CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

# The Crystal Structure of Strontium Dibromide

BY JOHN G. SMEGGIL AND HARRY A. EICK*

*Received September 30, 1970*

The crystal structure of $SrBr_2$ was found by single-crystal X-ray diffraction techniques to be consistent with space group $P4/n$ (no. 85). The tetragonal unit cell ($a = 11.630 \pm 7$, $c = 7.146 \pm 5$ Å; $d_x = 4.25$ g cm$^{-3}$) contains 10 formula units. One strontium atom is located uniquely in position 2c ($^1/_4$, $^1/_4$, $\simeq$0.848), in contrast to previous reports that this atom either randomly occupied this position and another ($^1/_4$, $^1/_4$, $\simeq$0.36) or was entirely in the second position. The structure is characterized by seven- and eight-coordinate Sr atoms and trigonally and tetrahedrally coordinated bromine atoms and may be considered a hybrid of the $SrCl_2$ and $SrI_2$ structure types. The bromine atoms form parallel to the $c$ axis a chain of antiprisms which are alternatively vacant and occupied. The Sr–Br bond distances vary from 3.106 to 3.593 Å, with an average value of 3.2 Å.

## Introduction

In 1963 Sass, Brackett, and Brackett,[1] reviewing earlier work, claimed that the structure proposed for $SrBr_2$ by Kammermans[2] on the basis of single-crystal X-ray investigation did not correctly explain the powder pattern reported by Döll and Klemm.[3] Sass, *et al.*, on the basis of intensity data for $SrBr_2$ taken with a powder diffractometer proposed a structure which located eight Sr atoms in a general position and distributed two Sr atoms randomly between two twofold positions. On the basis of comparably collected powder intensity data, Haschke and Eick[4] (HE) claimed that these latter two Sr atoms are not randomly distributed but rather totally occupy one of the twofold positions. However, they could not determine which position was occupied. This work was undertaken to solve definitely the $SrBr_2$ structure by single-crystal X-ray techniques and thereby settle the question of the Sr occupancy.

## Experimental Section

Strontium dibromide was prepared as described previously[4] by dissolving strontium hydroxide (reagent grade, J. T. Baker Chemical Co., Phillipsburg, N. J.) in 48% HBr and dehydrating the solution under vacuum at a maximum temperature of 800°. Single crystals of $SrBr_2$ were obtained by vapor transport; powdered $SrBr_2$ confined in an evacuated quartz tube was heated at approximately 1000° for 36–48 hr.

The space group was determined from Weissenberg and rotation photographs. Intensity data were collected using a multiple-film technique with a Charles Supper Weissenberg camera, and intensities were measured by visual comparison with a calibrated film strip. Nickel-filtered Cu K$\alpha$ radiation was used to collect $hkl$, $l = 0$–5, level intensity data (406 observed independent reflections) which were corrected for Lorentz and polarization effects. Absorption corrections, based on the crystal's approximately rectangular prismatic shape (about 100 $\mu \times$ 100 $\mu \times$ 180 $\mu$), were made using Busing and Levy's method for a general polyhedron[5] ($\mu = 461$ cm$^{-1}$). Lattice parameters determined at 25° from a Guinier powder photograph with Pt, $a = 3.9237 \pm 0.0003$ Å,[6] as an internal standard and Cu K$\alpha_1$ radiation are $a = 11.630 \pm 0.007$ Å, $c = 7.146 \pm 0.005$ Å; $Z = 10$ (see below); $d_x = 4.25$ g cm$^{-3}$.

## Structure Determination

The indices of the observed reflections were found to obey the following condition for reflection: $hk0$, $h + k = 2n$. This requirement is consistent with two centrosymmetric space groups: $P4/n$ or $P4/nmm$.

The positional parameters reported by HE were used as the starting model which was refined by full-matrix, least-squares calculation with the computer program ORFLS.[7] The scattering factors[8] for both Sr and Br were corrected for anomalous dispersion[9] according to the relationship $f = f_0 + \Delta f' + 0.5(\Delta f'')^2/(2(f_0 + \Delta f'))$, where $f_0$, $\Delta f'$, and $\Delta f''$ are the scattering factors uncorrected for anomalous dispersion and the real and imaginary parts of the anomalous correction, respectively.[10] In the structure proposed by HE for $SrBr_2$ there are 10 formula units per unit cell in space group $P4/n$ (no. 85) with three atoms in general eightfold (8g) positions, four atoms in two twofold (2a, 2b) positions, and two atoms in a twofold (2c) position. In addition to the ten corresponding positional parameters, six scale factors and six independent isotropic temperature factor coefficients were refined. The overdetermination of the structure was thus greater than 18-fold.

When in the least-squares refinement two Sr atoms were randomly located in the two 2c positions as suggested by Sass, *et al.*, the occupancy factor for the Sr atom situated at $\pm$($^1/_4$, $^1/_4$, $\simeq$0.36) and its isotropic temperature factor refined toward zero and an unreasonable high value, respectively. However, the occupancy factor for the atom at $\pm$($^1/_4$, $^1/_4$, $\simeq$0.86) refined to 0.250, the value expected for an atom in this position, and its isotropic thermal factor refined to a reasonable value. Accordingly, the structure was refined further with an Sr atom occupying fully the latter site.

The weights, $w$, were taken as unity for all reflections. The quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares procedure. An unweighted $R$ factor of 0.099 was obtained after several cycles of refinement. Additional cycles did not yield further refinement of the structure, and all parameter variations were <1% esd's of the parameters. The parameters which are presented in Table I refer to the origin at $\bar{1}$ at $^1/_4$, $^{\bar{1}}/_4$, 0 from $\bar{4}$. The Sr–Br atom distances implied by these parameters were calculated using a computer program DISTAN[11] and

---

[1] R. L. Sass, T. Brackett, and E. Brackett, *J. Phys. Chem.*, **67**, 2862 (1963).

[2] M. A. Kammermans, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **103**, 406 (1939).

[3] W. Döll and W. Klemm, *Z. Anorg. Allg. Chem.*, **241**, 239 (1939).

[4] J. M. Haschke and H. A. Eick, *J. Inorg. Nucl. Chem.*, **32**, 2153 (1970).

[5] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

[6] J. D. H. Donnay, Ed., "Crystal Data Determinative Tables," 2nd ed, American Crystallographic Association, Washington, D. C., 1963, p 841.

[7] W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[8] H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

[9] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[10] R. W. James, "The Crystalline State," Vol. II, G. Bell & Sons, Ltd., London, 1950, p 181.

[11] A. Zalkin, private communication.

TABLE I

POSITIONAL PARAMETERS OBTAINED BY LEAST-SQUARES REFINEMENT OF THE CRYSTAL STRUCTURE OF $SrBr_2$

| Atom | $10^4X/a$ | $10^4Y/b$ | $10^4Z/c$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Sr(1) | 1045 ± 4 | 5856 ± 4 | 2476 ± 8 | 2.75 ± 0.09 |
| Sr(2) | 2500 | 2500 | 8483 ± 13 | 1.85 ± 0.16 |
| Br(1) | 1531 ± 5 | 4590 ± 5 | 6258 ± 9 | 3.33 ± 0.12 |
| Br(2) | 3388 ± 4 | 4572 ± 4 | 963 ± 8 | 2.43 ± 0.10 |
| Br(3) | 2500 | 7500 | 0 | 2.90 ± 0.23 |
| Br(4) | 2500 | 7500 | 5000 | 2.44 ± 0.27 |

TABLE II

INTERATOMIC DISTANCES IN $SrBr_2$

| Ref atom | Coord atom | No. of coord atoms | Distance, Å |
|---|---|---|---|
| Sr(1) | Br(3) | 1 | 3.106 ± 5 |
| | Br(2) | 1 | 3.122 ± 8 |
| | Br(4) | 1 | 3.126 ± 5 |
| | Br(1) | 1 | 3.129 ± 8 |
| | Br(2) | 1 | 3.150 ± 7 |
| | Br(1) | 1 | 3.173 ± 8 |
| | Br(2) | 1 | 3.290 ± 7 |
| | Br(1) | 1 | 3.593 ± 8 |
| Sr(2) | Br(1) | 4 | 3.115 ± 8 |
| | Br(2) | 4 | 3.165 ± 7 |
| Br(1) | Sr(2) | 1 | 3.115 ± 8 |
| | Sr(1) | 1 | 3.129 ± 8 |
| | Sr(1) | 1 | 3.173 ± 8 |
| | Sr(1) | 1 | 3.593 ± 8 |
| | Br(4) | 1 | 3.678 ± 6 |
| | Br(1) | 2 | 3.788 ± 9 |
| | Br(2) | 1 | 3.830 ± 8 |
| | Br(2) | 1 | 3.861 ± 9 |
| | Br(2) | 1 | 3.996 ± 9 |
| Br(2) | Sr(1) | 1 | 3.122 ± 8 |
| | Sr(1) | 1 | 3.150 ± 7 |
| | Sr(2) | 1 | 3.165 ± 7 |
| | Sr(1) | 1 | 3.290 ± 7 |
| | Br(3) | 1 | 3.624 ± 5 |
| | Br(2) | 2 | 3.708 ± 7 |
| | Br(1) | 1 | 3.830 ± 7 |
| | Br(1) | 1 | 3.861 ± 9 |
| | Br(1) | 1 | 3.996 ± 9 |
| Br(3) | Sr(1) | 4 | 3.106 ± 5 |
| | Br(2) | 4 | 3.624 ± 5 |
| | Br(4) | 2 | 3.573 ± 2 |
| Br(4) | Sr(1) | 4 | 3.126 ± 5 |
| | Br(3) | 2 | 3.573 ± 2 |
| | Br(1) | 4 | 3.678 ± 6 |

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS

| | | |
|---|---|---|
| (H,0,0) | | |
| 2 | 8.3 | 4.0 |
| 4 | 8.5 | 6.6 |
| 6 | 24.8 | 23.4 |
| 8 | 9.3 | 6.8 |
| 10 | 28.2 | 27.1 |
| 12 | 14.9 | 13.2 |
| 14 | 12.7 | 14.6 |
| (H,1,0) | | |
| 1 | 8.6 | 6.0 |
| 7 | 49.5 | 49.2 |
| 9 | 29.6 | 27.2 |
| 13 | 14.8 | 13.6 |
| (H,2,0) | | |
| 2 | 10.7 | 9.3 |
| 4 | 53.2 | 55.7 |
| 6 | 38.2 | 42.0 |
| 8 | 17.8 | 14.3 |
| 14 | 8.4 | 10.3 |
| (H,3,0) | | |
| 1 | 19.6 | 17.6 |
| 3 | 37.5 | 34.6 |
| 5 | 20.5 | 20.0 |
| 7 | 27.5 | 26.7 |
| 9 | 27.6 | 27.4 |
| 11 | 13.0 | 11.8 |
| (H,4,0) | | |
| 2 | 73.6 | 73.5 |
| 4 | 22.8 | 19.2 |
| 6 | 14.0 | 10.7 |
| 8 | 26.1 | 22.4 |
| 10 | 24.2 | 20.0 |
| 12 | 12.1 | 9.5 |
| (H,5,0) | | |
| 1 | 17.5 | 14.3 |
| 5 | 45.6 | 49.4 |
| 9 | 15.7 | 13.1 |
| 11 | 18.4 | 13.4 |
| (H,6,0) | | |
| 2 | 27.4 | 28.3 |
| 6 | 28.9 | 31.7 |
| 8 | 19.0 | 17.4 |
| 12 | 17.1 | 20.3 |
| (H,7,0) | | |
| 1 | 31.3 | 31.9 |
| 3 | 26.4 | 29.6 |
| 5 | 13.0 | 8.6 |
| 11 | 13.5 | 9.5 |
| 13 | 6.4 | 8.1 |
| (H,8,0) | | |
| 2 | 12.4 | 10.2 |
| 4 | 21.4 | 22.3 |
| 6 | 26.0 | 28.8 |
| 12 | 7.7 | 8.3 |
| (H,9,0) | | |
| 3 | 19.6 | 19.9 |
| 7 | 13.8 | 11.1 |
| (H,10,0) | | |
| 2 | 18.9 | 19.1 |
| 4 | 16.2 | 16.0 |
| 6 | 15.0 | 16.6 |
| 8 | 13.5 | 12.6 |
| 10 | 20.4 | 22.3 |
| (H,11,0) | | |
| 3 | 16.3 | 15.2 |
| 5 | 15.2 | 13.6 |
| (H,12,0) | | |
| 2 | 12.2 | 9.0 |
| 4 | 16.9 | 19.3 |
| 6 | 16.4 | 18.0 |
| (H,0,1) | | |
| 2 | 8.9 | 7.3 |
| 3 | 6.5 | 3.6 |
| 4 | 9.5 | 6.6 |
| 5 | 20.3 | 18.0 |
| 11 | 13.5 | 12.5 |
| (H,1,1) | | |
| 1 | 12.6 | 9.1 |
| 2 | 8.2 | 7.6 |
| 3 | 36.5 | 34.9 |
| 4 | 54.6 | 57.1 |
| 7 | 24.8 | 19.4 |
| 8 | 15.9 | 12.1 |
| 9 | 14.8 | 11.2 |
| (H,2,1) | | |
| 1 | 32.4 | 31.0 |
| 3 | 45.7 | 44.6 |
| 4 | 25.4 | 25.7 |
| 5 | 24.1 | 27.5 |
| 6 | 31.8 | 31.7 |
| 7 | 13.1 | 11.7 |
| 9 | 18.8 | 16.4 |
| 10 | 14.6 | 12.2 |
| 11 | 19.7 | 18.0 |
| 13 | 13.4 | 15.1 |
| (H,3,1) | | |
| 1 | 46.1 | 47.4 |
| 2 | 30.4 | 29.8 |
| 4 | 29.5 | 29.7 |
| 5 | 19.6 | 17.9 |
| 9 | 17.5 | 13.1 |
| 11 | 15.6 | 11.6 |
| (H,4,1) | | |
| 1 | 41.5 | 43.5 |
| 2 | 35.8 | 38.9 |
| 5 | 12.3 | 9.8 |
| 6 | 15.3 | 10.8 |
| 8 | 22.2 | 20.1 |
| 9 | 19.1 | 16.8 |
| (H,5,1) | | |
| 1 | 13.9 | 10.1 |
| 2 | 37.4 | 40.0 |
| 4 | 18.3 | 17.1 |
| 6 | 24.4 | 25.4 |
| (H,6,1) | | |
| 1 | 12.2 | 8.3 |
| 2 | 16.6 | 16.2 |
| 3 | 21.1 | 21.8 |
| 5 | 24.3 | 24.4 |
| 7 | 17.0 | 15.9 |
| 8 | 20.0 | 20.8 |
| 11 | 16.8 | 17.3 |
| (H,7,1) | | |
| 1 | 18.1 | 17.5 |
| 3 | 12.7 | 12.2 |
| 6 | 15.2 | 13.8 |
| 9 | 13.4 | 11.0 |
| (H,8,1) | | |
| 1 | 37.4 | 38.4 |
| 2 | 10.9 | 10.5 |
| 3 | 20.5 | 22.3 |
| 4 | 22.4 | 24.9 |
| 6 | 13.7 | 11.6 |
| 7 | 19.8 | 23.4 |
| (H,9,1) | | |
| 2 | 11.8 | 9.4 |
| 3 | 22.1 | 23.7 |
| 6 | 12.5 | 12.7 |
| 10 | 15.2 | 15.6 |
| (H,11,1) | | |
| 2 | 17.6 | 18.6 |
| (H,12,1) | | |
| 1 | 12.8 | 12.0 |
| 3 | 14.6 | 13.6 |
| (H,13,1) | | |
| 1 | 14.0 | 12.9 |
| (H,0,2) | | |
| 2 | 34.5 | 37.8 |
| 3 | 54.6 | 53.9 |
| 4 | 54.4 | 51.2 |
| 5 | 15.8 | 11.3 |
| 6 | 27.1 | 24.5 |
| 7 | 53.8 | 55.3 |
| 9 | 22.9 | 19.8 |
| 10 | 32.3 | 32.4 |
| (H,1,2) | | |
| 1 | 11.6 | 9.4 |
| 2 | 41.1 | 41.2 |
| 3 | 75.6 | 80.6 |
| 4 | 8.0 | 4.5 |
| 5 | 16.4 | 14.0 |
| 6 | 25.8 | 23.3 |
| 8 | 22.1 | 18.3 |
| 9 | 28.2 | 28.9 |
| 10 | 20.3 | 16.2 |
| 11 | 13.4 | 12.3 |
| (H,2,2) | | |
| 1 | 49.2 | 46.4 |
| 2 | 11.7 | 12.8 |
| 3 | 17.0 | 16.8 |
| 4 | 12.1 | 9.2 |
| 5 | 28.9 | 31.8 |
| 6 | 26.6 | 26.3 |
| 8 | 11.6 | 9.5 |
| 10 | 13.2 | 14.1 |
| 11 | 20.4 | 16.6 |
| (H,3,2) | | |
| 1 | 43.8 | 42.2 |
| 2 | 16.9 | 18.4 |
| 3 | 18.5 | 18.7 |
| 5 | 28.0 | 26.4 |
| 6 | 17.2 | 16.2 |
| 7 | 34.3 | 34.8 |
| 10 | 26.3 | 23.4 |
| 13 | 13.4 | 15.6 |
| (H,4,2) | | |
| 2 | 13.9 | 10.6 |
| 4 | 11.1 | 8.1 |
| 5 | 39.3 | 43.5 |
| 6 | 44.3 | 43.6 |
| 9 | 15.8 | 16.2 |
| 12 | 17.9 | 20.4 |
| (H,5,2) | | |
| 1 | 19.7 | 16.9 |
| 2 | 35.6 | 36.5 |
| 3 | 21.4 | 20.3 |
| 4 | 48.8 | 49.3 |
| 5 | 29.3 | 31.2 |
| 6 | 27.6 | 30.3 |
| 7 | 19.5 | 18.3 |
| 12 | 16.7 | 15.8 |
| 13 | 9.8 | 12.0 |
| (H,6,2) | | |
| 1 | 15.3 | 12.8 |
| 2 | 33.6 | 34.0 |
| 4 | 19.7 | 17.9 |
| 5 | 32.4 | 35.6 |
| 6 | 11.7 | 9.7 |
| 7 | 16.9 | 11.8 |
| 8 | 21.8 | 18.8 |
| 9 | 18.7 | 14.8 |
| 10 | 16.7 | 12.3 |
| (H,7,2) | | |
| 1 | 23.7 | 23.9 |
| 3 | 41.9 | 42.8 |
| 6 | 16.8 | 13.4 |
| 9 | 25.8 | 27.4 |
| 10 | 20.6 | 20.9 |
| (H,8,2) | | |
| 1 | 21.6 | 21.4 |
| 2 | 17.9 | 16.0 |
| 4 | 19.5 | 20.3 |
| 8 | 11.3 | 11.2 |
| 9 | 13.1 | 9.6 |
| 11 | 11.0 | 12.2 |
| (H,9,2) | | |
| 1 | 19.2 | 16.4 |
| 2 | 13.2 | 10.9 |
| 5 | 19.6 | 21.1 |
| 6 | 17.7 | 18.4 |
| 7 | 18.0 | 19.3 |
| (H,10,2) | | |
| 2 | 16.4 | 13.4 |
| 3 | 15.5 | 16.8 |
| 6 | 19.0 | 19.1 |
| 7 | 20.3 | 24.6 |
| 9 | 10.3 | 9.3 |
| (H,11,2) | | |
| 1 | 12.8 | 12.3 |
| 2 | 21.2 | 23.5 |
| 5 | 15.4 | 13.5 |
| 7 | 12.4 | 11.4 |
| (H,12,2) | | |
| 1 | 17.1 | 16.0 |
| 2 | 14.6 | 10.2 |
| 3 | 12.4 | 8.9 |
| 4 | 10.8 | 7.3 |
| 5 | 13.8 | 13.7 |
| (H,13,2) | | |
| 1 | 9.3 | 7.3 |
| 3 | 14.4 | 16.2 |
| (H,14,2) | | |
| 2 | 10.4 | 12.4 |
| (H,0,3) | | |
| 2 | 19.6 | 17.7 |
| 3 | 10.6 | 9.0 |
| 4 | 14.7 | 12.7 |
| 5 | 11.6 | 9.5 |
| 6 | 19.3 | 20.4 |
| 7 | 20.7 | 20.4 |
| 9 | 12.1 | 8.5 |
| 11 | 14.3 | 12.9 |
| (H,1,3) | | |
| 1 | 10.2 | 7.5 |
| 2 | 61.7 | 63.2 |
| 3 | 10.8 | 7.7 |
| 4 | 21.5 | 19.0 |
| 6 | 27.9 | 26.6 |
| 7 | 26.0 | 24.7 |
| 8 | 14.0 | 9.6 |
| 10 | 14.0 | 16.6 |
| 11 | 10.0 | 7.7 |
| (H,2,3) | | |
| 1 | 51.7 | 54.0 |
| 2 | 17.7 | 17.4 |
| 3 | 40.2 | 41.6 |
| 4 | 19.6 | 16.4 |
| 5 | 27.4 | 28.8 |
| 6 | 23.6 | 21.4 |
| 7 | 33.9 | 33.6 |
| 10 | 14.6 | 14.3 |
| 11 | 13.6 | 10.4 |
| 13 | 12.1 | 14.7 |
| (H,3,3) | | |
| 1 | 43.1 | 44.5 |
| 2 | 19.3 | 18.2 |
| 5 | 13.5 | 12.7 |
| 6 | 26.8 | 25.7 |
| 8 | 46.1 | 45.6 |
| 11 | 14.7 | 13.3 |
| (H,4,3) | | |
| 1 | 12.8 | 11.3 |
| 2 | 24.3 | 24.7 |
| 4 | 18.6 | 17.4 |
| 5 | 17.5 | 17.6 |
| 6 | 17.4 | 14.2 |
| 7 | 21.7 | 19.4 |
| 8 | 11.1 | 9.4 |
| 9 | 28.9 | 26.3 |
| 11 | 12.6 | 10.6 |
| (H,5,3) | | |
| 1 | 8.7 | 6.0 |
| 2 | 30.0 | 31.6 |
| 4 | 45.6 | 46.1 |
| 5 | 19.5 | 19.6 |
| 8 | 21.7 | 18.7 |
| (H,6,3) | | |
| 1 | 40.1 | 43.0 |
| 2 | 14.6 | 12.1 |
| 3 | 15.4 | 14.2 |
| 6 | 17.8 | 16.8 |
| (H,7,3) | | |
| 2 | 23.4 | 23.6 |
| 3 | 13.0 | 10.4 |
| 4 | 14.7 | 13.9 |
| 6 | 10.8 | 9.8 |
| 8 | 16.2 | 16.1 |
| 9 | 15.2 | 13.8 |
| 10 | 12.2 | 9.1 |
| (H,8,3) | | |
| 1 | 14.3 | 10.9 |
| 2 | 13.1 | 13.7 |
| 3 | 21.6 | 24.3 |
| 4 | 20.1 | 18.5 |
| 5 | 20.7 | 20.7 |
| 11 | 15.3 | 18.7 |
| (H,9,3) | | |
| 3 | 19.5 | 20.6 |
| 4 | 33.7 | 34.0 |
| 6 | 18.1 | 20.5 |
| 8 | 13.9 | 14.9 |
| (H,10,3) | | |
| 1 | 15.9 | 14.2 |
| 6 | 10.2 | 9.2 |
| (H,11,3) | | |
| 4 | 22.9 | 22.8 |
| 7 | 9.0 | 9.3 |
| 8 | 8.8 | 12.0 |
| (H,12,3) | | |
| 1 | 11.1 | 9.44 |
| 5 | 10.1 | 14.1 |
| 7 | 7.6 | 10.2 |
| (H,13,3) | | |
| 1 | 10.4 | 11.2 |
| (H,0,4) | | |
| 1 | 18.2 | 18.3 |
| 2 | 13.2 | 9.5 |
| 3 | 6.9 | 2.8 |
| 4 | 12.1 | 10.1 |
| 5 | 7.6 | 6.1 |
| 6 | 49.7 | 49.5 |
| 7 | 18.0 | 8.7 |
| 8 | 17.9 | 15.5 |
| 9 | 11.9 | 9.1 |
| 10 | 30.1 | 31.7 |
| 11 | 9.6 | 7.2 |
| 12 | 12.0 | 10.7 |
| (H,1,4) | | |
| 1 | 44.8 | 48.6 |
| 2 | 12.5 | 9.0 |
| 3 | 16.6 | 14.1 |
| 5 | 32.8 | 35.3 |
| 6 | 13.8 | 9.8 |
| 7 | 16.9 | 13.3 |
| 9 | 14.3 | 11.0 |
| 10 | 15.0 | 13.2 |
| 11 | 12.4 | 10.4 |
| 13 | 13.7 | 16.6 |
| (H,2,4) | | |
| 1 | 11.9 | 8.2 |
| 2 | 27.3 | 31.6 |
| 3 | 12.1 | 8.7 |
| 4 | 12.9 | 10.8 |
| 5 | 15.5 | 14.8 |
| 6 | 11.1 | 7.3 |
| 12 | 12.2 | 12.5 |
| (H,3,4) | | |
| 1 | 12.6 | 11.5 |
| 2 | 17.0 | 15.0 |
| 3 | 48.0 | 50.0 |
| 4 | 10.9 | 6.3 |
| 5 | 25.2 | 23.0 |
| 6 | 16.9 | 17.4 |
| 7 | 18.6 | 14.9 |
| 9 | 17.7 | 16.7 |
| (H,4,4) | | |
| 1 | 21.6 | 19.6 |
| 2 | 8.7 | 4.5 |
| 3 | 15.6 | 12.1 |
| 4 | 33.4 | 35.7 |
| 6 | 13.6 | 10.6 |
| 10 | 20.3 | 19.7 |
| 12 | 11.1 | 14.0 |
| (H,5,4) | | |
| 1 | 37.3 | 37.4 |
| 2 | 17.4 | 17.3 |
| 3 | 30.5 | 30.3 |
| 4 | 11.8 | 9.2 |
| 6 | 21.5 | 20.2 |
| 7 | 18.4 | 16.3 |
| 9 | 17.0 | 13.5 |
| 11 | 16.3 | 20.7 |
| (H,6,4) | | |
| 2 | 30.1 | 28.8 |
| 4 | 10.0 | 8.9 |
| 6 | 18.9 | 19.3 |
| 7 | 13.3 | 12.1 |
| (H,7,4) | | |
| 5 | 26.3 | 31.0 |
| 7 | 33.1 | 36.1 |
| 8 | 10.4 | 10.6 |
| 9 | 13.9 | 12.0 |
| (H,8,4) | | |
| 3 | 16.3 | 15.2 |
| (H,9,4) | | |
| 1 | 20.1 | 21.6 |
| 3 | 19.8 | 18.5 |
| 9 | 14.0 | 17.3 |
| (H,10,4) | | |
| 2 | 21.0 | 22.2 |
| 8 | 9.3 | 9.8 |
| (H,11,4) | | |
| 3 | 10.3 | 10.5 |
| 5 | 11.6 | 12.5 |
| (H,12,4) | | |
| 2 | 9.1 | 6.9 |
| 4 | 8.2 | 7.8 |
| 5 | 9.8 | 8.9 |
| (H,0,5) | | |
| 1 | 18.1 | 19.1 |
| 9 | 15.6 | 15.3 |
| (H,1,5) | | |
| 2 | 19.9 | 23.0 |
| 3 | 26.3 | 30.0 |
| 7 | 10.7 | 8.2 |
| 8 | 11.7 | 8.9 |
| (H,2,5) | | |
| 1 | 25.0 | 24.2 |
| 3 | 14.6 | 10.8 |
| 4 | 16.3 | 17.8 |
| 5 | 28.9 | 33.9 |
| 6 | 19.0 | 19.7 |
| 11 | 8.1 | 9.0 |
| (H,3,5) | | |
| 1 | 23.3 | 20.7 |
| 8 | 21.2 | 19.8 |
| 9 | 14.3 | 12.8 |
| (H,4,5) | | |
| 1 | 18.3 | 16.1 |
| 2 | 23.4 | 21.9 |
| 5 | 14.0 | 11.1 |
| 7 | 13.7 | 13.7 |
| 8 | 17.5 | 16.1 |
| (H,5,5) | | |
| 4 | 17.5 | 15.0 |
| 8 | 12.1 | 6.3 |
| 10 | 10.0 | 9.0 |
| (H,6,5) | | |
| 1 | 18.4 | 18.6 |
| 2 | 12.3 | 10.8 |
| 3 | 10.9 | 10.6 |
| 5 | 10.7 | 8.6 |
| 7 | 11.7 | 13.9 |
| 8 | 12.5 | 13.7 |
| (H,7,5) | | |
| 1 | 17.7 | 16.7 |
| 2 | 12.5 | 13.3 |
| 6 | 11.3 | 10.8 |
| (H,8,5) | | |
| 1 | 13.0 | 11.2 |
| 4 | 13.8 | 16.1 |
| 5 | 15.0 | 17.6 |
| 6 | 10.8 | 9.7 |
| (H,9,5) | | |
| 2 | 10.3 | 8.1 |
| 3 | 13.4 | 13.7 |
| 4 | 10.4 | 8.9 |
| 7 | 8.5 | 8.0 |
| 8 | 9.2 | 9.9 |
| (H,10,5) | | |
| 1 | 12.9 | 12.0 |
| (H,11,5) | | |
| 3 | 11.2 | 9.6 |
| 4 | 12.4 | 15.5 |
| (H,12,5) | | |
| 1 | 10.1 | 6.7 |
| (H,13,4) | | |
| 1 | 6.7 | 4.0 |

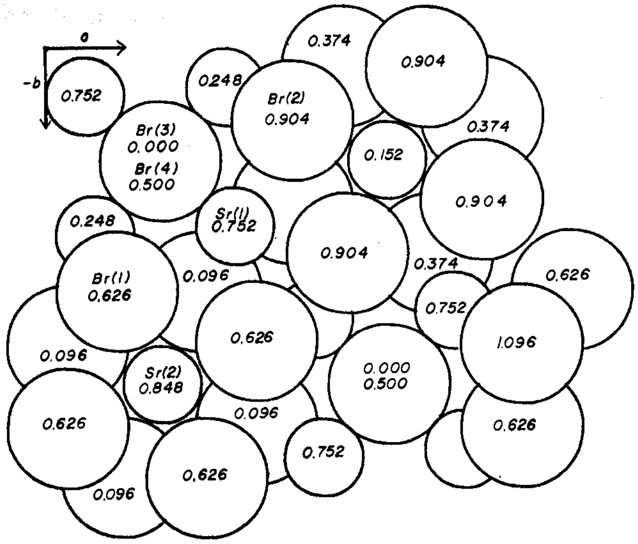

Figure 1.—Projection of the $SrBr_2$ structure onto the *xy* plane.

are listed in Table II. The final difference Fourier indicated random peaks less than 1 e$^-$/Å$^3$. A projection of the structure, drawn with a Hewlett-Packard 9125 plotter with $Sr^{2+}$ and $Br^-$ radii proportional to Goldschmidt's values,[12] 1.27 and 1.96 Å, respectively, is shown in Figure 1. Calculated and observed structure factors are listed in Table III.

## Discussion

In the $SrBr_2$ structure, the most noticeable feature is that all atoms are located in either one of two kinds of chains running parallel to the *c* axis of the crystal lattice and alternating in the *a* and *b* directions. The Sr(1) atoms form a chain of tetrahedral holes which are occupied by Br(3) and Br(4) atoms. The four Sr(1)–Br(3) and four Sr(1)–Br(4) distances are essentially equal, 3.106 and 3.126 Å, respectively. The Br(1) and Br(2) atoms form a chain of square antiprisms such that within every other antiprism along the chain is located a Sr(2) atom which is not precisely at the center of the antiprism but is closer to the four Br(1) atoms (3.115 Å) than to the Br(2) atoms (3.165 Å). The Sr(1)–Br(1) and Sr(1)–Br(2) bonds of which there are five with distances varying between 3.122 and 3.290 Å and possibly a sixth, if a Sr(1)–Br(1) distance of 3.593 Å is considered bonding, serve to stabilize the structure by holding the two different kinds of chains together.

Since $SrBr_2$ manifests many of the characteristics of the $SrCl_2$[13] and $SrI_2$[14] structures, it is both helpful and

---

[12] J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

[13] G. Brauer and O. Muller, *Z. Anorg. Allg. Chem.*, **295**, 218 (1958).

[14] E. Th. Rietschel and H. Baerninghausen, *ibid.*, **368**, 62 (1969).

meaningful to discuss them briefly. The $SrCl_2$ structure is of the familiar fluorite type: each Sr atom is located in a body-centered-cubic environment of Cl atoms, and each Cl atom is in a tetrahedral configuration of Sr atoms. The structure of $SrI_2$ is in many respects quite different, since the Sr atom is sevenfold coordinated by iodine atoms located in essentially two planes on either side of the Sr atom. Four of the iodine atoms form a slightly deformed square with the remaining three atoms describing a triangle. The two I atoms in $SrI_2$ are structurally different. One iodine atom is coordinated to three Sr atoms in the form of a triangular face; the other is tetrahedrally coordinated by four Sr atoms, reminiscent of the coordination polyhedron about the anion in $SrCl_2$.

The sevenfold Br atom coordination of the Sr(1) atom is comparable to that observed for Sr atoms in the $SrI_2$ structure. The Br(1) and Br(2) atoms are found trigonally and tetrahedrally coordinated to metal atoms, respectively, as are the two I atoms in $SrI_2$. However, the coordination polyhedra around the Sr(1), Br(1), and Br(2) atoms are not quite as regular as are their counterparts in the $SrI_2$ structure.

The presence of tetrahedrally coordinated Br atoms, namely, Br(2), Br(3), and Br(4), and an eightfold coordinated metal atom, Sr(2), in $SrBr_2$ is indicative of the similarity of this structure to that of $SrCl_2$ although in $SrCl_2$ the coordination about the Sr atom is cubic while in $SrBr_2$ it is square antiprismatic. The existence of the sevenfold coordinated Sr atoms and the trigonally coordinated halide atom in both $SrBr_2$ and $SrI_2$ establishes the similarity between these two structures. Therefore, this $SrBr_2$ structure may be considered a hybrid which incorporates features of both the $SrCl_2$ and the $SrI_2$ structures.

In addition to the above-mentioned common structural characteristics of $SrBr_2$, $SrCl_2$, and $SrI_2$, a unique feature of this structure is the alternation of Sr atoms and vacancies along the chain of antiprisms. At 25°, the temperature at which the work was done, the two kinds of antiprisms, one containing an Sr(2) atom and one containing a void region, are clearly different. The antiprism containing the Sr(2) atom exhibits significantly shorter distances from the metal atom to the bromine atoms at the corners of the surrounding polyhedron, namely, 3.115 and 3.165 Å, than analogous distances for the empty antiprism with the vacancy hypothetically located halfway along the $c$ axis from the Sr(2) atom, in this case, 3.181 and 3.333 Å. This difference is precisely what would be expected since Sr(2) is bonded to Br(1) and Br(2) while obviously the vacancy is not bonded to anything. However, at higher temperatures, it could be suggested that indeed the lattice would relax and allow partial occupancy of the Sr(2) atom in the two twofold positions with the two types of antiprism becoming structurally more similar to if, indeed, not identical with each other.

On the basis of certain similarities in powder photographs, earlier workers[1,3] have reported that $SrBr_2$, $SmBr_2$, and $EuBr_2$ are isostructural. In view of the considerable amount of controversy due in part to the insensitivity of the powder method to permit a determination of the occupancy parameter of one Sr atom in $SrBr_2$, we suggest that in $SmBr_2$ and $EuBr_2$ partial occupancy may well occur at 25°, to say nothing at all about the situation at higher temperatures. Only when single-crystal X-ray studies currently in progress have been completed can definitive statements be made about the isostructural character of these dibromides.[15]

**Acknowledgment.**—The support of the U. S. Atomic Energy Commission [Contract AT(11-1)-716] is acknowledged gratefully.

---

(15) H. Beck and H. Baerninghausen, private communication.

---

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

# The Crystal Structure of $H_2[Ta_6Cl_{18}]\cdot 6H_2O$[1]

BY CHARLES B. THAXTON AND ROBERT A. JACOBSON*

*Received October 30, 1970*

The structure of $H_2[Ta_6Cl_{18}]\cdot 6H_2O$ has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the cubic space group $Fd3m(O_h^7)$ with a unit cell dimension at 23 ± 3° of $a = 19.92$ (1) Å. The derived structure was refined by least-squares methods to a conventional $R$ index of 5.3%. The unit cell is composed of eight distinct and regular octahedral $Ta_6Cl_{18}^{2-}$ anion clusters ($O_h$ symmetry) with centers at ($^1/_8$, $^1/_8$, $^1/_8$), ($^1/_8$, $^5/_8$, $^5/_8$), ($^5/_8$, $^5/_8$, $^1/_8$), and ($^5/_8$, $^1/_8$, $^5/_8$), and the four others related to these by the center of symmetry. The Ta–Ta distance, uncorrected for thermal motion, is 2.962 (2) Å. The terminal Ta–Cl distance of 2.507 (9) Å is significantly longer than the bridging Ta–Cl distance of 2.414 (5) Å.

## Introduction

A number of compounds have been reported of the type $(M_6X_{12})Y_mL_{6-m}{}^{(n-m)+}$ where M = Nb, Ta; X = halogen; Y = halogen; L = neutral electron-donating ligand such as $H_2O$; $m$ = number of Y groups; and $n$ = charge on the $M_6X_{12}$ unit. Structural information on a number of $M_6X_{12}{}^{n+}$-containing compounds[2-7] has shown

---

(1) Research carried out at the Ames Laboratory of the U. S. Atomic Energy Commission. Ames Laboratory Contribution No. 2791.

(2) R. D. Burbank, *Inorg. Chem.*, **5**, 1491 (1966).

(3) D. Bauer, H. G. Schnering, and H. Schafer, *J. Less-Common Metals*, **8**, 388 (1965).

(4) D. Bauer and H. G. Schnering, *Z. Anorg. Allg. Chem.*, **361**, 259 (1968).

(5) V. A. Simon, H. G. Schnering, H. Wohrle, and H. Schafer, *ibid.*, **339**, 155 (1965).

(6) V. A. Simon, H. G. Schnering, and H. Schafer, *ibid.*, **361**, 235 (1968).

(7) H. Schafer, H. G. Schnering, K. J. Niehues, and H. G. Nieder-Vahrenholz, *J. Less-Common Metals*, **9**, 95 (1965).