

Redetermination of the Crystal Structure of Al_2Br_6 . A Comparison of Three Methods

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The structure of aluminium bromide has been reinvestigated by X-ray diffraction in three different ways: (a) on a single crystal grown in a glass capillary, (b) on powder in a Debye–Scherrer glass capillary and (c) on an area of powder placed in a protective container for Bragg–Brentano geometry. In accordance with previous results, the structure belongs to the monoclinic space group $P2_1/a$, no. 14, C_{2h}^5 , with $a=10.301(4)$, $b=7.095(2)$, $c=7.525(3)$ Å, and $\beta=96.44(3)^\circ$, and with two Al_2Br_6 molecules per unit cell. The single crystal was refined to $R=0.0746$. Rather similar structural results were obtained from full-profile Rietveld refinements of powder data [goodness of fit = 1.38 and 2.54 for (b) and (c), respectively]. The Al_2Br_6 molecule consists of two edge-sharing, almost regular AlBr_4 tetrahedra. The Al–Br bond distances are in the range 2.21–2.42 Å, in accordance with what should be expected from related structure determinations.

AlBr_3 (or rather Al_2Br_6) is a well known solid compound. In 1944 the crystal structure of aluminium bromide was determined by Renes and MacGillavry.¹ Owing to two printing errors in their report¹ and the resulting data inconsistency, the solved Al_2Br_6 structure has been left out in important databases.² Nevertheless, some crystallographers have resolved the errors and included the structure in their data collections.^{3,4} A reinvestigation of the structure is reported here, and the results are, except for the errors, closely similar to those obtained by Renes and MacGillavry.¹ Another aim of our work was to see if satisfactory structure solutions could be obtained from powder samples, when using a *hygroscopic* compound such as AlBr_3 , placed in a home-made moisture-protective container under Bragg–Brentano scattering geometry. For comparison also the Debye–Scherrer method was tried. In both cases, the structure was subsequently determined by Rietveld full-profile least-squares refinements.

Experimental

Preparation of AlBr_3 . Pure aluminium metal sponge (99.999%) was rinsed for surface oxides by treatment with concentrated NaOH solution, followed by a 12:10:3 volumetric mixture of 89% H_3PO_4 and concentrated H_2SO_4 and HNO_3 acids, respectively, washed with

water and ethanol, and quickly dried. Crude AlBr_3 was prepared by slowly letting bromine drip onto the metal sponge in a dry nitrogen-vented reflux-capped flask (carefully cooled with the reflux column and ice water). Owing to the extreme moisture sensitivity, all subsequent handlings of the aluminium bromide were performed in a glovebox under a nitrogen atmosphere, continuously dried to a level around 5 ppm H_2O . The obtained crude AlBr_3 was purified by sublimation at ca. 80–100 °C, in contact with aluminium metal (to reduce Br_2) and a NaBr–AlBr_3 phase (to dissolve oxide impurities), in a two-chamber evacuated and sealed cell of borosilicate glass (*note the danger of explosion when heating sealed cells; the melting point and critical temperature of AlBr_3 are 97.5 and 490 °C, respectively,⁵ and the critical pressure is 28.5 atm.⁶*). The crystals were isolated, transferred to another cell, and recrystallized at 97.5 °C using decantation, by turning the entire furnace (regulated to within ± 0.5 °C) upside down. Other experimental details are given elsewhere.⁷ The purity of the AlBr_3 crystals was investigated by Raman spectroscopy, and a small content of oxides (originating from the silica wall) was always found.⁷

X-Ray single crystal investigation. Some AlBr_3 crystals were transferred to a pyrex cell, ending in a narrow capillary tube. After sealing under high vacuum and condensing AlBr_3 in the tip of the capillary, crystals slowly grew by sublimation during some weeks. A suit-

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able single crystal was selected in a polarization microscope, and the capillary sealed off and placed on a goniometer head. The intensity data collection took place at 20 °C on an Enraf-Nonius CAD-4F four-circle diffractometer with monochromated Mo K α radiation (0.710 69 Å) and the ω -scan technique. The cell dimensions, in accordance with those of Renes and Mac Gillavry,¹ were determined by least-squares refinement based on the settings of 25 high-order reflections. Crystal data and other experimental details are included in Table 1, together with the powder results and previous data¹ on Al₂Br₆. The systematic absences were in accordance with the space group $P2_1/a$, C_{2h}^5 , no. 14 found by Renes and MacGillavry¹ (film-work). The raw intensities were corrected for Lorentz and polarization effects. Correction for the strong absorption was made by an empirical method in which the shape of the crystal was approximated by an ellipsoid, and in which the size (in units of μ^{-1}) and the orientation are treated as parameters. The refinement of the correction parameters was based on Ψ -scans on 12 reflections and their symmetry related reflections, which amounts to 368 observations. The quantity minimized was $R = \sum w(I_{\text{obs}} - I_{\text{corr}})^2$, where

A is the absorption coefficient. The initial and final values of $(R/\sum wI_{\text{obs}}^2)^{1/2}$ were 0.2899 and 0.0456, respectively. The minimum and maximum transmission coefficients were 0.0153 and 0.0834. The calculations, based on F^2 , were done using the SHELX program⁸ and included full-matrix least-squares refinements of positional and anisotropic thermal parameters. Atomic scattering factors (for Br⁻ and Al³⁺) and anomalous dispersion corrections given by Cromer and Mann⁹ were used. The five strongest reflections (006, 310, -202, 204 and 020) were omitted from the refinement. The weight function, $w^{-1} = \sigma^2(F_o^2) + (0.0697P)^2$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, gave a uniform distribution of $w|\Delta F|^2$.

X-Ray powder investigations. For Debye-Scherrer data collection, finely ground Al₂Br₆ powder was placed in a thin-walled Pyrex capillary tube (diameter 0.5 mm) and sealed. Diffractograms were obtained with a Stoe STADIP instrument with Cu K α_1 radiation ($\lambda_1 = 1.540 598$ Å; λ_2 was eliminated with a germanium primary monochromator) in transmission mode and with a moving linear PSD detector. The step size was 0.02°, the

Table 1. Crystal data (20 °C) of Al₂Br₆ in monoclinic space group $P2_1/a$, (no. 14), C_{2h}^5 .^a

Formula Al ₂ Br ₆ , sample	Single crystal of size 0.50 × 0.25 × 0.18 mm in tube	Powder in Debye-Scherrer tube	Powder in Bragg-Brentano container	Literature ^e (single crystals)
Formula weight/g mol ⁻¹		533.42		
Cell volume/Å ³	546.49	546.61	548.21	541
<i>a</i> /Å	10.301(4)	10.2992(1)	10.3082(1)	10.20(2)
<i>b</i> /Å	7.095(2)	7.0975(1)	7.1012(1)	7.09(4)
<i>c</i> /Å	7.525(3)	7.5253(1)	7.5364(1)	7.48(3)
β /°	96.45(3)	96.444(1)	96.418(2)	96
D_{calc} /g cm ⁻³	3.242	3.241	3.231	3.288
D_{meas} /g cm ⁻³			3.205 ^b	
<i>Z</i> (Al ₂ Br ₆)			2	
Radiation used	Mo K α		Cu K α	
μ /mm ⁻¹	22.1		27.5	
θ_{max} /°	25	53	55	> 38
Total no. of reflections	1909	677 (K α_1)	1444 (K α_1 + K α_2)	111
No. of unique reflections	956	677	722	111
R_{srr} ^c	0.0935			
Reflections with $I > 4\sigma(I)$	691			
No. of parameters	38	26	26	> 12
Extinction parameter	0.072(4)			
Residuals ^d	$R_1 = 0.0746$ $R_1^* = 0.0418$ $R_2 = 0.1066$	$R_p = 0.0530$ $R_{\text{wp}} = 0.0686$ $R_{\text{expt}} = 0.0500$ $S = 1.36$ Bragg R -factor = 0.1260	$R_p = 0.0870$ $R_{\text{wp}} = 0.1131$ $R_{\text{expt}} = 0.0448$ $S = 2.52$ Bragg R -factor = 0.0808	
Residual charge density/e Å ⁻³	-0.96 < ρ < 0.71			

^a Non-standard setting of space group $P2_1/c$ (no. 14); *a* and *c* interchanged. Estimated standard deviation of the last digit is given in parentheses in this and the following tables. ^b Ref. 10. ^c R_{srr} = residual index between symmetry related reflections = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^d $R_1 = \sum w||F_o| - |F_c|| / \sum |F_o|$ for all data. $R_1^* = R_1$ for data with $F_o > 4\sigma(F_o)$. $R_2 = \{\sum w(|F_o| - |F_c|)^2 / w\sum |F_o|^2\}^{1/2}$ for all data. $R_p = \sum |y_{\text{obs},i} - y_{\text{calc},i}| / \sum y_{\text{obs},i}$. $R_{\text{wp}} = [\sum w_i (y_{\text{obs},i} - y_{\text{calc},i})^2 / \sum w_i (y_{\text{obs},i})^2]^{1/2}$. $R_{\text{expt}} = [(N - P) / \sum w_i y_{\text{obs},i}^2]^{1/2}$. 'Goodness of fit', $S = R_{\text{wp}} / R_{\text{expt}}$. Bragg peak intensity R -factor = $\sum |I_{\text{obs},K} - I_{\text{calc},K}| / \sum I_{\text{obs},K}$. ^e Based on Weissenberg film intensities from two crystals, read visually and corrected for absorption by means of background measurements. The structure was solved by the Patterson method.¹

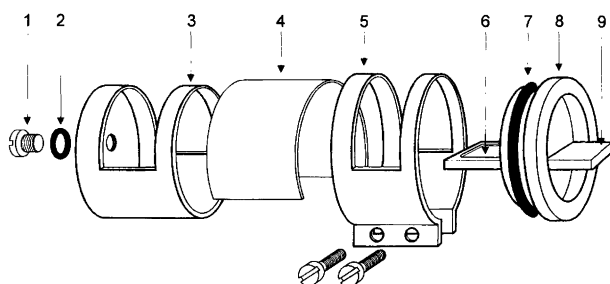


Fig. 1. Protective container for use with moisture- and oxygen-sensitive samples under Bragg-Brentano X-ray scattering geometry. 1, screw (for gas escape during assembling in glove box); 2, O-ring; 3, steel container with window slot and one open end; 4, thin polyethylene/aluminium/polyethylene laminated (coffee bag) foil; 5, foil holder with screws; 6, sampling area (ca. 1 cm²); 7, O-ring; 8, lid to close container; 9, plate for fixing to standard sample holder. Thin rubber gaskets between items 3, 4 and 5 are not shown.

counting time was 10 s per step and the temperature was ca. 20 °C.

For use under Bragg-Brentano scattering geometry, a sample of finely powdered Al₂Br₆ was placed in a homemade moisture-protective container, with a sampling area of ca. 1 cm², and with a window of thin polyethylene/aluminium/polyethylene laminated foil (Fig. 1). Diffractograms were obtained with a Philips PW1820/PW3711 automated $\theta/2\theta$ powder diffractometer using Cu K α radiation ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å, intensity ratio = 0.5), a variable slit-width, a step size of 0.02°, a counting time of 5 s per step, and a temperature of ca. 20 °C. Datasets were collected on different samples to check that crystallite orientation distributions were approximately random. Five successive recordings were obtained to ensure the tightness of the Bragg-Brentano container. These recordings were added to improve counting statistics and the final data set was corrected for the variation in slit-width.

Results and discussion

The results are shown in Tables 1–5; cell constants, other parameters and residual values given in Table 1, Rietveld

refinement parameters in Table 2, final atomic coordinates, and equivalent isotropic thermal parameters in Table 3, bond distances and angles of the AlBr₄ tetrahedra in Table 4 and powder diffraction data in Table 5. A list of observed and calculated squared single crystal structure factors as well as anisotropic thermal parameters (U_{ij}) can be obtained from the authors. The unit cell of the structure is depicted in Fig. 2. The obtained unit cell volume was somewhat larger than what was found by Renes and MacGillavry¹ (Table 1).

Figures 3 and 4 show the obtained X-ray diffraction patterns of the Al₂Br₆ powder in the two different experimental geometries. The diffractograms were subjected to Rietveld full-profile refinements,^{11,12} using the PC program of Young *et al.*¹³ Atomic scattering amplitudes (for Al³⁺ and Br⁻) and a monochromator polarization correction factor of 0.85 were used. The background was represented by linear interpolation between up to 29 points. The program uses a Newton-Raphson least-squares minimization algorithm and a weighting scheme of $w_i = 1/y_{i,obs}$ (where $y_{i,obs}$ represents the observed intensity at the i th step, after slit-width correction). The refinements included parameters for intensity scalings and zero shifts, pseudo-Voigt peak-profile parameters, and lattice and positional and thermal parameters. The refinements were conducted stepwise, involving more and more variable parameters until shifts were <5% of their associated e.s.d.s. Peaks below $2\theta = 37^\circ$ were Rietveld-Toraya corrected¹¹⁻¹³ for asymmetry. Correction for preferred orientation of crystallites on (001) faces was included, but surface roughness was left out because it was found to be of minor importance. No correction was applied for absorption effects (such corrections are normally not necessary for Bragg-Brentano geometry,¹³ but could have some influence on transmission Debye-Scherrer results). Refinement of site occupancies did not give significant deviation from stoichiometry.

The Rietveld refinement R -values (Table 1) are not as low as one would wish. The calculated standard deviations are generally considered to be underestimated, and should probably be multiplied by 2 or 3 to obtain realistic values. The isotropic thermal parameters

Table 2. Rietveld refinement data for Al₂Br₆.

	Debye-Scherrer geometry	Bragg-Brentano geometry
No. of data points, N	4801	5001
Peak range (in units of H_K) ^a	9	8
Pseudo-Voigt profile shape Lorentzian fraction, η ^b	0.31(1)	0.16(1)
Half-width parameter, U ^a	0.096(6)	-0.018(66)
Half-width parameter, V ^a	-0.042(5)	0.096(44)
Half-width parameter, W ^a	0.0159(8)	0.079(7)
Asymmetry parameter, ^c for peaks below $2\theta = 37^\circ$	0.40(8)	0.48(3)
Rietveld-Toraya preferred orientation parameter, G_1 , ^d along (0 0 1)	0.097	0.082

^a H_K is the full width at half maximum of the K th Bragg reflection. The angular dependence is represented by the expression $H_K^2 = U \tan^2 \theta + V \tan \theta + W$. ^b The profile function was a sum of a Lorentzian part, ηL , and a Gaussian part, $(1 - \eta)G$, as defined by Young *et al.*,^{12,13} here applied without angle dependence. ^c Peak asymmetry parameter as defined by Rietveld.¹¹ ^d $I_{corrected} = I_{observed} \exp(-G_1 a_K^2)$.

Table 3. Fractional coordinates and equivalent isotropic thermal parameters for the atoms in Al₂Br₆.^a

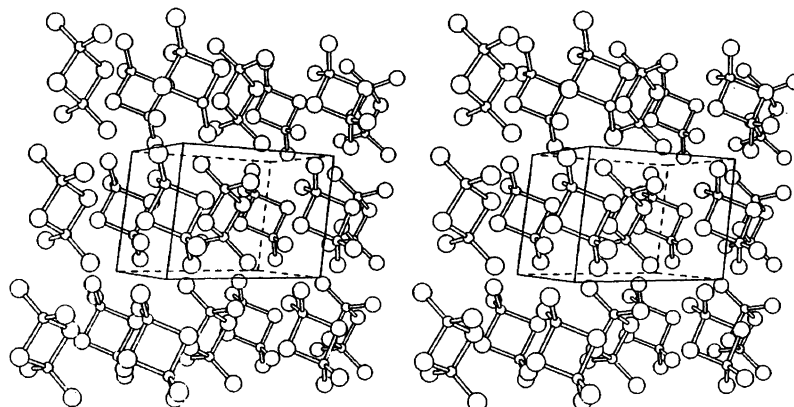
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} /Å ²
Al	0.0508(2)	0.0918(3)	0.1975(3)	3.17(4)
	0.0533(9)	0.0967(14)	0.1972(14)	–1.32(25) ^b
	<u>0.0533(16)</u>	<u>0.1128(20)</u>	<u>0.1950(21)</u>	<u>4.8(5)</u>
	<i>0.050</i>	<i>0.095</i>	<i>0.183</i>	
Br1	0.1463(1)	0.0686(1)	–0.0815(1)	4.16(2)
	0.1486(4)	0.0634(5)	–0.0840(7)	0.49(4) ^b
	<u>0.1470(7)</u>	<u>0.0633(9)</u>	<u>–0.0784(11)</u>	<u>6.01(7)</u>
	<i>0.150</i>	<i>0.075</i>	<i>–0.083</i>	
Br2	0.1676(1)	–0.0847(1)	0.4007(1)	4.92(2)
	0.1670(5)	–0.0857(6)	0.4007(7)	0.49(4) ^b
	<u>0.1650(7)</u>	<u>–0.0842(10)</u>	<u>0.4042(11)</u>	<u>6.01(7)</u>
	<i>0.169</i>	<i>–0.078</i>	<i>0.411</i>	
Br3	0.0096(1)	0.3925(1)	0.2499(1)	5.06(2)
	0.0114(4)	0.3938(4)	0.2534(7)	0.49(4) ^b
	<u>0.0131(7)</u>	<u>0.3927(7)</u>	<u>0.2511(10)</u>	<u>6.01(7)</u>
	<i>0.008</i>	<i>0.392</i>	<i>0.252</i>	

^aValues given in bold face are due to single crystal determination, normal and underlined parameters were obtained by means of Rietveld profile fitting on Debye–Scherrer and Bragg–Brentano geometry data, respectively, and values shown in italics are those of Renes and MacGillavry¹ (corrected for printing errors). All atoms are on Wyckoff sites 4e: $\pm(x, y, z; \frac{1}{2}-x, \frac{1}{2}+y, -z)$. *B*_{eq} is defined as $(8\pi^2/3) \sum_{i=1,3} \sum_{j=1,3} U_{ij} a_i^* a_j^* a_i \cdot a_j$. Anisotropic temperature parameters *U*_{ij} determined by the single-crystal structure determination can be obtained from the authors. ^bA simple estimation of the effect of absorption in a cylindrical sample of porosity *p*, with radius *r* and with absorption coefficient μ can be done by means of Hewat's formula.³³ To the refined *B*-values, one should add a term correcting for the absorption, $\Delta B = \lambda^2 [0.0368(\mu r p) + 0.3750(\mu r p)^2]$. In our case, for *p* = 0.5, one obtains $\mu r p = 3.4$ and $\Delta B = 10.3 \text{ \AA}^2$. Strictly, the procedure is valid only for neutron diffraction.

Table 4. Bond and contact lengths (in Å), and angles (in °) for Al₂Br₆, according to single crystal determinations.

Lengths and angles	This work ^a	Renes and MacGillavry ¹	Gas-phase geometry ¹⁷
Al–Br1(bridging)	2.422(2), 2.404(2)	2.42, 2.34	2.414(8)
Al–Br2 (terminal)	2.223(2)	2.33	2.222(5)
Al–Br3 (terminal)	2.219(2)	2.23	
Al–Al	3.125(14)	3.14	
Br1–Br1	3.582(15)	3.59	
Br1–Al–Br1'	93.52(8)		
Br1'–Al–Br2	108.46(9)		
Br1–Al–Br2	110.68(9)		
Br1'–Al–Br3	108.88(8)		
Br1–Al–Br3	110.45(8)		
Br2–Al–Br3	121.25(9)		122.8(3.3)
Al–Br1–Al'	86.48(8)		87.7(0.9)

^aEstimated standard deviations.

Fig. 2. Stereo plot of the unit cell of Al₂Br₆, seen along the *a*-axis. The *c*-axis is close to being vertical.

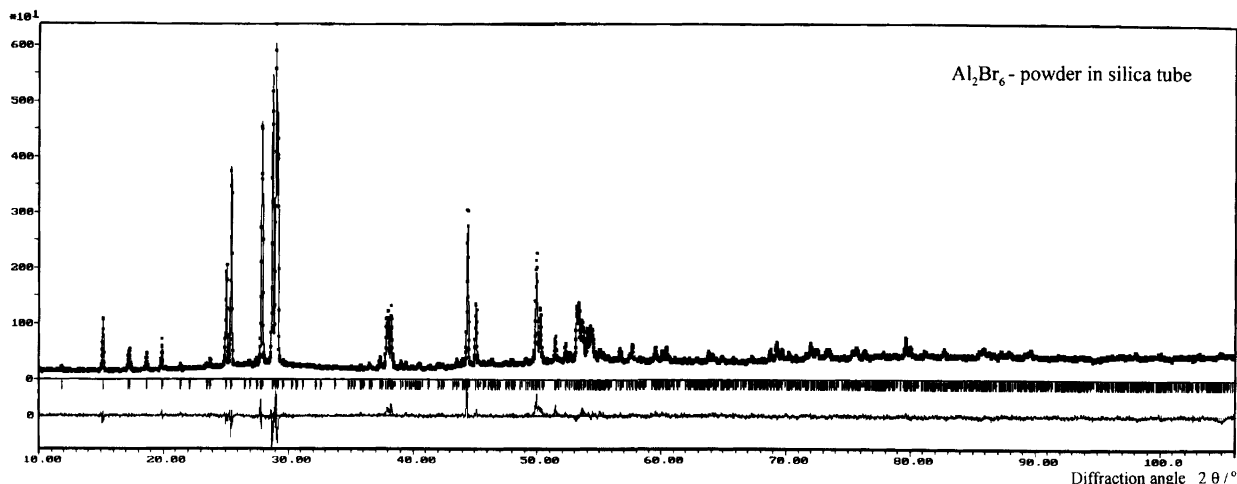


Fig. 3. Debye-Scherrer diffractogram of AlBr_3 (points) in 2θ ranges $10\text{--}106^\circ$. The solid line is the best-fit Rietveld profile. Tick marks below the profile indicate positions of all allowed copper $K\alpha_1$ (long) and $K\alpha_2$ (short) Bragg peaks. The difference between the observed and calculated intensities is shown in the bottom field.

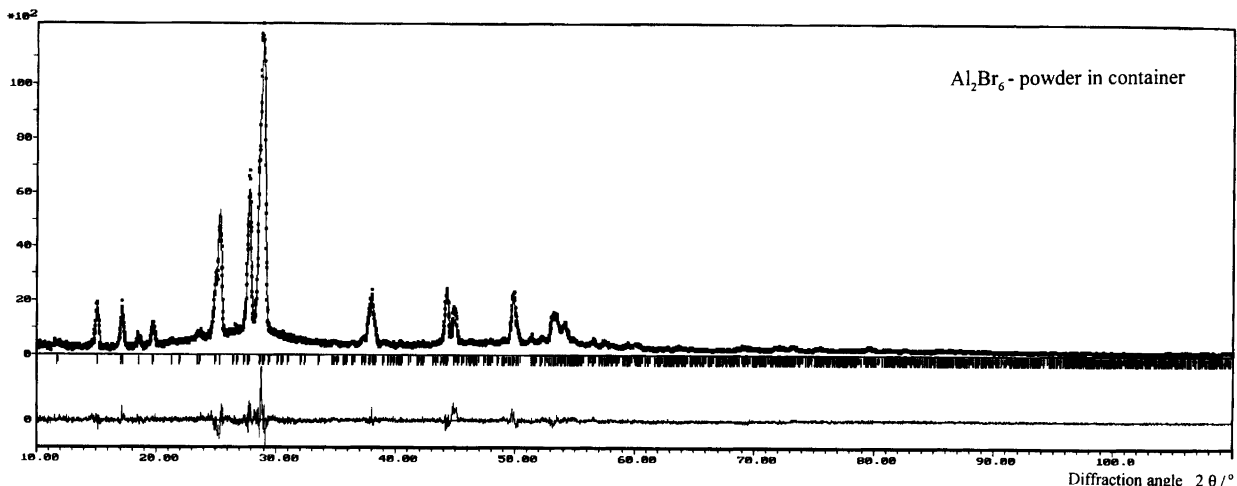


Fig. 4. Bragg-Brentano diffractogram of AlBr_3 (points) in 2θ ranges $10\text{--}110^\circ$. The solid line is the best-fit Rietveld profile. Tick marks below the profile indicate positions of all allowed copper $K\alpha_1$ (long) and $K\alpha_2$ (short) Bragg peaks. The difference between the observed and calculated intensities is shown in the bottom field.

(B -values) are in the case of the Bragg-Brentano data somewhat larger than those obtained from the single-crystal data. The reason is probably that the B -values cover some deficiencies in the model. The small B -values obtained in the case of Debye-Scherrer geometry are certainly due to the lack of correction for absorption which is of importance for absorbing samples under this geometry (Table 3, footnote b).

Discussion of the molecular structure. Crystals of aluminium bromide contain Al_2Br_6 molecules, consisting of two tetrahedra sharing a common edge (Fig. 6). The formation of such dimeric aluminium bromide molecules at moderate temperatures in the gas and liquid states has been known from vapor pressure measurements,^{14,15} gas- and liquid-phase electron diffraction experiments,^{16,17}

mass spectra,¹⁸ from infrared and Raman spectroscopy^{19–26} and *ab initio* quantum-mechanical calculations.²⁷ Similar M_2X_6 molecules are also known for many other halides ($\text{M}=\text{Al}$, Ga and In). The unit cell contains four AlBr_3 formula units, i.e. two Al_2Br_6 molecules. The space group, $P2_1/a$, requires that the two molecules are centrosymmetric. Bond lengths and angles of the molecule, given in Table 4, are generally close to the values of 2.3 Å and 109.47° for a regular AlBr_4 tetrahedron, to be expected from values of other solved structures containing aluminium bromide.^{28–31} The values are also close to those found from gas-phase electron diffraction experiments^{16,17} (Table 4) and to values calculated by the *ab initio* method.²⁷

The bond lengths between aluminium and the bridging bromine atoms (Br1 and $\text{Br1}'$) are, as expected, somewhat

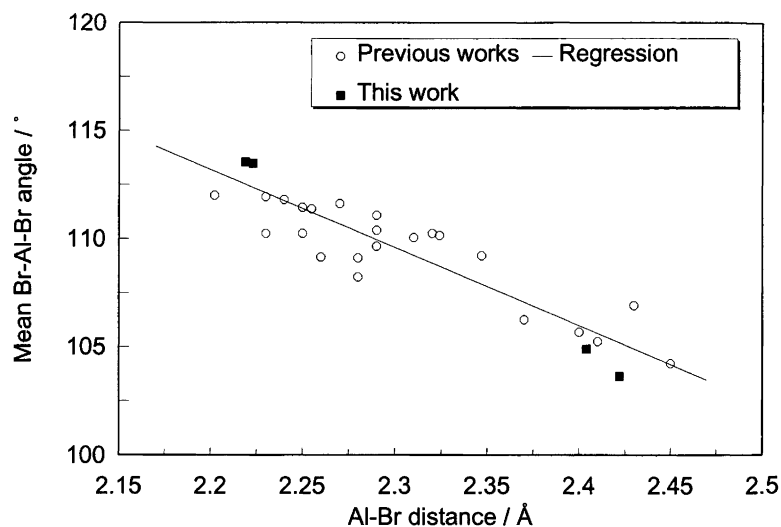


Fig. 5. Plot of the found average of the three Br–Al–Br angles involving a particular Al–Br bond vs. that Al–Br bond distance (four filled squares). Also shown (as circles) are some points calculated from data in the literature.^{28–31} The line is a regression line of all points.

Table 5. Observed Debye–Scherrer $\text{Cu K}\alpha_1$ intensities for selected intense reflections of Al_2Br_6 , with Miller indices and 2θ diffraction angle values in degrees.

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta/^\circ$	I_{obsd}^a
1	1	0	15.2	153
1	1	1	19.9	9
2	0	-1		
0	2	0	25.1	30
2	1	1	25.4	57
2	0	-2	27.9	70
1	2	-1	28.7	80
3	1	0	29.0	100
1	1	2	29.1	66
2	2	-2	37.9	15
4	1	-1	38	17
0	1	3	38.2	19
0	2	± 3	44.4	47
2	3	1		
4	0	2	45.1	18
2	3	2	49.9	33
5	1	-2		
1	1	-4	50.2	16
4	3	-1	53.2	16
0	3	± 3	53.3	17
1	3	-3		

^aExclusive background and normalized to 100 for reflection (3 1 0). An extended list of reflections can be obtained from the authors.

longer [2.404(2) and 2.422(2) Å] than the bonds between aluminium and the other *terminal* bromine atoms, Br2 and Br3, which are relatively short, 2.223(2) and 2.219(2) Å, respectively. Around each aluminium atom, distorted tetrahedral coordination is seen, the angles being deformed in such a way that the Br–Al–Br angles involving bridging bromine atoms (i.e. Br1 and/or Br1') tend to be smaller than the ideal tetrahedral angle of 109.47°. The terminal angle Br2–Al–Br3 is enlarged to 121.25°. The angle deformations and bond length changes

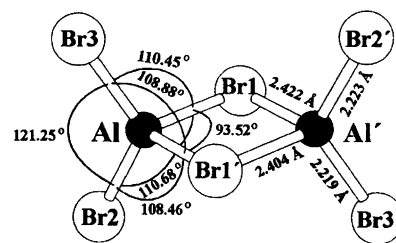


Fig. 6. Geometry of the Al_2Br_6 molecule.

are reasonably consistent with the occurrence of covalent Al–Br bonding involving sp^3 hybridization of the aluminium atom. With the four hybrid orbitals directed toward the bromine atoms, it is expected that *the higher* the *s* character of the bond, *the shorter* is the bond. If the variations in the distance depend on *differences* in hybridization, the Al–Br distance should be almost linearly correlated to the Br–Al–Br angles involving the bond. In fact, the Al–Br distances (Table 4) do depend on the angles: the larger the average of the three Br–Al–Br angles involving a particular bond, the smaller is the Al–Br distance. Figure 5 depicts the average of the three angles involving an Al–Br bond as a function of that Al–Br distance. An approximately linear relationship between the angles and distances can clearly be seen.

The Al–Br bond lengths found are near the value of 2.35 Å, which can be calculated as the sum of the ionic radii of four-coordinated Al^{3+} (0.39 Å) and Br^- (1.96 Å).³²

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