has been found to occur in enantiomorphous *trans* forms [7]. No crystal structure determination of an alkali pentathionate or selenopentathionate has been made; however, it appears likely that in alkali salts also these anions have *trans* forms, the occurrence of the *cis* form in the barium salts being due to the oxygen-coordinating powers of the barium ion, and favourable lattice conditions for the mirror-plane *cis* coordination complex.

The crystal structure of monoclinic barium telluropentathionate dihydrate has now been determined, and data obtained for a comparison of the *cis* and *trans* forms of the telluropentathionate ion. Apart from the rotational isomerism, the dimensions of the ion were found to be the same in the two forms. A further objective of the structure determination was to inquire more thoroughly into the indicated relationship [1] between the monoclinic dihydrate structure and the structures of the triclinic [1,2] and orthorhombic [3,4] dihydrates and the solvates [5,6]. As discussed earlier [1,5] and confirmed in the present work, monoclinic barium telluropentathionate dihydrate is built up of layers having the same internal structure as in the three other structure types. The layers are parallel to the *c* plane, and the structure types differ only in the way the layers are arranged relative to each other. In the triclinic dihydrates [1,2], of space group C_i^1—$P\bar{1}$ with $Z = 2$, the oblique β and α angles lead to relative displacements of successive layers in the directions of the *a* and *b* axes, while in the solvates [5,6], of space group C_{2h}^2—$P2_1/m$ with $Z = 2$, displacements occur in the *a*-axis direction only. In the orthorhombic dihydrates [3,4] of space group D_{2h}^{16}—*Pnma* with $Z = 4$, adjacent layers are related through glide planes *a* in the layer interface, and in the monoclinic dihydrate, through two-fold rotation axes in the interface.

The present structure is the fifth to be described for a telluropentathionic compound, and the first in which the S—S—Te—S—S chain has been found to have the *cis* instead of the *trans* configuration. Beside ammonium telluropentathionate [7], the earlier structures are those of tellurium dimethanethiosulphonate [8], dibenzenethiosulphonate [9] and di-*p*-toluenethiosulphonate [10].

CRYSTAL DATA

The monoclinic dimorph of barium telluropentathionate dihydrate, $BaTe(S_2O_3)_2 \cdot 2H_2O$, has the unit cell dimensions [1], $a = 4.99$ Å, $b = 10.59$ Å $c = 23.61$ Å, $\beta = 98°$. There are four formula units per unit cell; density, calc. 2.82, found 2.80 g/cm^3. The crystals occur as prisms along the *a* axis, with {001} dominant. There is a pronounced tendency of cleavage along the *c* plane.

On the basis of the systematic absences, *hkl* when $k+l$ is odd, and a comparison of the 0*kl* zone of reflections with the 0*kl* zones of orthorhombic barium pentathionate and selenopentathionate dihydrate, the space group, C_{2h}^3—$A2/m$, was originally chosen [1], and no later observations contradict this choise. The barium ion and the tellurium atom are thereby required to lie in special positions, and were found to lie in the mirror planes, as do also the water molecules.

The intensities of the 0*kl* and *h*0*l* reflections were estimated visually from Weissenberg photographs, taken with CuK_α radiation using a double-film, multiple-exposure technique. The crystals employed had cross-sections of 0.09×0.05 mm and 0.08×0.06 mm, respectively, in the case of the *a*- and *b*-axis photographs. 156 out of 172 $0kl$ reflections and 148 out of 156 $h0l$ reflections attainable with CuK_α radiation were observed and measured. The intensities were corrected for the Lorentz and polarization factors and converted to relative structure factors in the usual way, and were ultimately brought to an approximately absolute scale by comparison with the calculated values. Although the absorption coefficient for CuK_α radiation is 531 cm^{-1}, no correction for absorption was made, mainly because of the large amount of work it would involve, but reflections likely to be most heavily influenced by absorption were omitted from the $(F_o—F_c)$ syntheses in the final stages of refinement.

Summations were made by means of Beevers-Lipson strips, at 12°, 6° and 3° intervals, respectively, along the *a*, *b* and *c* axes, except for the F_o^2 and first F_o syntheses where the summations were made at 6° intervals also along the *c* axis.

The atomic scattering curves used in the calculation of structure factors were that of Berghuis *et al.*[11] and of Viervoll and Ögrim[12], respectively, for oxygen and sulphur, and the Thomas-Fermi curve[13] for tellurium. For the barium ion a curve was constructed based on the Thomas-Fermi values[13] for xenon at small scattering angles and for electroneutral barium at intermediate and larger scattering angles.

ANALYSIS OF THE STRUCTURE

The *y* and *z* coordinates of the barium ion and tellurium atom, and also of the two sulphur atoms of the asymmetric unit, were derived from a F_o^2 synthesis of the $0kl$ data. These first coordinates gave the signs of 117 of the largest $0kl$ terms, which were used for a F_o synthesis. The resulting electron density map revealed the approximate positions of the sulphonate oxygen atoms and water molecules, and allowed F_o refinement to be carried out. Finally, a series of $(F_o—F_c)$ refinements were made.

The *b*-axis projection was solved and refined in essentially the same way. Here, however, $(F_o—F_c)$ refinement did not proceed quite satisfactorily and was therefore abandoned at a relatively early stage. One reason may be that in this projection the water molecule $(H_2O)_2$ is obscured by the tellurium atom and therefore cannot be located with any certainty; also, the overlapping makes the tellurium *x* coordinate less reliable.

The difference maps indicated individual and partly anisotropic temperature vibrations of the atoms. In temperature factor $\exp [—B(\sin^2\Theta/\lambda^2)]$ the following values of *B* were adopted in the last stages: For the $0kl$ data, 3.0 Å^2 for tellurium, 2.8 Å^2 for the sulphur and oxygen atoms except for $(H_2O)_2$ where $B = 5.0$ Å^2, and $(2.6+0.8 \cos^2\varphi)$ Å^2 for the barium ion, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the ion. This direction is parallel to the *c* axis. For the $h0l$ data, $B = 2.8$ Å^2 for the sulphur and oxygen atoms, and $(2.6+1.0 \cos^2\varphi)$ Å^2 and $(3.0+2.0 \cos^2\varphi)$ Å^2, respectively, for the barium ion and tellurium atom. Here, the directions of maximum vibration make angles of 34° and 45°, respectively,

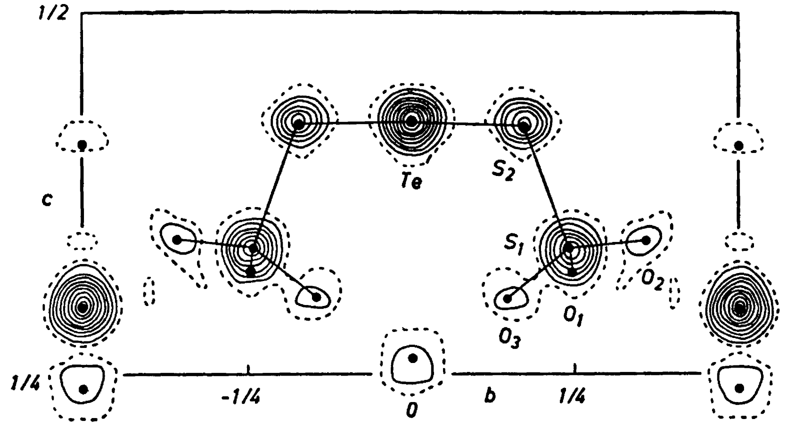

Fig. 1. Electron density projection of monoclinic barium telluropentathionate dihydrate along the *a* axis. Contour intervals: 10 e · Å^{-2} for the barium ion and tellurium atom, and 5 e · Å^{-2} for the sulphur and oxygen atoms and water molecules. The 5-electron line is dashed.

with the *c* axis in the acute angle. The temperature factors may have little physical reality in terms of thermal motions of the atoms; rather, they also represent absorption and other errors in the observed structure factors.

The final electron density maps are shown in Figs. 1 and 2, and the final atomic coordinates are listed in Table 1. The *z* coordinates are from the *a*-axis projection, since attempts to establish independent *z* coordinates from the *b*-axis projection were not made. One exception is that of O_1. It should be noted that the *b*-axis projection did not indicate changes in the *z* coordinates of the heavier atoms including sulphur.

In Table 2, observed and calculated values of structure factors are compared for all 0*kl* and *h*0*l* reflections within the range of CuK_α radiation. The strong reflections 002, 004, 006, 008, 011, 013, 015, 026 in the 0*kl* zone and 002, 004, 006, 008, 108, $\bar{1}$08, $\bar{3}$04, $\bar{3}$ 0 12 in the *h*0*l* zone have observed values markedly

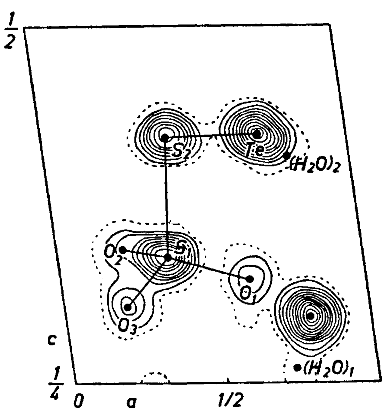

Fig. 2. Electron density projection along the *b* axis. Contours are at intervals of 8 e · Å^{-2} for the barium ion and tellurium atom, and the 8-electron line is dashed; otherwise as in Fig. 1. Each sulphur and sulphonate oxygen peak represents two exactly overlapping atoms, one on each side of the mirror plane.

lower than the calculated ones, probably due to absorption and extinction effects. These reflections were omitted from the (F_o—F_c) syntheses and from the calculation of scale factors for the respective zones, and were included in the final F_o syntheses with their calculated values. The relatively weak reflections 0 0 28, 031, 062, 0 10 2 in the $0kl$ zone and 0 0 28, 1 0 24, 206, $\bar{2}$ 0 28, 300, 304, $\bar{3}$ 0 26, 408, 4 0 16, $\bar{4}$08, 602, 606, $\bar{6}$ 0 12 in the $h0l$ zone have small calculated values and therefore uncertain signs, and were not included in the F_o or (F_o—F_c) syntheses.

Table 1. Atomic coordinates, in fractions of monoclinic cell edges. Origin at a centre of symmetry ($2/m$).

	x	y	z		x	y	z
Ba	0.802	0	0.2045	S_1	0.365	0.240	0.3382
Te	0.712	0	0.4238	S_2	0.413	0.171	0.4224
$(H_2O)_1$	0.739	0	0.262	O_1	0.623	0.241	0.322
$(H_2O)_2$	0.200	0	0.091	O_2	0.240	0.360	0.343
				O_3	0.211	0.146	0.303

The reliability index, $R = \Sigma||F_o|—|F_c||/\Sigma|F_o|$, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.082 for the $0kl$ reflections and 0.170 for the $h0l$ reflections, if the above-mentioned groups of strong reflections with high calculated values are omitted. With these reflections included, the R values become 0.108 and 0.190, respectively.

ASSESSMENT OF ACCURACY

The standard deviations of the coordinates of the heavier atoms were estimated from the root-mean-square gradients of the difference maps and the curvatures of the electron density peaks [14,15]. The gradients were 2.3 e · Å^{-3} in the y and z directions of the $0kl$ difference map, and 5.8 e · Å^{-3} in the x direction of the less refined $h0l$ map. The derived standard deviations are: $\sigma(x) = 0.005$ Å, $\sigma(z) = 0.002$ Å for the barium ion; $\sigma(x) = 0.006$ Å, $\sigma(z) = 0.003$ Å for the tellurium atom; $\sigma(x) = 0.010$ Å, $\sigma(y) = 0.007$ Å, $\sigma(z) = 0.008$ Å for the sulphur atoms. The y coordinates of barium and tellurium are fixed by symmetry relations. $\sigma(x)$ for sulphur is relatively low despite the large gradient because in the b-axis projection exact overlapping of two and two sulphur atoms (and likewise of sulphonate oxygen atoms) occurs. $\sigma(z)$ and $\sigma(x)$ for S_1 may be larger than the given values due to overlapping with oxygen atoms in both projections. The s.d. for resolved oxygen atoms may be taken as about three times those of the sulphur atoms, except for the x coordinate of $(H_2O)_1$ and particularly $(H_2O)_2$ where the uncertainties are larger.

The above values give s.d. of 0.009 Å and 0.011—0.014 Å, respectively, for S—Te and S—S distances, and 0.3—0.4° for angles involving these atoms. Considering uncertainties in the estimates due to overlapping in some cases, and non-random errors in the observed structure factors due to absorption and other effects, s.d. of about 0.02 Å for S—S and S—Te distances and about 1° for the angles may be more realistic. Similar estimates lead to s.d. of about 0.04 Å for S—O bond lengths, 2—3° for S—S—O and O—S—O bond angles, and 0.03 Å for distances from barium to sulphonate oxygen atoms.

Table 2. Observed and calculated 0*kl* and *h*0*l* structure factors for monoclinic barium telluropentathionate dihydrate.

l	F_o	F_c	*l*	F_o	F_c	*l*	F_o	F_c
	0*kl* zone		5	213	+231	14	149	+163
	00*l*		7	110	−110	16	22	+ 24
2	87	−176	9	96	+118	18	114	−123
4	57	−120	11	16	+ 14	20	18	− 12
6	44	− 74	13	139	−147	22	57	− 58
8	316	−372	15	75	+ 79	24	51	+ 48
10	119	+117	17	97	− 91	26	33	+ 36
12	139	+145	19	86	+ 80			
14	209	+189	21	18	+ 11		07*l*	
16	40	− 37	23	<16	− 5	1	40	− 44
18	100	− 92	25	23	+ 17	3	122	−127
20	42	− 29	27	53	− 52	5	184	+170
22	130	−127	29	12	+ 15	7	51	+ 49
24	102	+104				9	45	+ 43
26	61	+ 54		04*l*		11	36	− 36
28	26	+ 1	0	350	+364	13	81	− 86
30	13	+ 16	2	103	− 93	15	19	− 13
			4	11	− 5	17	41	− 39
	01*l*		6	48	− 56	19	103	+107
1	109	−140	8	160	−171	21	<14	+ 9
3	134	−177	10	68	+ 80	23	<12	− 7
5	239	+291	12	30	+ 41	25	<8	− 3
7	85	+ 81	14	86	+ 91			
9	107	+129	16	24	− 18		08*l*	
11	75	− 75	18	28	− 31	0	243	+235
13	190	−185	20	20	− 15	2	88	− 90
15	15	+ 4	22	82	− 74	4	16	− 6
17	70	− 67	24	70	+ 62	6	19	+ 13
19	163	+155	26	<12	+ 5	8	110	−110
21	40	+ 36	28	<8	+ 7	10	48	+ 48
23	<16	− 11				12	20	+ 11
25	16	− 20		05*l*		14	56	+ 59
27	78	− 72	1	121	−119	16	19	− 19
29	<9	+ 12	3	98	− 93	18	19	− 19
			5	236	+222	20	<13	+ 12
	02*l*		7	19	+ 12	22	60	− 61
0	205	+189	9	121	+138	24	31	+ 42
2	<7	− 8	11	61	− 60			
4	137	+120	13	177	−182		09*l*	
6	218	−268	15	29	+ 34	1	<16	− 19
8	96	−108	17	51	− 54	3	41	− 43
10	153	+181	19	113	+113	5	97	+ 87
12	105	−100	21	43	+ 43	7	55	− 54
14	154	+157	23	16	− 11	9	71	+ 71
16	29	+ 33	25	20	− 22	11	21	− 10
18	115	−111	27	55	− 60	13	69	− 72
20	17	+ 18				15	49	+ 50
22	52	− 49		06*l*		17	51	− 51
24	33	+ 33	0	278	+281	19	39	+ 37
26	<13	+ 10	2	13	− 1	21	20	+ 12
28	24	+ 26	4	36	+ 31			
			6	200	−203		0,10,*l*	
	03*l*		8	160	−158	0	79	+ 73
1	9	+ 2	10	131	+141	2	18	− 4
3	142	−161	12	22	− 17	4	35	+ 35

l	F_o	F_c
	$0,10,l$	
6	75	−84
8	55	−49
10	68	+67
12	31	−37
14	60	+64
16	12	+15
18	45	−47
20	<7	0
	$0,11,l$	
1	31	−32
3	69	−68
5	119	+109
7	16	+14
9	31	+36
11	16	−18
13	72	−73
15	<10	+4
17	18	−20
	$0,12,l$	
0	126	+130
2	20	−19
4	<13	−8
6	27	−33
8	68	−73
10	36	+35
12	10	+20
14	41	+53
	$0,13,l$	
1	21	−26
3	18	−17
5	46	+49
7	<8	−5
	$h0l$ zone	
	$00l$	
2	87	−176
4	64	−120
6	51	−72
8	307	−375
10	113	+124
12	132	+135
14	203	+186
16	44	−38
18	108	−96
20	46	−18
22	139	−120
24	112	+97
26	65	+48
28	26	−6
30	15	+17
	$10l$	
0	129	−121
2	148	−180
4	65	+37
6	148	−160
8	278	+323
10	84	+90
12	145	−163
14	56	+53
16	146	−126
18	24	−13
20	80	+79
22	49	+33
24	26	+2
26	41	−39
28	<10	+16
	$\bar{1}0l$	
2	36	+25
4	156	+187
6	202	+230
8	144	−200
10	56	+56
12	129	−143
14	85	−88
16	141	+136
18	18	+8
20	73	+58
22	22	−20
24	45	−29
26	26	−23
28	19	−33
30	43	+56
	$20l$	
0	292	−327
2	45	+22
4	74	+72
6	14	+2
8	151	+161
10	94	−92
12	17	+19
14	116	−108
16	20	−27
18	128	+121
20	52	−58
22	73	+75
24	19	−12
26	53	−54
	$\bar{2}0l$	
2	191	+192
4	80	−79
6	70	+77
8	113	+118
10	77	−86
12	<15	−8
14	73	−74
16	41	+64
18	<18	−21
20	27	+14
22	40	+46
24	68	−73
26	31	+36
28	15	−4
30	<6	−16
	$30l$	
0	38	+5
2	211	+223
4	39	+2
6	44	+46
8	103	−113
10	168	−179
12	95	+94
14	23	+17
16	82	+92
18	34	+32
20	58	−61
22	35	−30
24	38	−49
	$\bar{3}0l$	
2	22	−31
4	127	−171
6	86	−91
8	104	+126
10	38	−45
12	169	+199
14	47	−56
16	75	−98
18	20	+24
20	79	−81
22	59	+62
24	35	+41
26	13	−4
28	<9	+4
	$40l$	
0	19	+15
2	19	−23
4	92	−107
6	20	−7
8	19	−6
10	105	+107
12	19	+14
14	18	−21
16	16	+4
18	101	−96
20	21	+38
	$\bar{4}0l$	
2	22	+18
4	145	+163
6	101	−90
8	18	−1
10	24	−47
12	69	−83
14	74	+78

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
	$\bar{4}0l$		14	14	− 6		$60l$	
16	20	+ 22	16	<4	− 7	0	13	− 7
18	30	+ 41				2	11	− 5
20	18	− 12		$\bar{5}0l$		4	38	+ 46
22	15	− 26	2	51	− 57	6	8	− 3
24	15	− 21	4	24	+ 10			
26	17	− 21	6	40	+ 28		$\bar{6}0l$	
			8	24	− 32	2	30	− 36
	$50l$		10	34	+ 43	4	33	− 25
0	67	+ 77	12	51	− 42	6	43	+ 50
2	105	− 77	14	35	+ 38	8	27	− 21
4	19	+ 13	16	<15	− 28	10	31	+ 41
6	56	+ 43	18	<14	− 16	12	9	0
8	25	− 45	20	29	+ 36	14	22	− 42
10	55	+ 54	22	20	− 28			
12	37	− 27						

DESCRIPTION OF THE STRUCTURE

The telluropentathionate ion consists of a divalent tellurium atom to which are attached two thiosulphate groups, through Te—S bonds. The S—S—Te—S—S chain thus resulting has the dimensions listed in Table 3. The ion possesses mirror plane symmetry, and a prime is used to denote the equivalent of an atom across the mirror plane.

Table 3. S—S and S—Te bond lengths and angles.

$S_1-S_2 = 2.10$ Å
$S_2-Te = 2.34$
$\angle S_1-S_2-Te = 105.7°$
$\angle S_2-Te-S_2' = 101.2°$
S_1S_2Te/S_2TeS_2' (dihedral angle) $= 103°$

Non-bonded S—S and S—Te distances.

$S_1-S_1' = 5.08$ Å
$S_1-S_2' = 4.78$
$S_1-Te = 3.55$ Å
$S_2-S_2' = 3.62$

The bond lengths and angles found in ammonium telluropentathionate [7], where the two halves of the ion are not related by symmetry, are: S—S = 2.11 Å and 2.12 Å, S—Te = 2.35 Å and 2.36 Å, ∠ S—S—Te = 105° and 104°, ∠ S—Te—S = 103°, and the non-bonded distances not dependent on rotation about the S—Te bonds: S_1—Te = 3.57 Å, S_5—Te = 3.52 Å, S_2—S_2' = 3.68 Å. The differences between these values and those of Table 3 are not significant.

Whereas the telluropentathionate ion in the ammonium salt occurs in the *trans* form, with the two terminal sulphur atoms located on different sides of the plane of the tellurium and two middle sulphur atoms, the ion in the barium salt has the *cis* form, with the terminal sulphur atoms on the same side of the plane. This is reflected in the shorter S_1—S_1' separation, 5.08 Å, in the barium salt as compared with 6.11 Å in the ammonium salt. In the latter the SSTe/STeS dihedral angles are 86° and 95°, and thus smaller than in the barium salt.

The sulphonate groups have S_1—O_1 = 1.39 Å, S_1—O_2 = 1.43 Å, S_1—O_3 = 1.45 Å, $\angle O_1-S_1-O_2 = 117°$, $\angle O_1-S_1-O_3 = 107°$, $\angle O_2-S_1-O_3 = 117°$.

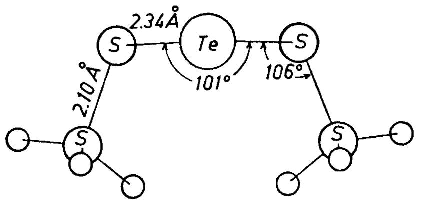

Fig. 3. The *cis* form of the telluropentathionate ion, with principal bond lengths and angles.

The small value of the second angle may be due to maximum error in the y coordinate of O_1, since this atom in the a-axis projection is overlapped by S_1.

The barium-oxygen coordination is as in the four structures of barium pentathionates determined earlier [2-4,6]. The barium ion is surrounded by nine oxygen atoms, at an average distance of 2.82 Å. The extreme values are 2.68 Å and 2.98 Å. The arrangement has been described in detail earlier [3,4] and shall not be repeated here. As in the other structures, the water molecule $(H_2O)_1$ probably forms hydrogen bonds to the sulphonate oxygen atoms O_1 and O_1'; the distances are in the present structure 3.01 Å and the O_1—$(H_2O)_1$—O_1' angle 116°.

The structure within layers parallel to the c plane is the same as in the triclinic [2] and orthorhombic [3,4] dihydrates and, apart from the replacement of a water molecule by an organic molecule, as in the acetone and tetrahydrofuran solvates [5,6]. In the present space group, adjacent layers are related through twofold rotation axes which run parallel to the b axis in the layer interfaces at $z = 0$ and $\frac{1}{2}$. The layers are held together through non-bonded contacts between atoms of the S_2—Te—S_2' groups across the interfaces. The closest approaches are: Te—Te = 4.28 Å over twofold axis at $(1,y,\frac{1}{2})$, and Te—Te = 4.42 Å, Te—S = 4.18 Å, S—S = 3.65 Å over twofold axis at $(\frac{1}{2},y,\frac{1}{2})$.

It may be noted that the origin chosen in the present work (at $2/m$ in accordance with the *International Tables* [16]) lies in a layer interface and in a mirror plane, and not in the middle of a layer and midway between mirror planes as in the earlier structure determinations [2-4,6]. To make the present b-axis projection correspond with those of the triclinic dihydrate [2] and the solvate [6] structures, another c axis should, furthermore, be chosen. The new cell, still A-centered, would have $c = 24.32$ Å, $\beta = 106°$ and be derived from the first by means of the transformation matrix, $\bar{1}00/010/201$.

SOLVATES WITH DIOXANE

In the crystals of the acetone solvate [5,6], $BaS(S_2O_3)_2 \cdot H_2O \cdot (CH_3)_2CO$, the internal layer structure differs from the dihydrate structures only in the substitution of an acetone molecule for one of the water molecules of the dihydrates. The oxygen atom of the acetone molecule is coordinated to the barium ion, like the oxygen atom of the replaced water molecule, and is located between the barium ion and the nearest layer interface, with the methyl groups directed towards the interface. A symmetrical molecule with two oxygen atoms, like dioxane, might be thought to be able to extend across the layer interfaces and replace two water molecules, one in each of two adjacent layers. Crystal symmetry and layer structure would permit such a replacement in the triclinic dihydrate structure, space group C_i^1—$P\bar{1}$ with $Z = 2$, and in the monoclinic dihydrate structure, space group C_{2h}^3—$A2/m$ with $Z = 4$, but not in the orthorhombic dihydrate structure or in the acetone and tetrahydrofuran solvate structure. In the two permitted space groups, $P\bar{1}$ and $A2/m$, the molecular symmetries, $\bar{1}$ and $2/m$, respectively, would be required for the dioxane molecule.

Experiments have shown that barium pentathionate, selenopentathionate and telluropentathionate readily give solvates with dioxane. The seleno- and telluropentathionate solvates have been analyzed and found to have the expected composition, *i. e.*, one mole of water and half a mole of dioxane per mole of salt. The solvates are relatively stable, more so than the acetone and tetrahydrofuran solvates, and the perfect cleavage displayed by the latter crystals and those of the dihydrates is absent, in agreement with the idea that dioxane molecules extend across the layer interface and hold the layers more firmly together.

The solvate of barium selenopentathionate with dioxane, $BaSe(S_2O_3)_2 \cdot H_2O \cdot \frac{1}{2}C_4H_8O_2$, was studied crystallographically. The pale green crystals are monoclinic, and formed relatively large, short prisms extended along the a axis and bounded by {011} and {001}. The specimens examined were all persistently twinned. From oscillation and Weissenberg photographs taken with copper radiation, $\lambda(\mathrm{Cu}K_\alpha) = 1.542$ Å, the unit cell dimensions are: $a = 5.02$ Å, $b = 10.59$ Å, $c = 22.72$ Å (all ±0.5 %), $\beta = 102°$. There are four formula units per unit cell; density, calc. 2.83, found 2.81 g/cm^3. Systematic absences, hkl when $k+l$ is odd. The $0kl$ zone of reflections has the same symmetry and intensity distribution as the $0kl$ zone of orthorhombic barium selenopentathionate dihydrate [4], of space group D_{2h}^{16}—$Pnma$, and the a-axis projections of the two salts have also very like dimensions. The unit cell dimensions and systematic absences indicate that the solvate is isostructural with monoclinic barium telluropentathionate dihydrate. These analogies leave little doubt that the space group of the dioxane solvate is the centrosymmetric one, C_{2h}^3—$A2/m$, and that replacement of two crystallographically equivalent water molecules, one in each of two adjacent layers, by one dioxane molecule occurs as indicated above.

EXPERIMENTAL

Solutions of about 1 g of barium pentathionate [2], selenopentathionate [4] and telluropentathionate [1] hydrates in 12 ml of 0.2 N perchloric acid were filtered, when necessary, then warmed to about 40 °C, and about 3 ml of 1,4-dioxane was added. On standing, the solvates crystallized, and were filtered off, washed with dioxane and then with ether, and dried for a short time in a vacuum over sulphuric acid.

The dioxane solvates are less soluble and crystallize more rapidly than the acetone and tetrahydrofuran solvates [5]. As usual, the solubilities decrease in the order, pentathionate, selenopentathionate and telluropentathionate. The crystals of the latter were very small and not suited for single-crystal X-ray work.

For analysis, the selenopentathionate was oxidized with potassium bromate and subsequently analyzed iodometrically by means of the Norris and Fay method, as described earlier [17]. The telluropentathionate was titrated directly with iodine [18].

0.2850 g substance: 22.71 ml of 0.09954 N sodium thiosulphate.
$BaSe(S_2O_3)_2 \cdot H_2O \cdot \frac{1}{2}C_4H_8O_2$ (502.7). Mol. weight found, 504.3.
0.2557 g substance: 18.31 ml of 0.1001 N iodine.
$BaTe(S_2O_3)_2 \cdot H_2O \cdot \frac{1}{2}C_4H_8O_2$ (551.3). Mol. weight found, 558.1.

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