metal halide complexes and must be related to a change in structure between the two phases.[12] The spectrum of $BiCl_3$(solv) has been interpreted in terms of C_{3v} pyramidal symmetry;[9] judging from the partial Raman spectrum of $BiBr_3$(solv), this molecule probably possesses C_{3v} symmetry in solution as well.

It is not difficult to understand why previous Raman and infrared studies failed to uncover the lower solid-state symmetry for $BiBr_3$ and $BiCl_3$. First, the early photographic Raman technique applied to crystalline samples probably lacked the resolution necessary to detect the multiplicity of overlapping bands which can be observed photoelectrically. Based on the reported frequencies, it also appears as though the early workers might mistakenly have been investigating $BiCl_3 \cdot H_2O$, and not anhydrous $BiCl_3$. Second, since the polyethylene-matrix method used to obtain the far-infrared spectrum of $BiBr_3$ was specifically designed to break down the intermolecular structure of related iodides, it could very well have isolated discrete $BiBr_3$ molecules as well. The spectrum so obtained, then, was not that of crystalline $BiBr_3$; in fact, 196 cm^{-1} in the infrared spectrum very closely matches 200 cm^{-1} in the Raman spectrum of the methanolic $BiBr_3$ solution.

[12] P. J. Hendra, *Spectrochim. Acta*, **23A**, 2871 (1967).

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The Crystal Structure of Potassium Perbromate[1]

By Stanley Siegel, Benjamin Tani, and Evan Appelman

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A description of the synthesis of perbromates has been published recently by one of us.[2]

The symmetry of $KBrO_4$ is orthorhombic with a = 8.930 (4), b = 5.921 (4), and c = 7.488 (4) Å. The extinctions are: $0kl$ with $k + l$ odd and $hk0$ with h odd, which leads to space group C_{2v}^{9}-Pn2$_1$a or D_{2h}^{16}-Pnma. A pycnometric determination of the density gave a value of 3.08 (3) g cm^{-3}. The computed density, based on four molecules in the cell, is 3.07 g cm^{-3}.

Experimental Section

Crystals of $KBrO_4$ were grown by evaporation at room temperature of a saturated solution of the salt. All symmetry information was deduced from Weissenberg patterns obtained with each crystal axis serving as a rotation axis, using Cu $K\bar{\alpha}$ radiation. Cell dimensions and errors were determined from counter and diffractometric data after calibration of the instrumental settings with a sodium chloride crystal. Mo $K\bar{\alpha}$ radiation ($\lambda(K\bar{\alpha})$ 0.71069 Å) was used for this purpose and in the subsequent collection of diffraction information.

A spherical crystal of 0.021-cm diameter was used in the structural analysis. Intensity data were obtained by counter methods utilizing a single-crystal orienter mounted on a General Electric XRD-5 diffraction unit. One quadrant only was investigated because of the onset of radiation damage. The scattering angle was limited to $2\theta = 50°$, for line intensities were quite reduced beyond this value.

Radiation damage was found to be very pronounced. In order to limit the exposure time of the crystal to irradiation and thereby reduce the radiation damage, the following data collection procedure was adopted.

The intensities of all reflections hkl within a quadrant were obtained rapidly with balanced filters based on a stationary crystal and counter technique and using 10-sec counting times for each filter. Examination of a number of reflections with a θ–2θ scan indicated that the weak maxima, those with intensities less than approximately 1% of the value of the most intense ones, could be evaluated more reliably with the scan technique. Accordingly, data for the weaker reflections were obtained by scanning, with a scan interval of 2° on either side of the Bragg angle and a scanning rate of 2°/min. The intensity distribution was recorded on a chart recorder in order to obtain a visual display of line position, line width, and background and to permit evaluation of the intensity. Numerical values for the intensities were obtained with a planimeter. A diffraction line intensity observed as zero was given a value corresponding to our estimated lower limit of the measurement of the line above the background noise level of the tracing. The radiation damage was kept to a minimum by exposing the crystal to X-rays only long enough to obtain intensity readings. Reflections $h00$, $0k0$, and $00l$ served as standards, and curves displaying changes in intensities with time were used to deduce corrections to the intensities for all classes of reflections. Following the data collection, a number of reflections for which intensities had been obtained initially from the fresh nonirradiated crystal were reexamined. It was found that corrections so applied led to reasonable agreement with the initial values.

Spherical absorption corrections were applied based on a linear absorption coefficient of 118.7 cm^{-1}. This absorption correction is contained in our data reduction program. Following corrections for radiation damage and absorption, the data were scaled and the Lorentz and polarization corrections were applied in the usual manner.

Approximate K and Br positions, found by trial, gave y-coordinate values near $^1/_4$, indicating the fourfold special positions of Pnma, 4c, but not necessarily eliminating the general positions of Pn2$_1$a.[3] Improvement of these trial coordinates, based on space group Pnma, was obtained with the Busing–Martin–Levy "Fortran Crystallographic Least-Squares Program." In these calculations, the scattering factors for K and Br were taken from ref 4. Two-dimensional Fourier syntheses were then computed with the signs of the coefficients determined from the improved K and Br coordinates. The electron density maps showed three sets of peaks corresponding to the oxygen positions—two in the special fourfold positions and one in the general eightfold position.

Refined coordinates for all atoms were obtained by a least-squares analysis on all atomic positions, using the oxygen-scattering curve reported by Tokonami.[5] In this and subsequent analyses, a total of 383 independent reflections was used. The final values for the coordinates are given in Table I. The conventional R factor for this refinement is 0.076.

The coordinates were then subjected to a new refinement based on the space group Pn2$_1$a, with no essential improvement in the R factor. We have therefore chosen space group Pnma as representing the symmetry of $KBrO_4$. The observed and calculated structure factors based on Pnma are presented in Table II.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

[3] "International Tables for Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

[4] "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

[5] M. Tokonami, *Acta Cryst.*, **19**, 486 (1965).

TABLE I

POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	B, Å^2
	Pnma			
K	0.1776 (5)	0.25	0.1623 (6)	2.27 (8)
Br	0.07019 (18)	0.25	0.6847 (2)	1.59 (4)
O (1)	0.207 (2)	0.25	0.548 (2)	3.1 (3)
O (2)	0.914 (2)	0.25	0.577 (2)	3.7 (3)
O (3)	0.0811 (10)	0.0277 (17)	0.809 (1)	3.2 (2)

[a] Numbers in parentheses are standard deviations in the last figure(s).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c	h	k	l	.78F_o	.78F_c
0	2	0	112.8	-123.8	1	0	4	35.2	34.7	2	6	2	10.6	11.9	3	6	2	21.8	20.4	4	2	2	7.3	-6.2	5	6	2	11.5	11.6	6	1	3	8.7	9.5	8	1	0	7.4	10.0
0	4	0	102.9	111.1	1	1	4	53.9	55.8	2	6	3	8.7	9.0	3	6	3	20.2	-18.9	4	3	2	30.4	-31.2	5	5	3	29.2	-31.1	6	0	3	3.6	-4.1	8	2	0	49.0	50.5
0	6	0	46.6	-54.2	1	2	4	46.9	-48.9	2	5	3	10.3	-10.2	3	5	3	35.2	-35.9	4	4	2	13.2	11.1	5	4	3	31.9	-31.8	6	0	4	4.5	-5.8	8	3	0	3.6	-5.4
0	5	1	35.2	38.6	1	3	4	54.8	-56.2	2	4	3	21.4	-19.2	3	4	3	32.2	30.4	4	5	2	25.7	27.1	5	3	3	51.1	49.7	6	1	4	6.9	4.2	8	4	0	41.2	-43.6
0	3	1	30.3	-33.9	1	4	4	26.0	27.0	2	3	3	13.7	11.4	3	3	3	68.7	65.3	4	6	2	2.1	-4.8	5	2	3	60.0	57.1	6	2	4	2.0	4.0	8	4	1	19.3	-17.8
0	1	1	55.0	61.7	1	5	4	30.2	32.3	2	2	3	17.7	16.0	3	2	3	47.9	-45.4	4	6	3	8.0	10.7	5	1	3	60.2	-56.2	6	3	4	4.8	-3.6	8	3	1	18.9	20.6
0	0	2	67.9	-79.0	1	6	4	21.0	-20.7	2	1	3	20.2	-17.4	3	1	3	69.7	-70.3	4	5	3	5.1	3.2	5	0	3	48.4	-43.1	6	4	4	2.0	-3.8	8	2	1	15.3	14.6
0	2	2	29.0	24.4	1	5	5	7.8	8.0	2	0	3	41.0	-38.2	3	0	3	55.6	51.6	4	4	3	21.8	-21.6	5	0	4	27.0	26.0	6	4	5	2.1	-0.6	8	1	1	24.2	-27.0
0	4	2	43.5	-46.6	1	4	5	23.3	-24.0	2	0	4	3.8	3.5	3	0	4	55.2	51.6	4	3	3	1.7	-1.8	5	1	4	18.4	-17.5	6	3	5	21.4	-22.4	8	0	1	26.9	-27.6
0	6	2	22.0	24.6	1	3	5	14.0	-16.3	2	1	4	12.0	11.5	3	1	4	0.8	0.9	4	2	3	24.3	22.8	5	2	4	35.7	-35.1	6	2	5	1.9	-0.2	8	0	2	33.0	34.0
0	5	3	11.4	-11.6	1	2	5	44.7	46.0	2	2	4	7.6	-1.9	3	2	4	77.0	-75.0	4	1	3	5.1	3.7	5	3	4	20.9	19.7	6	1	5	28.9	27.7	8	1	2	7.4	-7.4
0	3	3	2.6	3.8	1	1	5	16.9	15.8	2	3	4	8.4	-10.0	3	3	4	1.7	-1.3	4	0	3	45.2	-40.8	5	4	4	20.6	20.8	6	0	5	1.8	0.2	8	2	2	24.8	-25.5
0	1	3	2.6	-2.8	1	0	5	27.3	-25.6	2	4	4	1.8	2.4	3	4	4	38.9	39.0	4	0	4	1.5	6.3	5	5	4	7.6	-9.3	6	0	6	14.0	-14.3	8	3	2	4.5	4.1
0	0	4	21.3	-21.4	1	0	6	15.9	-11.1	2	5	4	8.6	6.6	3	5	4	2.0	0.6	4	1	4	10.2	-8.9	5	4	5	15.8	16.2	6	1	6	17.8	-17.2	8	4	2	23.2	23.5
0	2	4	20.8	21.1	1	1	6	29.2	-27.8	2	6	4	2.1	-1.4	3	5	5	25.9	26.1	4	2	4	5.9	-6.2	5	3	5	32.0	-33.2	6	2	6	6.2	7.3	8	3	3	8.1	-8.6
0	4	4	12.0	-13.1	1	2	6	19.9	16.8	2	5	5	20.5	-18.5	3	4	5	15.1	-13.2	4	3	4	6.8	6.3	5	2	5	30.1	-30.0	6	3	6	15.2	14.4	8	2	3	1.9	-2.6
0	6	4	12.4	8.6	1	3	6	27.6	26.5	2	4	5	3.7	-5.1	3	3	5	46.5	-46.2	4	4	4	1.9	3.7	5	1	5	36.7	37.1	6	1	7	32.5	-32.6	8	1	3	11.0	10.9
0	5	5	4.8	-1.7	1	4	6	9.0	-8.4	2	3	5	25.8	25.7	3	2	5	20.2	18.2	4	5	4	2.0	-4.5	5	0	5	19.3	19.3	6	0	7	11.3	12.8	8	0	3	4.9	7.3
0	3	5	6.2	-3.9	1	5	6	15.7	-14.8	2	2	5	1.6	1.3	3	1	5	53.5	49.4	4	5	5	2.1	1.0	5	0	6	19.4	-19.2	7	5	1	2.1	-2.8	8	0	4	6.4	8.6
0	1	5	6.2	6.5	1	4	7	8.9	10.6	2	1	5	36.0	-33.5	3	0	5	21.9	-19.3	4	4	5	30.3	-32.7	5	1	6	10.7	13.1	7	4	1	18.3	17.6	8	1	4	3.9	4.3
0	0	6	56.0	59.6	1	3	7	12.9	12.1	2	0	5	7.0	-7.5	3	0	6	19.7	-17.8	4	3	5	1.8	-0.3	5	2	6	22.3	22.8	7	3	1	3.5	4.8	8	2	4	5.3	-8.3
0	2	6	40.2	-43.1	1	2	7	20.1	-18.7	2	0	6	17.8	15.3	3	1	6	7.7	-6.6	4	2	5	42.1	40.7	5	3	6	11.3	-13.5	7	2	1	29.7	-29.2	8	3	4	3.6	-3.2
0	4	6	37.2	40.3	1	1	7	16.8	-13.4	2	1	6	48.5	-46.9	3	2	6	31.0	28.8	4	1	5	4.3	1.1	5	4	6	12.5	-14.5	7	1	1	5.4	-4.4	8	2	5	6.0	-8.2
0	3	7	23.2	-23.9	1	0	7	16.6	14.5	2	2	6	10.9	-8.7	3	3	6	7.3	5.9	4	0	5	53.6	-51.0	5	2	7	2.1	1.7	7	0	1	27.1	26.0	8	1	5	2.0	2.9
0	1	7	33.1	32.2	1	0	8	19.0	-15.4	2	3	6	36.1	35.8	3	4	6	15.5	-15.5	4	0	6	13.8	-11.2	5	1	7	2.0	-1.3	7	0	2	26.9	-24.8	8	0	5	10.2	11.0
0	0	8	50.6	-47.2	1	1	8	9.8	-8.7	2	4	6	9.9	10.6	3	3	7	2.0	5.2	4	1	6	22.3	-22.0	5	0	7	3.6	2.1	7	1	2	38.9	39.0	9	3	1	4.9	6.7
0	2	8	34.7	34.0	1	2	8	16.6	13.3	2	5	6	29.6	-27.8	3	2	7	6.5	6.9	4	2	6	6.0	6.4	6	0	0	52.2	-53.0	7	2	2	18.7	17.1	9	2	1	2.0	-2.4
1	6	1	15.0	14.0	1	3	8	8.4	7.0	2	4	7	22.5	19.2	3	1	7	3.5	-3.7	4	3	6	15.9	16.2	6	1	0	46.5	-45.7	7	3	2	35.6	-35.0	9	1	1	5.1	-6.4
1	5	1	1.7	0.8	2	0	0	45.9	38.9	2	3	7	23.9	-23.1	3	0	7	6.8	-8.0	4	4	6	7.6	-7.5	6	2	0	23.2	21.9	7	4	2	16.0	-15.2	9	0	1	1.9	1.8
1	4	1	20.7	-19.0	2	1	0	93.8	-97.9	2	2	7	20.4	-17.7	3	0	8	5.0	-3.1	4	3	7	2.1	1.7	6	3	0	35.1	35.4	7	5	2	19.9	21.0	9	0	2	20.7	21.4
1	3	1	7.2	-4.7	2	2	0	1.0	-1.1	2	1	7	30.9	29.0	3	1	8	10.4	10.2	4	2	7	35.0	-35.5	6	4	0	31.9	-31.3	7	4	3	26.3	-26.6	9	1	2	24.0	25.3
1	2	1	45.4	46.9	2	3	0	61.6	62.3	2	0	7	33.4	29.2	3	2	8	2.1	1.6	4	1	7	2.0	-3.2	6	5	0	22.8	-24.3	7	3	3	14.8	-13.4	9	2	2	25.0	-26.6
1	1	1	1.0	1.1	2	4	0	27.9	24.9	2	0	8	22.8	-20.6	4	0	0	38.7	-37.6	4	0	7	48.9	47.0	6	5	1	41.0	-41.2	7	2	3	42.4	43.6	9	3	2	20.6	-21.7
1	0	1	34.1	-28.8	2	5	0	55.5	-54.1	2	1	8	31.3	28.2	4	1	0	21.8	-18.1	4	0	8	6.7	8.4	6	4	1	15.4	14.5	7	1	3	16.4	14.8	9	2	3	8.7	12.4
1	0	2	50.2	-50.2	2	6	0	13.8	-12.4	2	2	8	16.2	14.5	4	2	0	14.5	11.6	4	1	8	25.6	23.8	6	3	1	50.7	50.1	7	0	3	33.0	-33.8	9	1	3	11.9	14.7
1	1	2	82.1	-81.8	2	6	1	15.8	-14.1	3	6	1	8.2	7.7	4	3	0	15.6	14.4	5	6	1	10.2	-11.2	6	2	1	17.9	-17.5	7	0	4	16.7	14.6	9	0	3	8.8	-12.4
1	2	2	59.1	63.4	2	5	1	39.4	38.6	3	5	1	10.0	10.6	4	4	0	19.8	-18.4	5	5	1	16.0	15.3	6	1	1	72.7	-69.6	7	1	4	31.9	-33.6	9	0	4	24.0	-23.6
1	3	2	65.5	68.9	2	4	1	34.9	31.5	3	4	1	13.4	-11.1	4	5	0	27.2	-25.1	5	4	1	15.2	14.6	6	0	1	22.4	21.3	7	2	4	10.3	-8.2	9	1	4	28.3	-29.0
1	4	2	32.7	-32.5	2	2	1	1.0	-0.1	3	3	1	21.1	-16.7	4	6	0	8.1	8.0	5	3	1	25.7	-24.6	6	0	2	31.4	31.2	7	3	4	31.2	32.3	10	0	0	2.0	-2.4
1	5	2	31.7	-36.0	2	3	1	49.1	-48.1	3	2	1	18.3	14.6	4	6	1	31.5	-35.1	5	2	1	29.2	-27.1	6	1	2	19.5	16.0	7	4	4	9.3	9.7	10	1	0	36.2	39.2
1	6	2	22.3	22.7	2	1	1	75.9	72.6	3	1	1	9.4	5.6	4	5	1	8.4	-6.7	5	1	1	28.6	28.0	6	2	2	14.0	-12.3	7	3	5	2.7	4.2	10	2	0	2.1	5.6
1	6	3	24.5	-24.7	2	0	1	61.0	57.2	3	0	1	19.3	-14.5	4	4	1	62.5	63.8	5	0	1	21.4	19.0	6	3	2	15.8	-13.8	7	2	5	32.5	-33.3	10	2	1	8.9	12.9
1	5	3	1.8	1.3	2	0	2	48.3	-45.5	3	0	2	10.5	-5.9	4	3	1	1.5	2.9	5	0	2	14.5	-12.7	6	4	2	21.3	19.9	7	1	5	5.1	-3.8	10	0	1	18.5	-21.3
1	4	3	26.6	27.0	2	1	2	58.6	59.4	3	1	2	27.6	24.6	4	2	1	63.9	-60.0	5	1	2	11.3	8.7	6	5	2	11.6	10.7	7	0	5	25.9	26.5	10	1	1	7.5	-8.6
1	3	3	1.8	1.0	2	2	2	18.5	17.7	3	2	2	47.1	43.4	4	1	1	9.9	-8.8	5	2	2	25.0	24.2	6	5	3	8.5	7.9	7	0	6	2.0	-1.8	10	0	2	3.6	4.5
1	2	3	55.2	-58.7	2	3	2	38.6	-37.5	3	3	2	16.2	-14.4	4	0	1	111.8	108.3	5	3	2	14.9	-12.7	6	4	3	5.1	-3.8	7	1	6	23.4	21.6	10	1	2	26.9	-26.0
1	1	3	15.0	13.0	2	4	2	26.2	-24.0	3	4	2	22.9	-20.5	4	0	2	24.8	21.7	5	4	2	15.0	-13.4	6	3	3	5.1	-6.5	7	2	6	2.1	-1.0	10	0	3	12.5	13.3
1	0	3	24.4	17.5	2	5	2	33.6	32.8	3	5	2	6.4	7.6	4	1	2	51.4	47.6	5	5	2	4.0	4.7	6	2	3	1.9	3.5	8	0	0	43.2	-65.1					

Results

$KBrO_4$ belongs to the $BaSO_4$ structure type and is therefore isostructural with several perchlorates reported in the literature.[6] Bond distances for $KBrO_4$ were computed with the Busing–Martin–Levy "Fortran Crystallographic Function and Error Program" and are shown in Table III.

TABLE III[a]

BOND DISTANCES (Å)

Br–O(1)	1.593 (14)	O(3)–O(3)	2.63 (2)
Br–O(2)	1.614 (16)	K–O(2′)	2.77 (2)
Br–(2)O(3)	1.617 (10)	K–(2)O(3‴)	2.93 (1)
O(2)–(2)O(3)	2.65 (2)	K–O(1)	2.90 (2)
O(1)–(2)O(3)	2.61 (2)	K–(2)O(3)	3.08 (1)
O(1)–O(2)	2.63 (2)	K–(2)O(3″)	2.84 (1)

[a] Numbers in parentheses are standard deviations in the last figure(s).

The BrO_4^- configuration is tetrahedral with Br–O(1) = 1.593 (14) Å, Br–O(2) = 1.614 (16) Å, and Br–(2)O(3) = 1.617(10) Å. Within error, the bond distances are equal, leading to an average value of 1.610 Å. This may be compared with values of 1.44–1.46 Å for Cl–O distances in the perchlorate ion and 1.79 Å for I–O distances in the periodate ion.[7–9] The oxygen–oxygen distances within the configuration are: O(2)–(2)O(3) = 2.65 (2) Å, O(1)–(2)O(3) = 2.61 (2) Å, O(1)–O(2) = 2.63 (2) Å, and O(3)–O(3) = 2.63 (2) Å. The corresponding bond angles are: O(1)BrO(3) = 108° 48′, O(2)BrO(3) = 110° 12′, O(1)BrO(2) = 110° 11′, and O(3)BrO(3) = 108° 50′. Eight K–O distances are observed with contacts less than 3.08 Å as shown in Table III. The average weighted K–O distance is 2.92 Å, corresponding essentially to the ionic radii sum corrected for the eightfold coordination.[10]

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Coordination Chemistry of Phosphoryl Compounds. III. Transition Metal Complexes of Trimorpholinophosphine Oxide[1]

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In a set of earlier papers, the coordination chemistry of hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, was reported.[4–6] This ligand, found to be an oxygen donor in

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