

SHORT-FORMAT PAPERS

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A Neutron Diffraction and Electron Microscopy Examination of Barium Bromide-Barium Chloride (2/1)

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Abstract. $2\text{BaBr}_2 \cdot \text{BaCl}_2$, $\text{BaBr}_{1.333}\text{Cl}_{0.667}$, $M_r = 282.312$, $Pnma$, $a = 8.2031$ (3), $b = 4.8606$ (2), $c = 9.6359$ (4) Å, $V = 384.20$ Å³, $Z = 4$, $D_x = 4.880$ Mg m⁻³, $\lambda = 1.5500$ Å, $\mu = 0.023$ mm⁻¹, $T = 298$ K; $wR = 0.0773$ for 330 reflections. The anions occupy two crystallographic sites in an arrangement such that the larger square-pyramidal site is filled only with bromine atoms; the smaller tetrahedral site is occupied randomly by both chlorine and bromine atoms. No evidence for ordering of the chlorine and bromine atoms in the tetrahedral site was found.

Experimental. Two separate batches of sample were prepared by fusing in alundum crucibles confined in high vacuum (1.33 mPa) an intimately ground mixture of $2\text{BaBr}_2 \cdot 1\text{BaCl}_2$. The two batches were subsequently ground together in an agate mortar. BaCl_2 was purchased from Cerac, Inc., Milwaukee, WI; BaBr_2 was prepared from BaO (Fisher Scientific Co.) by conventional $\text{NH}_4\text{Br}/\text{HBr}$ bromination procedure. Both BaCl_2 and BaBr_2 were melted in alundum crucibles in high vacuum prior to use.

Data collected on the NBS, Gaithersburg, MD, five-detector neutron-diffractometer system in step-scan mode. Details of data collection and refinement procedure are presented in Table 1. Scattering lengths: Ba: 5.25; Br: 6.79; Cl: 9.579 fm. X-ray and neutron diffraction data revealed following extinctions: $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$. These are consistent with space groups $Pnma$ and $Pn2_1a$. Refinement undertaken initially in centrosymmetric space group.

Initial atomic parameters were those reported for BaBrCl (Hodorowicz, Hodorowicz & Eick, 1983) and

Table 1. *Data collection and refinement parameters*

Sample container	Cylindrical, aluminium
2θ range (°)	17-122
[2θ range of each detector (°)]	[17-42, 37-62, 57-82, 77-102, 97-122]
Step-scan increment (°)	0.05
Number of steps	2505
Number of contributing reflections	330
Absorption correction	None
Preferred orientation	None
Number of structure parameters	21
Number of segment/slope parameters	5/5
Total number of parameters	36
$R = \sum Y_i(\text{obs}) - (1/c)Y_i(\text{calc}) / \sum Y_i(\text{obs})$ *	0.0606
$wR = [\sum w_i Y_i(\text{obs}) - (1/c)Y_i(\text{calc}) ^2 / \sum w_i Y_i(\text{obs}) ^2]^{1/2}$	0.0773
$R_{\text{exp}} = [(n-p) / \sum w_i Y_i(\text{obs}) ^2]^{1/2}$	0.0497
Halfwidth (H) parameters; U, V, W	4178(151), 230(47), 716(11)
$H = [U(\tan\theta - 0.6)^2 + V(\tan\theta - 0.6) + W]^{1/2}$	
Max shift/e.s.d.	0.05
Computer programs	PREP, REFINE, DISTAN

* Definitions: Y_i = background-corrected intensity at 2θ point i ; $w_i = 1/Y_i(\text{obs})$; n = number of observations; p = number of variable parameters; H = full width of single reflection at half height in $0.01^\circ 2\theta$.

lattice parameters determined from Guinier X-ray powder diffraction analysis of the specimen. Reflections were assigned Miller indices and background removed by program *PREP* (E. Prince, private communication). Structure refinement was carried out with program *REFINE*, a profile-fitting program (Rietveld, 1969) modified by E. Prince and adapted to run on a Vax 11/750 computer. Refinement began with lattice parameters and scale factors. After these had stabilized, half-width parameters U, V and W were refined. The barium atom was refined isotropically. Two anion positions were refined subsequently with anion site

occupancy variable subject to the constraints that the total bromine content equal that of the mixed composition ($\text{Br}/\text{Ba} = 1.333$) and that each anion site occupancy be unity. Isotropic thermal parameters and occupancy were refined in alternate cycles. Under these conditions, occupancy of anion site 1 refined to 1.009 (16) with $wR = 0.0789$. Occupancy of anion site 2 was then 0.679 (16) chloride ion and 0.321 (16) bromide ion. Refinement process was repeated with all atoms anisotropic to determine if site-occupancy parameter would change. It did not. Occupancy was then removed as a variable; anion site 1 was refined with occupancy of 1.0 bromine atom and anion site 2 with occupancy of 0.6667 chlorine atom and 0.3333 bromine atom. Refinement was continued to convergence. These refined centrosymmetric coordinates were then converted to those required for non-centrosymmetric space group (No. 33), and refinement was begun again. The 'y' parameter of Ba was fixed at 0.25, and with both anions isotropic the occupancy parameter of Br(2) was varied. Refinement converged when occupancy of anion site 1 was 1.05 (2) bromine atom, $wR = 0.0780$. Since the occupancy parameter again indicated that anion site 1 contained only bromine atoms, occupancy was again removed as a variable, site 1 occupancy was set to 1.0 bromine atom; site 2 occupancy was set to 0.6667 chlorine and 0.3333 bromine atom. Both positions were converted anisotropic, and refinement continued to convergence. The 'y' parameters of anion sites 1 and 2 refined, respectively, to 0.231 (3) and 0.241 (4), $wR = 0.0776$. On the basis of Hamilton's (1965) test, the hypothesis that the molecule is non-centrosymmetric can be rejected at the 95% confidence level.*

Another portion of the sample was examined by high-resolution electron microscopy. The sample was ground vigorously to create crystal fragments, which were then suspended in dry acetone and picked up by dipping a microscope grid covered with a holey carbon film into the suspension. These fragments were examined in a Philips 400T electron microscope maintained for high-resolution work to determine if the anions which occupied anion site 2 evidenced a further level of order at the microscopic level. Two primary zones were examined. The electron diffraction patterns of the crystal fragments did not evidence either the presence of superstructure reflections or of streaking. Thus, the occupancy of anion site 2 must be considered random.

Positional and equivalent isotropic thermal parameters for this material are presented in Table 2.

* Tables of positional and anisotropic thermal parameters, and observed and calculated intensity data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42817 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and equivalent isotropic thermal parameters (\AA^2) for $2\text{BaBr}_2 \cdot \text{BaCl}_2$*

The digit in parentheses indicates the e.s.d. of the least significant digit.

	Site	occupancy	x	y	z	B_{eq}^*
Ba	4(c)	1.0	0.2603 (4)	0.25	0.1203 (3)	1.43 (6)
Br(1)	4(c)	1.0	0.0293 (3)	0.25	0.8292 (3)	1.59 (4)
Br(2)	4(c)	0.3333	0.1446 (2)	0.25	0.4329 (2)	1.38 (5)
Cl(2)	4(c)	0.6667				

$$* B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

Table 3. *Bond distances (\AA) and e.s.d.'s in $2\text{BaBr}_2 \cdot \text{BaCl}_2$*

Ba-Br(1)	3.385 (4)	Ba-Cl/Br(2)	3.158 (4)
2 × Ba-Br(1)	3.433 (3)	2 × Ba-Cl/Br(2)	3.126 (2)
2 × Ba-Br(1)	3.597 (4)	2 × Ba-Cl/Br(2)	3.194 (4)
		2 × Ba-Ba	4.803 (3)

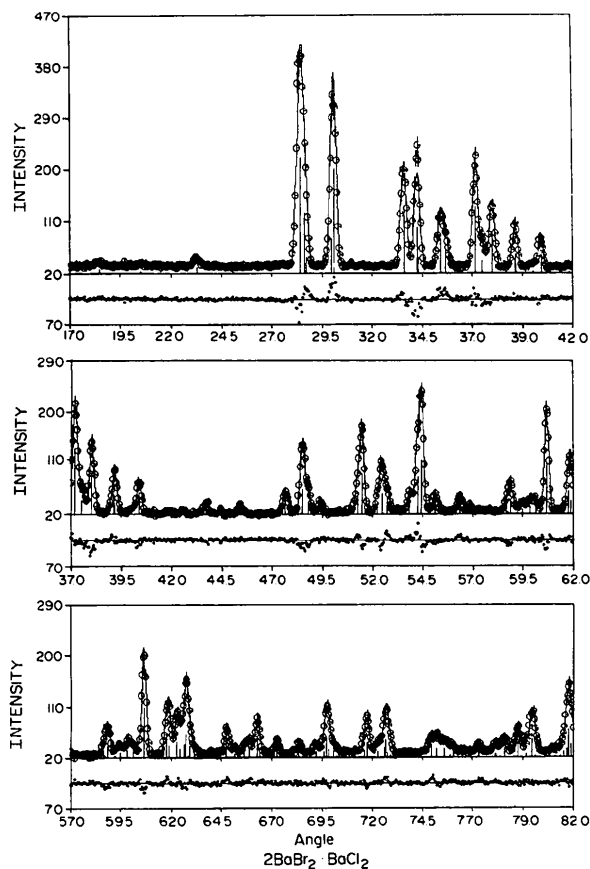


Fig. 1. Rietveld line-profile fit (—) of the observed intensity data over the region $17 \leq 2\theta \leq 82^\circ$. The difference between the calculated line and the observed data is plotted underneath on a separate scale.

Bond distances and their e.s.d.'s (program *DISTAN*; E. Prince, private communication) are presented in Table 3. A plot of the observed and calculated intensity data over the region $17 \leq 2\theta \leq 82^\circ$ is presented in Fig. 1. An examination of the plot output indicates a good fit of the data throughout the entire spectrum. A Hamilton's (1965) test of the *R* values obtained with and without all thermal parameters anisotropic (0.0773 vs 0.0786, respectively) indicated the isotropic case could be rejected at the 0.995 confidence level.

Related literature. The positional parameters are in excellent agreement with those derived for BaBrCl by a Rietveld line-profile fit of X-ray powder diffraction data (Hodorowicz, Hodorowicz & Eick, 1983), substantiating the previous report that even though a Rietveld treatment of X-ray powder diffraction data may give erroneous thermal parameters, it yields accurate positional parameters (Malmros & Thomas, 1977). The positional parameters differ somewhat from

those expected from a comparison with parameters reported for BaCl₂ and BaBr₂ (Brackett, Brackett & Sass, 1963).

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Structure of Mercury Tellurate(IV)

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Abstract. HgTeO₃, $M_r = 376.2$, triclinic, $P\bar{1}$, $a = 6.139$ (1), $b = 7.361$ (8), $c = 7.459$ (3) Å, $\alpha = 84.76$ (3), $\beta = 65.72$ (4), $\gamma = 87.11$ (2)°, $V = 305.94$ Å³, $Z = 4$, $D_x = 8.154$ g cm⁻³, $\lambda(\text{Ag } K\alpha) = 0.56083$ Å, $\mu = 333.4$ cm⁻¹, $F(000) = 624$, room temperature, final $R = 0.065$ for 2318 independent observed reflections. The structure consists of slightly distorted trigonal TeO₃ pyramids (mean Te–O distance 1.89 Å) with single connective bonds to each of three adjacent pyramids [Te–O distances 2.54 (2)–3.13 (2) Å]; with these longer bonds a framework of edge-sharing distorted TeO₆ octahedra is formed, in which the mercury atoms are incorporated. The resulting Hg–O coordination polyhedra are an octahedron [Hg–O 2.07 (2)–2.74 (2) Å] and a mono-capped trigonal prism [Hg–O 2.15 (2)–2.94 (2) Å], both distorted.

Experimental. Colourless single crystals prepared by annealing a mixture of HgO + TeO₂ in an evacuated quartz ampoule for two days at 770 K. Irregular-shaped crystal of 0.0032 mm³ selected; D_m not measured. Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Ag $K\alpha$ radiation; lattice parameters from refinement of 16 reflections in range $9 < \theta < 23^\circ$; scan width 1.2°, ω – 2θ scan mode; max. $\sin\theta/\lambda = 0.837$ Å⁻¹; hkl range: h 0 to 12, k –12 to 12, l –11 to 12. *SHELX76* (Sheldrick, 1976) and *XRAY* systems (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); two standard reflections: no significant variation; 3828 total reflections, 3015 independent, 2318 with $I > 3\sigma(I)$; $R_{\text{int}} = 0.061$ (on F , 639 contributors); corrections for Lorentz–polarization, absorption (numerical integration with subprogram *ABSORB*: A^* 9.92 to 44.58) and ex-