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The Crystal Structure of Barium Dithionate Dihydrate, $BaS_2O_6.2H_2O$

BY J. A. RAUSELL-COLOM AND S. GARCIA-BLANCO
Consejo Superior de Investigaciones Cientificas, Instituto de Quimica Fisica 'A. de Gregorio Rocasolano', Seccion de Rayos X, Serrano 119, *Madrid, Spain*

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The crystal structure of barium dithionate dihydrate, $BaS_2O_6.2H_2O$, has been determined by means of two-dimensional X-ray analysis with the use of photographic data. Refinement by differential synthesis led to final agreement indices of $R_{h0l}=0·065$ and $R_{hk0}=0·079$. The crystals are monoclinic, with $a=12·483$, $b=6·660$, $c=9·195$ Å and $\beta=111°38'$. The space group is $C2/c$. There are four formula units per unit cell. The dithionate ions are located in symmetry centres and the barium ions lie in special positions along the twofold axes. Each barium ion is ten-coordinated to four water molecules and six oxygen atoms from six different dithionate groups.

Introduction

The determination of the crystal structure of $BaS_2O_6.2H_2O$ has been previously attempted by Abbad & Rivoir (1945), Garcia-Blanco & Gomis (1953), Garcia-Blanco (1953), and Garcia-Blanco, Gomis & Abbad (1953). In a series of papers these authors reported progressively the cell dimensions, space group and positional parameters of the atoms. More recently Martinez and Garcia-Blanco (1959) proceeded to the refinement of the (010) projection to an agreement index of $R=0·166$.

The structure reported was that of a pseudo-rhombic crystal, space group $B2_1/a$, with cell constants $a=12·36$, $b=6·66$, $c=17·05$ Å, $\beta=90°36'$, and eight formula units per elementary volume.

In an attempt to refine further the above structure new X-ray diffraction data were collected from a crystal of this substance. It was seen on interpretation that the data corresponded to a different structure, which is described in the following sections.

Experimental

Barium dithionate was prepared by reaction of MnS_2O_6 and $Ba(OH)_2$ in aqueous suspension. The solution of BaS_2O_6 was evaporated and purified by succesive crystallizations at room temperature. The majority of the crystals grew in form of twinned pseudo-rhombic tables such as those described by Abbad & Rivoir (1945). A few had the habit of thin monoclinic needles elongated along the *b* unique axis. Because of their suitable shape, one of these needles was selected for X-ray determinations. That the crystal was of the dihydrate of BaS_2O_6 was ascertained by goniometric determinations of interfacial angles. Stereographic representation of the interfacial angles led to the following constants

$$a:b:c::0·9369:1:1·3799 \text{ and } \beta=111°38'\,,$$

in good agreement with the values given by Groth (1908) for $BaS_2O_6.2H_2O$.

Cell dimensions and space group were determined from Weissenberg photographs (Mo $K\alpha=0·7107$ Å) of the zero, first and second levels along the *b* axis. They are shown in Table 1.

Table 1. *Unit-cell parameters and space group*

$a=12·483\pm0·010$ Å
$b=\ 6·660\pm0·010$
$c=\ 9·195\pm0·010$
$\beta=111°38'\pm6'$
$Z=4$
D_{calc} 3·118 g.cm^{-3}
Volume 710·28 Å^3

Systematic absences
hkl when $h+k=2n+1$
$h0l$ $l=2n+1$ $(h=2n+1)$
$0k0$ $(k=2n+1)$
Space group $C2/c$

Determination and refinement of the structure

The $h0l$ reflexions were recorded from the needle-like crystal (dimensions 0·19 mm × 0·275 mm × 4·5 mm) on a zero layer Weissenberg diagram. A small piece of the same crystal was used for obtaining the $hk0$ reflexions by the same technique. Six different photographs of each setting were made with decreasing time exposures, using Mo $K\alpha$ radiation. The relative intensities were measured with a microphotometer.

Intensities, after scaling, were corrected by the Lorentz and polarization factors, and, in the case of the $h0l$ reflexions, a cylindrical absorption correction was applied (*International Tables for X-ray Crystallography*, 1959). μR was equal to 0·82 for the crystal used. No extinction corrections were applied.

Patterson projections normal to the *b* and *c* axes gave the *y* coordinate of the barium atom and approximate *x*, *y* and *z* coordinates of the one sulphur atom, three oxygen atoms and one water molecule of the asymmetric unit of the structure. As the barium atom is in a special position $(0,y,\frac{1}{4})$, interpretation of the $h0l$ Patterson projection was straightforward. The $hk0$

projection was interpreted by means of Buerger's (1951) method of the minimum function.

Fig. 1 shows two-dimensional Fourier maps normal to [010] and to [001]. They reveal the positions of all atoms in the structure. Certain ambiguities in the positional parameters of the light atoms arise, however. The *y* coordinate of the O(*w*) atom cannot be obtained accurately owing to the proximity of the barium atom, while the presence of the sulphur atom obscures the *x*, *z* coordinates of the O(3) atom and the *y* coordinate of the O(1) atom. In addition, the *y* coordinate of the O(3) atom is undetermined owing to superposition in projection of two of these atoms belonging to two different dithionate ions.

Refinement of the structure was accomplished as follows. Fourier syntheses on both projections, where the contribution of the barium atom to the electron density was excluded, gave the coordinates of the O(*w*) atom with greater accuracy. Two cycles of differential synthesis using all observed *h*0*l* and *hk*0 reflexions afforded the final coordinates of the Ba, S, and O(2) atoms. From the positions of the last two atoms the final coordinates of the O(1) and O(3) atoms were determined geometrically on the basis of the spatial

Table 2. *Final positional parameters and standard deviations in coordinates*

	Point position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ba	4(*e*)	0·00000	0·00000	0·19171	0·00027	0·25000	0·00000
S	8(*f*)	0·20811	0·00012	0·37651	0·00061	0·02892	0·00026
O(1)	8(*f*)	0·17500	0·00041	0·30443	0·00149	0·15670	0·00110
O(2)	8(*f*)	0·11057	0·00041	0·42000	0·00149	−0·11562	0·00110
O(3)	8(*f*)	0·29634	0·00041	0·53430	0·00149	0·07395	0·00110
O(*w*)	8(*f*)	0·07237	0·00035	0·16300	0·00179	0·60076	0·00048

Table 3. *Comparison of calculated and observed structure factors*

H	K	L	FOBS	FCAL
2			78.5	73.2
4			173.0	180.7
6			137.8	150.3
8			66.2	64.4
10			210.0	199.3
12			60.1	56.0
14			124.6	118.6
16			72.3	68.2
18			68.1	69.9
20		2	28.4	33.1-
16		2	86.6	92.3-
14		2	41.7	47.6-
12		2	129.6	125.4-
10		2	36.1	20.9-
8		2	156.5	170.9-
6		2	196.0	206.3-
4		2	113.5	115.4-
2		2	274.1	287.9-
		2	57.9	66.0-
- 2		2	250.7	270.4-
- 4		2	151.3	143.0-
- 6		2	124.6	132.1-
- 8		2	158.4	166.2-
-10		2	109.9	114.2-
-12		2	192.7	188.4-
-14		2	61.8	36.4-
-16		2	88.3	83.3-
-18		2	62.1	61.5-
-22		2	84.9	90.7-
-24		2	19.9	16.7-
16		4	26.8	25.0
14		4	94.0	101.5
12		4	67.0	64.2
10		4	108.9	99.1
8		4	134.7	128.3
6		4	122.4	115.1
4		4	171.9	178.9
2		4	108.9	114.3
		4	122.7	117.8
- 2		4	100.1	108.8
- 4		4	254.0	277.8
- 6		4	192.7	196.6
- 8		4	105.5	105.2
-10		4	151.5	155.9
-12		4	45.6	41.5
-14		4	135.9	124.4
-16		4	93.1	86.6
-18		4	43.6	46.9
-20		4	81.9	90.4
12		6	79.7	82.5-
-24		4	48.8	54.3
-26		4	27.6	24.3
10		6	102.6	111.0-
8		6	67.8	61.0-
6		6	117.4	97.8-
4		6	81.6	73.5-
2		6	169.5	183.7-
		6	128.7	138.9-
- 2		6	149.1	150.0-
- 4		6	161.0	170.5-
- 6		6	79.7	79.5-
- 8		6	178.0	185.8-
-10		6	73.1	63.8-
-12		6	108.6	91.3-
-14		6	124.3	121.6-
-16		6	82.2	77.9-
-18		6	103.9	96.2-
-22		6	48.5	44.4-
8		8	110.6	111.9
4		8	148.9	149.2
2		8	88.0	79.4
		8	129.6	124.3
- 2		8	176.3	174.8
- 6		8	166.4	153.4
- 8		8	97.0	87.6
-10		8	144.9	134.8
-12		8	137.3	124.5
-14		8	62.3	53.0
-16		8	97.6	91.6
-20		8	82.7	79.0
14		10	20.4	24.8-
10		10	76.3	71.5-
6		10	125.2	138.8-
4		10	53.3	48.8-
2		10	74.7	72.9-
		10	100.3	93.1-
- 2		10	54.7	53.5-
- 4		10	155.5	158.4-
- 6		10	64.0	60.1-
- 8		10	128.7	127.3-
-10		10	79.9	75.6-
-12		10	97.3	85.6-
-14		10	101.4	96.9-
-18		10	98.4	102.7-
-22		10	60.7	66.4-
4		12	67.9	74.6
- 2		12	97.9	97.0
- 6		12	124.1	137.6
- 8		12	29.0	32.3
-10		12	77.2	68.7
-12		12	79.7	82.2
-16		12	110.5	117.7
-20		12	59.5	56.3
-18		12	27.1	29.3
		14	69.2	82.3-
- 4		14	81.1	78.5-
-10		14	81.1	82.2-
-12		14	41.9	40.7-
-14		14	83.5	81.2-
-16		14	43.6	48.3-
-20		14	28.7	32.1-
-16		16	35.0	39.5
-20		16	45.2	49.7
	2		127.8	130.6-
	4		58.0	57.0-
	6		74.4	78.4
	8		61.3	70.6-
	10		55.4	61.0
1	1		52.4	48.6
1	3		156.1	148.6-
1	5		145.0	154.4
1	7		45.7	38.9-
1	9		27.0	28.3-
2			74.9	70.9
2	2		166.7	163.5-
2	4		46.8	40.7
2	6		65.1	67.8
2	8		117.7	115.8-
2	10		43.9	50.4
3	1		137.7	126.1
3	3		218.8	236.5-
3	5		88.4	99.4
3	7		46.5	46.9-
4			163.2	180.7
4	2		120.3	116.2-
4	4		3.6	3.1
4	6		66.4	73.3
4	8		54.3	51.9-
4	10		46.6	51.3
5	1		63.5	53.5
5	3		26.9	24.4-
5	5		127.0	129.2
5	7		87.9	88.4-
5	9		40.0	35.2-
6			142.4	150.3
6	2		124.4	125.2-
6	4		30.9	36.7
6	6		58.3	61.0
6	8		69.9	81.0-
6	10		47.8	64.9
7	1		58.9	51.9
7	3		150.9	147.0-
7	5		54.5	54.8
7	7		26.4	27.1-
8			72.1	64.4
8	2		83.9	79.3-
8	4		30.9	30.9
8	6		26.6	26.8
8	8		78.5	83.4-
8	10		44.4	52.7
9	1		8.7	8.0
9	3		75.5	74.5-
9	5		141.8	142.2
9	7		60.2	61.1-
10			185.3	199.3
10	2		61.8	58.3-
10	4		23.9	24.2-
10	6		45.4	39.4
10	8		40.9	45.6-
10	10		41.5	47.2
11	1		44.1	43.2
11	3		104.8	89.8-
11	5		80.4	69.8
12			50.1	56.0
12	2		112.3	102.8-
12	4		49.8	42.4
12	6		55.1	59.6
12	8		76.3	92.5-
13	1		65.0	52.2
13	3		102.6	104.2-
13	5		66.7	61.5
13	7		37.2	33.7-
14			126.8	118.6
14	2		66.1	58.6-
14	4		18.0	22.2-
14	6		43.9	53.0
15	1		30.6	33.3
15	3		62.3	57.3-
15	5		83.0	91.1
15	7		40.8	46.3-
16			82.5	68.2
16	2		62.3	59.4-
17	1		33.4	28.1
17	3		83.3	78.0-
17	5		32.9	31.3
18			79.2	69.9
18	2		49.8	48.3-
19	5		60.2	71.7
20			68.0	60.0

configuration of the $S_2O_6^{2-}$ ion, which requires equal O–S and O–O distances and equal O–S–S angles.

Final positional parameters are shown in Table 2. Standard deviations in coordinates were calculated by Cruickshank's (1949) formulae. With these parameters the agreement index R was brought down to 0·065 for the $h0l$ projection and to 0·079 for the $hk0$ projection. No attempt was made to introduce individual temperature factors; the temperature factor finally used was $\exp(-0{\cdot}56 \sin^2\theta/\lambda^2)$ which was determined by the method of Wilson (1942). Values of f_0 were taken from *International Tables* (1959) on the basis of atoms being charged thus: Ba^{2+}, S^0, $O^{1/3-}$. Observed and calculated structure factors are given in Table 3.

Description and discussion of the structure

The structure is shown in projection in Fig. 2. The dithionate ions are located in symmetry centres and the barium ions are located in special positions along the twofold axes. Each sulphur atom of the dithionate ion is surrounded by the other sulphur atom and three oxygen atoms of the ion, forming an irregular tetrahedron. Interatomic distances and angles and standard deviations (calculated by the formulae of Cruickshank & Roberston, 1953) are

S–S = 2·150 ± 0·004 Å	O–S–S = 104°23′ ± 22′
S–O = 1·462 ± 0·009	O–S–O = 114 3 ± 30
O–O = 2·455 ± 0·012	O–O–O = 60 0 ± 37

These values agree well with those previously reported for the dithionate ion in similar compounds (Martinez, Garcia-Blanco & Rivoir, 1956; Stanley, 1956).

Table 4 gives the details of distances and ionic coordination around the cations and the water molecules. Each barium ion is surrounded by ten oxygen atoms at distances between 2·67 and 3·05 Å (average distance 2·88 Å). These are supplied by six different dithionate ions and by four molecules of water of crystallization (each water molecule being coordinated to two barium ions). The irregular coordination polyhedra thus formed are linked together in a pattern of zigzag chains parallel to [001], where each polyhedron shares with its neighbours two opposite edges consisting of two water molecules. Such chains are bounded side by side into a layer arrangement through parallel chains of dithionate ions, the connecting link being in the sequence Ba · · · O–S–O · · · Ba. The coordinated ionic structure may thus be considered as a stacking of such layers along the direction of [010], the linkage between them being also provided by the $S_2O_6^{2-}$ ions in the sequence

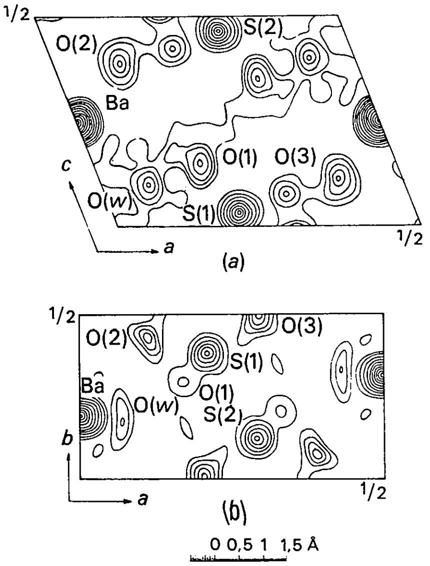

Fig. 1. Electron density maps. (*a*) Projection normal to [010]. (*b*) Projection normal to [001]. Contours drawn at equal but arbitrary levels. Contours of Ba atom drawn at wider intervals.

Table 4. *Ionic coordination of* $BaS_2O_6.2H_2O$

The following roman numbers give the symmetry relationship of the atoms concerned:

I	x	y	z	VI	$-x$	$-y$	$1-z$
II	x	$-y$	$1-z$	VII	$-x$	$1-y$	$-z$
III	x	$-y$	$-\frac{1}{2}+z$	VIII	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
IV	x	$1-y$	$\frac{1}{2}+z$	IX	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
V	$-x$	y	$\frac{1}{2}-z$	X	$-\frac{1}{2}+x$	$-\frac{1}{2}+y$	z

Atom	Point position	Neighbour	Point position	Symmetry code	Number of atoms	Bond length
Ba	(*e*)	O(*w*)	(*f*)	III and VI	2	3·03 Å
		O(*w*)	(*f*)	I and V	2	3·01
		O(1)	(*f*)	I and V	2	2·73
		O(2)	(*f*)	IV and VII	2	2·98
		O(3)	(*f*)	VIII and X	2	2·67
O(*w*)	(*f*)	O(*w*)	(*f*)	VI	1	2·99
		O(1)	(*f*)	IX	1	3·12
		O(2)	(*f*)	II	1	3·00
		O(2)	(*f*)	V	1	2·90
		O(3)	(*f*)	VIII	1	2·82
		O(3)	(*f*)	IX	1	3·12
		Ba	(*e*)	I	1	3·01
		Ba	(*e*)	II	1	3·03

Ba···O–S–S–O···Ba. In total, each $S_2O_6^{2-}$ group connects six different barium ions through its six different oxygen atoms, none of which is coordinated to more than one barium ion.

X-ray diffractograms of compressed powder specimens of this compound show strong variations in the relative intensities of the diffraction peaks, indicating preferred orientation of the (001), (100), (111), and $(\bar{1}13)$ planes, and less markedly of the (101), $(\bar{1}01)$, (010), (023), and (301) planes. All these are planes of cleavage of the crystal, and may easily be recognized as such in terms of the layer arrangement of the structure.

In the present structure no attempt has been made to determine the positions of the hydrogen atoms, and therefore the existence of hydrogen bonding can only be inferred from theoretical considerations. Neutron diffraction studies of hydrates (Hamilton, 1962) indicate that in most cases hydrogen atoms of the water molecules participate in hydrogen bonding. In hydrates where each water molecule is coordinated to two cations the geometrical disposition of the water molecules tends to be such that each molecule is tetrahedrally coordinated to the two cations and to two other anions presenting negative charges towards it, and with which it is hydrogen bonded. In the present case each water molecule is surrounded by two barium ions and by six other hydrogen accepting neighbours at distances between 2·82 and 3·12 Å (Table 4). A geometrical arrangement for hydrogen bonding which is quasi-tetrahedral in configuration is shown in Fig. 2. Here the Ba···O(*w*)···Ba and the O···O(*w*)···O angles are 120°40′ and 122° respectively, the Ba···O(*w*) distances being 3·01 and 3·03 Å and the O···O(*w*) distances 2·89 and 3·12 Å. That there is such a favourable disposition within the structure does not necessarily imply that the water molecule will adopt that particular orientation; a hydrogen bond may occur with some other atom in a less favourable position, or it may not even occur at all, as is the case with one of the hydrogen atoms of $MgSO_4.4H_2O$ (Baur, 1964). The main factor governing the orientation of the water molecule, and hence the geometry of the hydrogen bond, is, according to Baur (1965), the electrostatic interaction between the water molecule and the surrounding atoms, rather than the possibility of a geometrical disposition with linear or nearly linear hydrogen bonds. Baur quotes a list of selected values of distances and angles of some well determined hydrogen bond arrangements, showing that there is a wide range of possibilities between the geometrically different types of hydrogen bond.

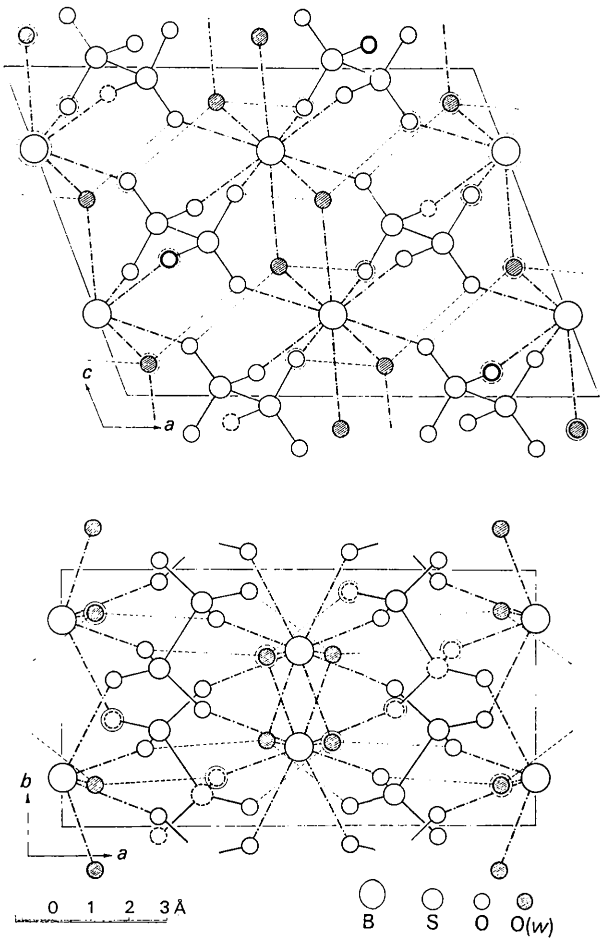

Fig. 2. Structure of $BaS_2O_6.2H_2O$. Atoms drawn with thicker lines have a coordinate greater than unity. Atoms drawn with broken lines have a negative coordinate. A continuous line encircling an atom represents the same atom at a positive translation of unity. A discontinuous line encircling an atom represents same atom at a negative translation of unity. Coordination bonds are represented by chain-dotted lines, possible hydrogen bonds by broken lines.

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