Acta Cryst. (1975). B31, 2905

Barium Disulphide

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(*Received* 11 *June* 1975; *accepted* 7 *July* 1975)

Abstract. BaS_2, monoclinic, $C2/c$, $a=9{\cdot}299$ (4), $b=4{\cdot}736$ (2), $c=8{\cdot}993$ (4) Å, $\beta=118{\cdot}37$ (3)°, $Z=4$, $D_x=3{\cdot}84$ g cm^{-3}. Crystals were prepared by heating an equimolar mixture of BaS and S up to 800 °C in a graphite tube placed in an evacuated Vycol glass ampoule. S_2^{2-} ions (S–S bond length 2·118 Å) form arrays parallel to ⟨110⟩. Ba ions are located between these arrays and coordinated to eight S atoms.

Introduction. The single crystals obtained were lemon-yellow. The specimen examined by X-rays had approximately the shape of a hemisphere with a radius of about 0·08 mm. The intensity data were collected on a Rigaku four-circle diffractometer with Mo $K\alpha_1$ ($\lambda=0{\cdot}70926$ Å) radiation monochromatized by graphite. For $2\theta<90{\cdot}0°$, 2787 independent reflexions were measured, of which 2145 were considered to be zero. The observed intensities were rather weak for the specimen size, indicating that only a part of the specimen was crystalline. For this reason, an absorption correction was not applied.

The systematic absences were hkl: $h+k=2n+1$ and $h0l$: $l=2n+1$, giving possible space groups $C2/c$ (No. 15) and Cc (No. 9). The structure determination verified the former space group.

The position of the Ba atom was obtained from a Patterson map. A difference Fourier synthesis revealed the position of the S atom. The structure was refined by the full-matrix least-squares method with *ORFLS* (Busing, Martin & Levy, 1962) with anisotropic tem-

Table 1. *Atomic parameters* ($\times 10^4$)

Temperature factors are expressed as $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0	1446 (3)	2500	47 (1)	160 (4)	56 (1)	0	27 (1)	0
S	1603 (3)	3545 (8)	206 (3)	53 (3)	163 (11)	73 (4)	5 (7)	38 (3)	2 (1)

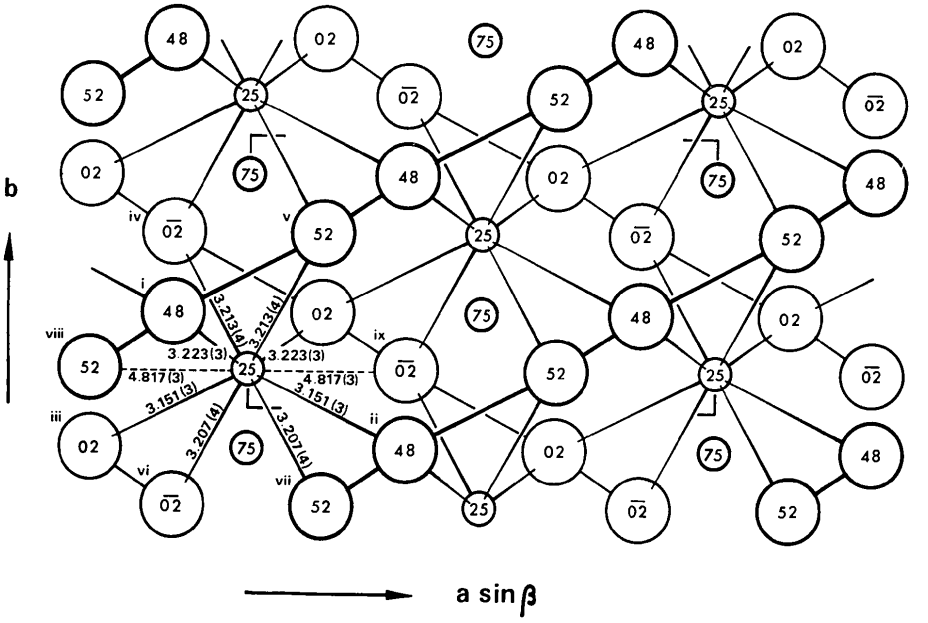

Fig. 1. The structure of BaS_2 projected along **c**. Small circles are Ba atoms and large circles S atoms. Fractional z coordinates ($\times 10^2$) are shown in the circles. Ba–S distances are also indicated. For the symmetry-operation superscripts see Table 2.

Table 2. *Bond angles* (°) *around* Ba (∠ S–Ba–S)

	S^{i}	S^{ii}	S^{iii}	S^{iv}	S^{v}	S^{vi}	S^{vii}
S	144·1 (1)	85·9 (1)	109·9 (1)	58·5 (1)	93·9 (1)	86·1 (1)	121·6 (1)
S^{i}		109·9 (1)	85·9 (1)	93·9 (1)	58·5 (1)	121·6 (1)	86·1 (1)
S^{ii}			128·3 (1)	141·1 (1)	82·3 (1)	97·8 (1)	38·9 (1)
S^{iii}				82·3 (1)	141·1 (1)	38·9 (1)	97·8 (1)
S^{iv}					84·8 (1)	95·1 (1)	179·9 (21)
S^{v}						179·9 (21)	95·1 (1)
S^{vi}							85·0 (1)

Symmetry code

i	$-x$,	y,	$\frac{1}{2}-z$
ii	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
iii	$-\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	z
iv	$-x$,	$1-y$,	$-z$
v	x,	$1-y$,	$\frac{1}{2}+z$
vi	$-x$,	$-y$,	$-z$
vii	x,	$-y$,	$\frac{1}{2}+z$

perature factors. No parameter shift occurred in the last least-squares cycle. The final R value was 0·056 and the weighted R 0·049 for 642 observed reflexions.* The atomic scattering factors for Ba and S were taken from Hanson, Herman, Lea & Skillman (1964).

Discussion. The atomic parameters of BaS_2 are given in Table 1. In the structure of BaS_2, arrays of disulphide ions S_2^{2-} with an S–S bond length of 2·118 Å run parallel to ⟨110⟩ at approximately $z=0$ and $z=\frac{1}{2}$ (Figs. 1 and 2). Compared with the non-bonded S–S distances ranging from 3·21 to 3·98 Å found in the closely related compounds Ba_2S_3 and BaS_3, the S–S distance of 3·143 Å between neighbouring disulphide ions in BaS_2 is rather short, possibly suggesting the existence of some weak bonding between them. The S–S–S angle in these arrays is 165·08°. The Ba ion is located between the arrays of disulphide ions and surrounded by eight S atoms; the Ba–S distances range from 3·151 to 3·223 Å.

The structures of the above-mentioned barium polysulphides were determined by Yamaoka, Lemley, Jenks & Steinfink (1975) using single crystals obtained under high pressure. Ba_2S_3 contains a divalent S ion and an S_2^{2-} disulphide ion with an S–S bond length of 2·32 Å. The barium ions are each surrounded by nine S atoms which are 3·11 to 3·91 Å distant from the Ba ions. In BaS_3 the S atoms form S_3^{2-} polysulphide ions with a bond length of 2·074 Å and the Ba is surrounded by 12 S atoms; the Ba–S distances range from 3·204 to 3·541 Å. It should be noted that in this series of barium polysulphides, including BaS_2, the bond lengths in the polysulphide ions decrease with increasing S content in the compounds, probably indicating increasing bond strengths.

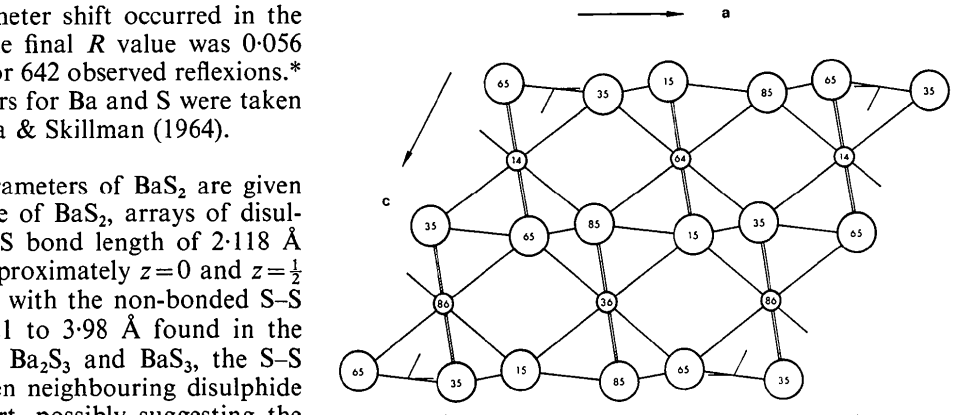

Fig. 2. Projection of the structure along **b**. Small circles are Ba atoms and large circles S atoms. Fractional y coordinates ($\times 10^2$) are shown in the circles.

Interatomic distances and angles were calculated with *ORFFE* (Busing, Martin & Levy, 1964). The Ba–S distances in the coordination polyhedron are indicated in Fig. 1. The bond angles at Ba are listed in Table 2. The calculations were carried out on the FACOM 270-20 of this Institute.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31277 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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