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## Barium Thiocyanate Trihydrate

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## Abstract

$\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ ,  $M_r = 307.55$ , is monoclinic,  $C2/m$ , with  $a = 15.981$  (1),  $b = 4.441$  (1),  $c = 13.333$  (1) Å,  $\beta = 104.65$  (1)°,  $V = 915.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.23$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 4.74$  mm<sup>-1</sup>. The salt, which was reported in a previous structural study as a dihydrate [Zvonkova & Zhdanov (1950), *Zh. Fiz. Khim.* **24**, 1345–1349], is actually a trihydrate. The third water molecule has been located and the structure has been refined to  $R = 0.032$  for 1059 observed reflections. Ba has a tricapped trigonal prismatic coordination: four N, four O and one S (Ba–N = 2.90–2.91, Ba–O = 2.71–2.90, Ba–S = 3.39 Å). Bond lengths within the two independent thiocyanate groups are N–C = 1.15 and C–S = 1.65–1.66 Å. The water molecules are involved in O–H...S hydrogen bonds with O...S = 3.36–3.77 Å. E.s.d.'s for distances involving non-hydrogen atoms are  $\leq 0.01$  Å. A reversible phase transition was found to occur at about 135 K by Raman spectroscopy.

## Introduction

During continuing studies on hydrogen bonds between H<sub>2</sub>O molecules and S in crystalline hydrates we became interested in structures of thiocyanate hydrates (Mereiter & Preisinger, 1982). Zvonkova & Zhdanov (1950) reported the structure of a salt stated to be  $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ , monoclinic, space group  $C2/m$ , with lattice parameters  $a = 15.98$ ,  $b = 4.26$ ,  $c = 13.26$  Å

and  $\beta = 104.5^\circ$ . The structure was determined from X-ray film data by Patterson and Fourier projections. No  $R$  values, but only a table of  $F_o$ 's without  $F_c$ 's were given. Several errors in this paper were pointed out and partly corrected in *Structure Reports* (1950). Unfortunately it was not realized that barium thiocyanate crystallizes as a trihydrate rather than a dihydrate, an error which seems to date back to the first description of the salt and which has been retained in many later references [see Foote & Hickey (1937)]. After becoming aware of this problem we decided to start a re-examination.

## Experimental

The title compound was prepared by boiling an aqueous solution of  $\text{NH}_4\text{SCN}$  and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  until all  $\text{NH}_3$  was expelled. The excess of  $\text{Ba}(\text{OH})_2$  was then precipitated with  $\text{CO}_2$  as  $\text{BaCO}_3$ . Filtration, evaporation and cooling of the solution, followed by recrystallization from water below 323 K, yielded needle-like crystals which are stable in air. A thermogravimetric analysis confirmed that the salt is a trihydrate. When heated in a stream of dry air with continuously rising temperature (4 K min<sup>-1</sup>) the salt starts to lose water above 345 K, a process which continues until 430 K. The resulting anhydrous salt is stable until 720 K and decomposes then to BaS which subsequently oxidizes slowly to  $\text{BaSO}_4$ . Raman spectra showed that the title compound is subject to a reversible phase transformation at about 135 K (see *Discussion*).

Preliminary Weissenberg photographs were in accordance with the data given by Zvonkova & Zhdanov (1950). Accurate cell parameters (see *Abstract*) and diffraction intensities were measured on a Philips PW 1100 four-circle diffractometer with graphite monochromated Mo  $K\alpha$  radiation. A needle-shaped crystal of 0.04 mm diameter and 0.4 mm length was used for data collection in the  $\omega$ - $2\theta$  scan mode with a scan range of  $1.2^\circ$  and counting times of 40 and  $2 \times 10$  s for the scan and the stationary backgrounds, respectively. Standard reflections monitored every 2 h were constant with time. 1553 independent reflections were measured ( $3 < \theta < 30^\circ$ ), of which 1059 with  $I > 3\sigma(I)$  were used for the subsequent calculations. The data were corrected for absorption; transmission factors ranged from 0.78 to 0.87.

A structure factor calculation with the revised atomic parameters given in *Structure Reports* (1950) showed them to be basically correct ( $R = 0.1$ ). The third, missing water molecule of the structure was located in a Fourier map. Least-squares refinement with anisotropic temperature factors resulted in  $R = 0.034$ . H atoms could be recognized in a difference map and were included in the refinement with isotropic temperature factors fixed at  $B = 6 \text{ \AA}^2$ ; positional parameters were allowed to vary while intramolecular O—H distances and H—O—H angles were restricted to  $0.96 \text{ \AA}$  and  $108^\circ$ , respectively. The final refinement converged to  $R = 0.032$ ,  $R_w = 0.033$  and  $S = [\sum w(F_o - F_c)^2 / (1059 - 71)]^{1/2} = 1.44$ , where  $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$ . An additional refinement indicated that the O positions are fully occupied. Calculations were carried out with *SHELX 76* (Sheldrick, 1976). Atomic coordinates and equivalent isotropic temperature fac-

Table 1. Atomic coordinates ( $\times 10^5$  for Ba and S,  $\times 10^4$  for N, C, O and H) and equivalent isotropic  $B$ 's ( $\text{\AA}^2$ )

The H atoms were refined as parts of rigid  $\text{H}_2\text{O}$  molecules (see text); the e.s.d.'s for the  $[010]$  rotation around the oxygens are  $8^\circ$  for  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(2)$ , and  $5^\circ$  for  $\text{H}_2\text{O}(3)$ .  $B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ .

|       | <i>x</i>   | <i>y</i> | <i>z</i>   | <i>B</i> <sub>eq</sub> |
|-------|------------|----------|------------|------------------------|
| Ba    | 12482 (3)  | 0        | 27137 (4)  | 2.18 (2)               |
| S(1)  | 34179 (13) | 0        | 37409 (15) | 3.2 (1)                |
| S(2)  | 33290 (14) | 0        | 8837 (18)  | 4.2 (1)                |
| C(1)  | 3413 (5)   | 0        | 4986 (6)   | 2.4 (3)                |
| C(2)  | 4359 (5)   | 0        | 1516 (6)   | 2.8 (3)                |
| N(1)  | 3397 (5)   | 0        | 5843 (5)   | 3.0 (3)                |
| N(2)  | 5083 (5)   | 0        | 1940 (6)   | 3.8 (3)                |
| O(1)  | 9998 (4)   | 0        | 3757 (7)   | 5.2 (3)                |
| O(2)  | 890 (5)    | 0        | 576 (5)    | 5.1 (3)                |
| O(3)  | 7129 (4)   | 0        | 2030 (6)   | 4.8 (3)                |
| H(1)  | 9664       | 1749     | 3825       |                        |
| H(2)  | 1134       | 1749     | 335        |                        |
| H(31) | 7665       | 0        | 2556       |                        |
| H(32) | 7261       | 0        | 1366       |                        |

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Symmetry code: None  $x, y, z$ ; (i)  $x - 1, y, z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (iii)  $\frac{1}{2} + x, y - \frac{1}{2}, z$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (v)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (vi)  $1 - x, -y, -z$ ; (vii)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (viii)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ ; (ix)  $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$ ; (x)  $\frac{1}{2} - x, -\frac{1}{2} - y, -z$ .

(a) Ba coordination polyhedron

|                          |           |                        |           |
|--------------------------|-----------|------------------------|-----------|
| Ba—S(1)                  | 3.391 (2) | Ba—O(1 <sup>i</sup> )  | 2.708 (9) |
| —N(1 <sup>vii,ix</sup> ) | 2.899 (4) | —O(2)                  | 2.762 (7) |
| —N(2 <sup>ix,v</sup> )   | 2.914 (5) | —O(3 <sup>ix,v</sup> ) | 2.897 (5) |

(b) Thiocyanate groups

|           |            |                                          |           |
|-----------|------------|------------------------------------------|-----------|
| N(1)—C(1) | 1.149 (11) | N(1)—C(1)—S(1)                           | 179.0 (8) |
| C(1)—S(1) | 1.662 (9)  | C(1)—N(1)—Ba <sup>vii,ix</sup>           | 127.6 (2) |
| N(1)—S(1) | 2.811 (7)  | Ba <sup>ii</sup> —N(1)—Ba <sup>ix</sup>  | 100.0 (2) |
|           |            | C(1)—S(1)—Ba                             | 98.1 (3)  |
| N(2)—C(2) | 1.152 (10) | N(2)—C(2)—S(2)                           | 178.7 (9) |
| C(2)—S(2) | 1.649 (8)  | C(2)—N(2)—Ba <sup>ii,iii</sup>           | 130.3 (2) |
| N(2)—S(2) | 2.801 (8)  | Ba <sup>ii</sup> —N(2)—Ba <sup>iii</sup> | 99.3 (2)  |

(c) Hydrogen-bond geometry ( $\text{H}_2\text{O}$  geometry fixed at O—H =  $0.96 \text{ \AA}$  and H—O—H =  $108^\circ$ )

|                                                   | H...S    | O...S     | $\angle$ O—H...S     |
|---------------------------------------------------|----------|-----------|----------------------|
| O(1)—H(1)...S(1 <sup>ii</sup> )                   | 2.44 (3) | 3.359 (5) | 160 (4)              |
| O(2)—H(2)...S(2 <sup>viii</sup> )                 | 2.48 (3) | 3.392 (6) | 158 (4)              |
| O(3) { —H(31)...S(1 <sup>ii,iii</sup> )           | 2.81 (2) | 3.464 (5) | 126 (2)*             |
| { —H(32)...S(2 <sup>ii,iii</sup> )                | 2.97 (5) | 3.525 (7) | 118 (4) <sup>†</sup> |
| { —H(32)...S(2 <sup>vi</sup> )                    | 2.91 (5) | 3.767 (8) | 150 (7)              |
| S(1 <sup>ii</sup> )...O(1)...S(1 <sup>iii</sup> ) | 82.8 (2) |           |                      |
| S(2 <sup>viii</sup> )...O(2)...S(2 <sup>x</sup> ) | 81.8 (2) |           |                      |

\* Bifurcated.

† Trifurcated.

tors are given in Table 1, interatomic distances and angles in Table 2.\*

## Results and discussion

Our study left no doubt that Zvonkova & Zhdanov (1950) investigated  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  and not a dihydrate. Unit-cell dimensions and the corrected atomic parameters given in *Structure Reports* (1950) agree reasonably well with those obtained here, except for the third water molecule,  $\text{H}_2\text{O}(3)$ , which had apparently been overlooked in the previous study. This was proved by calculating a Fourier map with Zvonkova & Zhdanov's published  $h0l$  data, which showed the third O as a peak slightly larger than those of the two already known O atoms.

The structure of  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  (Fig. 1) contains two independent, almost linear thiocyanate groups, one of which is bonded *via* N and S to three Ba and the other one *via* N to two Ba atoms. The observed N—C and C—S bond lengths agree well with those found for

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36371 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

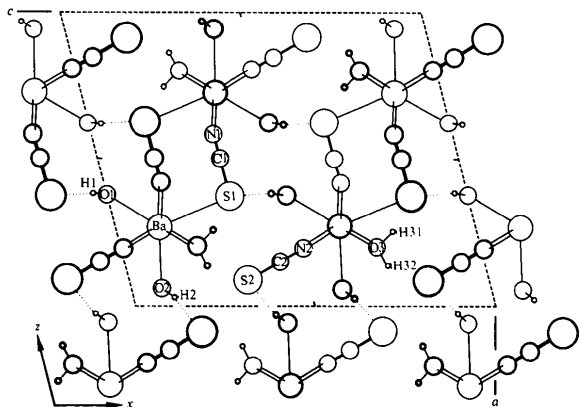


Fig. 1. A view of the structure along *b*. All atoms, except H(1) and H(2), lie on mirror planes at  $y = 0$  and  $y = \frac{1}{2}$ .

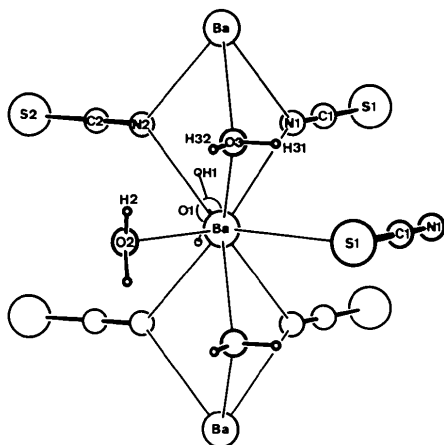


Fig. 2. View of a  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  single chain.

other thiocyanate hydrates (Brattås, Jagner & Ljungström, 1978; Drew & Hamid bin Othman, 1975; Mereiter & Preisinger, 1982).

Barium has a regular tricapped trigonal prismatic coordination (Fig. 2). The trigonal prism is defined by three pairs of mirror-plane-related atoms, two N(1), two N(2) and two O(3), which are at very similar distances to Ba (2.897–2.914 Å). Each of these N and O atoms bridges and connects two Ba atoms parallel to *b*. The coordination around Ba is supplemented by O(1), O(2) and S(1), which are at terminal positions bonded to only one Ba. Ba–O bonds for the two terminal water molecules are slightly shorter than those of the bridging molecule, a feature which has been observed also in  $\text{Ba}_6(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  (Masse, Guitel & Durif, 1976). The cation coordination in  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  closely resembles those found in  $\text{Ba}(\text{N}_3)_2 \cdot \text{H}_2\text{O}$  (Walitzki & Krischner, 1973) and  $\text{Ba}(\text{N}_3)_2$  (Choi, 1969; Walitzki & Krischner, 1970). In the first, Ba is surrounded by seven N at 2.85–3.00 Å and two O ( $\text{H}_2\text{O}$  bridging two Ba) at 2.85–2.98 Å. In the second, Ba is surrounded by nine N at 2.883–2.985 Å.

The crystal structure consists of continuous chains which extend along *b*. The single chains shown in Fig. 2 are connected in pairs *via* the Ba–S(1) bonds to form double chains which are linked only by hydrogen bonds (Fig. 1). The single chains are topologically identical with the  $M(\text{H}_2\text{O})_6$  chains (*M* in tricapped trigonal prismatic coordination) present in the  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ -type structures (Leclaire & Borel, 1977), to which  $\text{BaI}_2 \cdot 6\text{H}_2\text{O}$  is reported to belong (Hermann, 1931). There is also a striking similarity between the structures of  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ba}(\text{N}_3)_2$ . The double chains mentioned above can be regarded as a fragment of the  $\text{Ba}(\text{N}_3)_2$  framework structure, where some of the N ligands have been replaced by  $\text{H}_2\text{O}$ . The cell dimensions parallel to the chain directions,  $b = 4.44$  Å for the title compound and  $b = 4.39$  Å for  $\text{Ba}(\text{N}_3)_2$ , are thus very similar. The structure of  $\text{Ba}(\text{N}_3)_2 \cdot \text{H}_2\text{O}$  does not show this close relationship with the title compound.

### Hydrogen bonds

Although we cannot claim high accuracy for the H atoms, they seem to be sufficiently well established from X-ray data and stereochemical considerations to justify discussion of the hydrogen bonds. All  $\text{H}_2\text{O}$  molecules are involved in O–H...S-type interactions (Table 2c). Molecules  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(2)$  are in very similar environments, each being bonded to one Ba and *via* H atoms to a pair of S atoms. The coordination is flat pyramidal. The O...S distances,  $2 \times 3.36$  Å for O(1) and  $2 \times 3.39$  Å for O(2), are close to the mean value of 3.324 Å reported for about sixty O–H...S bonds (Mereiter, Preisinger & Guth, 1979). The small S...O...S angles, 82.8 and 81.8°, effect a considerable bending of the hydrogen bonds. Two  $\text{H}_2\text{O}(2)$  molecules are located very close to each other. The corresponding O...O distance, 2.87 Å, is shorter than usually found between non-bonded  $\text{H}_2\text{O}$  molecules and might indicate the presence of an O–H...O hydrogen bond, a case which we cannot completely rule out without neutron data. If present, however, the O–H...O bond would replace only one of four equivalent O–H...S bonds.

An unusual situation is encountered with  $\text{H}_2\text{O}(3)$ . This molecule bridges two Ba and has five neighbouring S atoms at distances appropriate for O–H...S-type bonds (O–S = 3.46–3.77 Å), but all of them in positions which are unfavourable to the formation of a pair of straight hydrogen bonds. To form such a pair of bonds the H–O–H plane of the molecule should be either parallel or inclined at  $\sim 45^\circ$  to the Ba–O–Ba plane, which would cause an unfavourably short separation between H and Ba. Comparisons with structures where  $\text{H}_2\text{O}$  molecules bridging two Ba were studied by neutron diffraction show that the angles between the H–O–H planes and

the corresponding Ba—O—Ba planes do not deviate by more than  $10^\circ$  from  $90^\circ$ , even in the case of furcated hydrogen bonds in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (Padmanabhan, Busing & Levy, 1978) and  $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  (Maffly, Johnson & Williams, 1977). This permits us to trust our X-ray results, according to which the  $\text{H}_2\text{O}(3)$  molecule is oriented parallel to (010) and consequently exhibits one bifurcated and one trifurcated  $\text{O—H} \cdots \text{S}$  interaction. The situation for H(31), which is directed towards two mirror-plane-related S atoms ( $\text{H} \cdots \text{S} = 2 \times 2.81$ ,  $\text{O} \cdots \text{S} = 2 \times 3.46$  Å), compares well with the bifurcated hydrogen bond in  $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$ , for which  $\text{D} \cdots \text{S}$  distances of 2.76 and 2.85 Å ( $\text{O} \cdots \text{S} = 3.55$  and 3.58 Å) have been established by neutron diffraction (Mereiter, Preisinger, Guth, Heger, Hiebl & Mikenda, 1979). Neglecting geometrical criteria for the detection of hydrogen bonds (Hamilton & Ibers, 1968), the coordination around H(32) might be described as that of a trifurcated hydrogen bond. This seems to be justified despite the rather large  $\text{H}(32) \cdots \text{S}$  distances (2.91–2.97 Å), in view of the effects observed for bifurcated  $\text{O—H} \cdots \text{S}$  hydrogen bonds (Mikenda & Preisinger, 1980), which do not have much shorter  $\text{H}, \text{D} \cdots \text{S}$  distances.

#### Phase transition

A reversible phase transition was found to occur at about  $135 \pm 5$  K by Raman spectroscopy. Raman spectra above the transition temperature exhibit only two N—CS valence stretching vibration lines ( $\tilde{\nu}_1$  vibrations at 2064 and 2074  $\text{cm}^{-1}$ ), which is in full agreement with the structure described above. Below 135 K four different N—CS vibrations are observed in the spectrum ( $\tilde{\nu}_1 = 2062\text{--}2102$   $\text{cm}^{-1}$ ), which proves that at this temperature the structure has a lower symmetry. Structural changes at the transition temperature are certainly of a distortional nature, most likely accompanied by modifications of the hydrogen-bond system. This is not surprising in view of the rather unusual hydrogen-bond system in the room-temperature structure.

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