Space Group Data on Barium Pentathionate

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Crystals of barium pentathionate dihydrate [1] have been obtained in two modifications, one triclinic (I) by crystallization from water, and one orthorhombic (II) by crystallization from aqueous methanol. The dimensions of the unit cells, from oscillation and Weissenberg photographs taken with CuK_α radiation, $\lambda = 1.54$ Å, are:

I, $a = 5.00 \pm 0.02$ Å, $b = 10.36 \pm 0.04$ Å, $c = 11.53 \pm 0.04$ Å, $\alpha = 110°$, $\beta = 98°$, $\gamma = 90°$. Two molecules per unit cell; density, calc. 2.56, found 2.59. No absent reflections. The Wilson [2] ratio, $\varrho = \langle|F_{obs}|\rangle^2 / \langle F^2_{obs}\rangle$, is 0.59 for 274 $0kl$ reflections in the range $\sin\vartheta$ from 0.25 to 1. The predicted value being 0.637 for centrosymmetric crystals and 0.785 for noncentrosymmetric crystals, this indicates that the space group is $C_i^1-P\bar{1}$.

II, $a = 5.00 \pm 0.02$ Å, $b = 10.30 \pm 0.04$ Å, $c = 21.78 \pm 0.06$ Å. Four molecules per unit cell; density, calc. 2.55, found 2.53. Absent reflections, $0kl$ when $k + l$ is odd, $hk0$ when h is odd. The Wilson ratio, calculated for $0kl$ reflections as above, is 0.57, which is in favour of the centrosymmetric space group $D_{2h}^{16}-Pnma$.

The crystals, for both modifications, appear as prisms elongated along the a axis and flattened along the b axis. In both cases there is perfect cleavage along (001). The relative distribution of the intensities of the $00l$ reflections, with the c axis of I doubled, is very similar for the two crystals.

A Patterson synthesis based on the $0kl$ data of I gave the y and z parameters of the barium atom, the space group being chosen as $C_i^1-P\bar{1}$. Subsequent Fourier syntheses, starting with the strongest reflections and signs calculated from the barium contributions alone, revealed the positions of the five sulphur atoms, in agreement with the barium-sulphur vectors of the Patterson map. The pentathionate ion is unbranched, and there is an apparent mirror plane perpendicular to the b axis at $z = 0$, $y = 1/4$ and passing through the barium atom and the central sulphur atom of the pentathionate ion at $z = -0.11$ and $z = 0.34$, respectively.

A mirror plane as a molecular symmetry element is in accordance with the requirements of the space group $D_{2h}^{16}-Pnma$ for II. A Patterson synthesis based on the $0kl$ data of II was carried out. The positions and numbers of vector peaks on the resulting map show that the structure of the pentathionate ion in this crystal is the same as in I, and that the space group of II is $D_{2h}^{16}-Pnma$. The barium atom and the central sulphur atom of the pentathionate ion lie in the fourfold positions *(c)* of this space group [3].

The pentathionate ion in barium pentathionate thus possesses a mirror plane of symmetry. The configuration of the sulphur chain is similar to that of the S_8 ring of orthorhombic sulphur [4] with three adjacent sulphur atoms removed.

Work on the crystal structure of barium pentathionate (I and II) is being continued. Also, work is being done on strontium and barium selenopentathionate and telluropentathionate, and on solvates of the above salts with ethanol and acetone.

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