Potassium Heptabromodialuminate, KAl₂Br₇

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Abstract. Potassium heptabromodialuminate, KAl_2Br_7, is monoclinic with $a = 12.373$ (2), $b = 10.822$ (2), $c = 14.444$ (3) Å, $\beta = 133.87$ (1)°, $Z = 4$, space group $P2_1/c$ and calculated density 3.107 g cm^{-3}. The crystals were prepared by zone refinement. The Al_2Br_7 anion consists of two $AlBr_4$ tetrahedra sharing one corner, in staggered arrangement with a bent Al–Br–Al bridge (109.3°). The potassium ion is surrounded by nine bromine ions at distances of 3.3 to 4.0 Å.

Introduction. $AlBr_3$ was prepared by reacting HBr with Al (purity 99.999%, Vigelands Brug, Norway) at 450°C. The product was purified by repeated vacuum distillations. The dry HBr used, containing only traces of Br_2, was prepared by reacting 85% H_3PO_4 with a mixture of NaBr and P_2O_5 in the weight ratio 1:3. KBr was obtained in *pro analysi* quality from Merck, Darmstadt.

The final crystals were picked out from a solid matrix of KAl_2Br_7, prepared by zone refinement of a 2·1/1 mixture of $AlBr_3$ and KBr sealed in a small glass tube. All operations were carried out in a dry box filled with N_2 or under vacuum, since the crystals were very hygroscopic.

A single-crystal fragment approximating a prismatic needle with dimensions $0.19 \times 0.26 \times 0.59$ mm was used. Intensities and cell dimensions were measured with an on-line Picker automatic diffractometer using Mo $K\alpha$ radiation, λ(Mo $K\alpha_1) = 0.7093$ Å. From the total of 2258 independent reflexions measured up to $\theta = 25°$, the 2053 reflexions with intensities larger than zero were used in the calculations.

The observed systematic extinctions were consistent with the space group $P2_1/c$. However, a statistical test of the structure factors gave no clear indication of a centre of symmetry. The measured intensities were converted into structure factors and corrected for absorption (linear absorption coefficient = 216·8 cm^{-1}).

Signs for the largest structure factors were determined by the symbolic addition method, using the program *SYMBOL* by Hjortås (1969). An E map revealed the Br positions quite clearly and the Al atoms were placed in the centre of the Br_4 tetrahedra. A difference Fourier map revealed a peak which was assigned to the potassium atom. The structure was refined by the full-
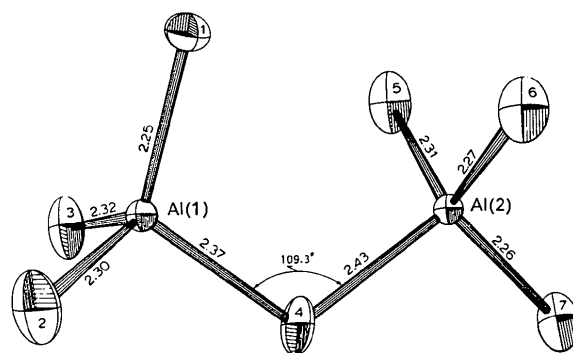

Fig. 1. The $Al_2Br_7^-$ ion.

Table 1. *Final atomic parameters*

Positional and anisotropic thermal parameters are multiplied by 10⁴. Standard deviations are given in parentheses. The anisotropic temperature factors for Br and K are of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The isotropic temperature factor for Al is given as exp $[-B \sin^2 \theta/\lambda^2]$.

	x/a	y/b	z/c	$\beta_{11}(B)$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	5641 (7)	1042 (9)	4440 (7)	107 (12)	77 (10)	106 (10)	14 (11)	62 (10)	32 (9)
Br(2)	7842 (8)	3986 (11)	5779 (7)	96 (12)	185 (16)	67 (9)	−31 (14)	31 (9)	−40 (10)
Br(3)	6176 (8)	2747 (11)	2495 (6)	131 (14)	216 (18)	67 (9)	−5 (13)	75 (10)	10 (10)
Br(4)	3820 (7)	4156 (11)	2912 (8)	46 (11)	158 (15)	142 (12)	23 (12)	43 (10)	17 (12)
Br(5)	1546 (8)	1308 (11)	1005 (7)	110 (13)	209 (19)	52 (9)	−20 (12)	40 (9)	−26 (9)
Br(6)	2091 (8)	2130 (10)	3847 (6)	100 (13)	181 (16)	40 (8)	16 (12)	32 (9)	21 (9)
Br (7)	9778 (8)	4210 (11)	971 (7)	94 (11)	199 (17)	74 (9)	35 (13)	45 (9)	53 (10)
Al(1)	5958 (22)	2897 (24)	3951 (18)	3·3 (0·5)					
Al(2)	1738 (19)	2882 (20)	2191 (16)	1·7 (0·4)					
K	8830 (15)	3796 (26)	2696 (14)	41 (23)	392 (53)	71 (20)	−12 (29)	30 (19)	−50 (25)

matrix least-squares refinement program *LSFVO*1 (Borgen & Mestvedt, 1973). Atomic scattering factors for Br, Al and K$^+$ were taken from Doyle & Turner (1968), and values for $\Delta f'$ and $\Delta f''$ used for anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1. These parameters gave an R value of 0·25 and a weighed R_w value of 0·18.*

The R_w value was rather high for diffractometer data. The possibility of an error in the assignment of the space group was therefore tested by lowering the sym-

metry from that of $P2_1/c$. However, the new refinements did not give any significant improvement. In support of the present results one may observe that the interatomic distances given in Tables 2 and 3 are reasonable and that the structure, which was solved by a direct method, exhibits a plausible anion configuration. The high R_w value was probably due largely to an imperfect absorption correction. The crystal had a somewhat irregular shape, which was difficult to measure accurately through the capillary walls. This may have caused considerable errors, since the absorption corrections were quite large and strongly dependent on direction. In addition decreasing intensity of the standard reflexions during data collection indicated that the crystal deteriorated, thus giving rise to still another source of error. (Presumably humidity leaked into the sealed off capillary during the run.) The nature of the available crystalline material makes it very difficult to obtain better experimental data, and we feel that this justifies presenting the structure with the present level of accuracy.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *within the* Al$_2$Br$_7^-$ *ion*

Standard deviations, multiplied by 10^2 for the distances, are given in parentheses.

Al(1)–Br(1)	2·25 (3)	Br(1)–Al(1)–Br(2)	111·1 (0·9)
Al(1)–Br(2)	2·29 (2)	Br(1)–Al(1)–Br(3)	112·2 (1·2)
Al(1)–Br(3)	2·32 (3)	Br(1)–Al(1)–Br(4)	111·0 (1·1)
Al(1)–Br(4)	2·37 (2)	Br(2)–Al(1)–Br(3)	114·3 (1·1)
		Br(2)–Al(1)–Br(4)	103·5 (1·1)
		Br(3)–Al(1)–Br(4)	104·2 (0·8)
Al(2)–Br(4)	2·43 (2)	Br(4)–Al(2)–Br(5)	105·9 (1·1)
Al(2)–Br(5)	2·31 (3)	Br(4)–Al(2)–Br(6)	112·0 (0·6)
Al(2)–Br(6)	2·27 (3)	Br(4)–Al(2)–Br(7)	102·8 (1·0)
Al(2)–Br(7)	2·26 (2)	Br(5)–Al(2)–Br(6)	111·2 (1·1)
		Br(5)–Al(2)–Br(7)	113·0 (0·7)
		Br(6)–Al(2)–Br(7)	111·6 (1·2)
		Al(1)–Br(4)–Al(2)	109·3 (0·9)

Non-bonding distances $< 6·0$ Å

Al(1)–Al(2)	3·91 (3)	Br(2)–Br(3)	3·87 (1)
Al(1)–Br(5)	4·32 (2)	Br(2)–Br(4)	3·66 (1)
Al(1)–Br(6)	4·74 (3)	Br(2)–Br(6)	5·91 (1)
Al(1)–Br(7)	5·77 (2)	Br(3)–Br(4)	3·69 (2)
Al(2)–Br(1)	4·02 (2)	Br(3)–Br(5)	4·77 (1)
Al(2)–Br(2)	5·58 (2)	Br(4)–Br(5)	3·78 (1)
Al(2)–Br(3)	5.20 (3)	Br(4)–Br(6)	3·90 (2)
Br(1)–Br(2)	3·75 (1)	Br(4)–Br(7)	3·66 (1)
Br(1)–Br(3)	3·79 (2)	Br(5)–Br(6)	3·78 (2)
Br(1)–Br(4)	3·80 (1)	Br(5)–Br(7)	3·80 (2)
Br(1)–Br(5)	3·94 (1)	Br(6)–Br(7)	3·74 (1)
Br(1)–Br(6)	4·02 (1)		

Table 3. *Interatomic distances* (Å) *less than* 5·0 Å

Distances within the Al$_2$Br$_7^-$ ion are not included.

| Al(1)–Br(7) | 4·12 (2) | Al(2)–Br(2) | 4·23 (2) |
Al(1)–Br(5)	4·80 (3)	Al(2)–Br(2)	4·27 (3)
Al(1)–Br(3)	4·97 (3)	Al(2)–Br(7)	4·73 (3)
Al(1)–Br(4)	4·98 (3)		
Br(1)–Br(1)	3·70 (2)	Br(3)–Br(4)	3·93 (2)
Br(1)–Br(7)	3·94 (1)	Br(3)–Br(6)	4·05 (1)
Br(1)–Br(6)	4·02 (1)	Br(3)–Br(7)	4·30 (1)
Br(1)–Br(3)	4·11 (1)	Br(3)–Br(5)	4·37 (2)
Br(1)–Br(3)	4·19 (2)	Br(3)–Br(5)	4·92 (1)
Br(1)–Br(4)	4·40 (2)	Br(4)–Br(7)	4·45 (1)
Br(2)–Br(5)	4·03 (2)	Br(4)–Br(6)	4·86 (1)
Br(2)–Br(6)	4·06 (1)	Br(4)–Br(4)	4·88 (2)
Br(2)–Br(7)	4·10 (2)	Br(5)–Br(5)	3·96 (2)
Br(2)–Br(4)	4·15 (2)	Br(5)–Br(6)	3.99 (2)
Br(2)–Br(6)	4·23 (2)	Br(6)–Br(7)	4·04 (2)
Br(2)–Br(5)	4·38 (2)	Br(7)–Br(7)	3·64 (2)
Br(2)–Br(3)	4·58 (2)		
K–Br(3)	3·29 (3)	K–Br(2)	3·87 (2)
K–Br(5)	3·44 (2)	K–Br(6)	3·97 (3)
K–Br(7)	3·45 (3)	K–Br(1)	4·72 (2)
K–Br(1)	3·47 (1)		
K–Br(5)	3·50 (3)	K–Al(2)	4·26 (4)
K–Br(6)	3·61 (2)	K–Al(1)	4·31 (3)
K–Br(2)	3·69 (3)	K–Al(2)	4·49 (4)
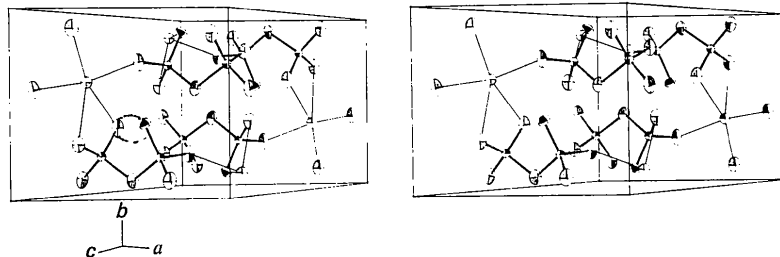
Fig. 2. Stereographic view of the KAl$_2$Br$_7$ structure, the *ab* plane being parallel to the paper. For clarity only five of the nine bromine ions surrounding the potassium are shown.

Discussion. This investigation was undertaken as a part of a project to clarify the structure of $Al_2X_7^-$ ions in the solid and liquid state. A linear Al–X–Al bridge gave better correspondence between observed and calculated Raman frequencies for the melt (Rytter *et al.*, 1973). However, a bent bridge was found for solid $Pd_2(C_6H_5)_2(Al_2Cl_7)_2$ and $Te_4(Al_2Cl_7)_2$ (Couch, Lokken & Corbett, 1972), the former with an eclipsed and the latter with a staggered conformation, indicating that environmental effects are important.

The anion in the present structure, shown in Fig. 1, is very similar to the anion in the $Te_4(Al_2Cl_7)_2$ structure. It is noteworthy that the Al–Br–Al angle (109·3°) is very close to the tetrahedral angle and that the bridging Al–Br distances are about 5% larger than the terminal ones. The $Al_2Br_7^-$ ion is staggered with almost C_s symmetry, the main discrepancy being the angle of 14·8° between the planes through the atoms Br(1), Al(1), Br(4) and Br(4), Al(2), Br(7). A stereographic view of the structure is given in Fig. 2.

The potassium ion is surrounded by 9 bromine ions in the range 3·3 to 4·0 Å in an irregular way.

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Mescaline Hydrobromide

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Abstract. Mescaline hydrobromide (3,4,5-trimethoxyphenethylamine hydrobromide, $C_{11}H_{18}NO_3Br$), triclinic space group $P\bar{1}$, $a = 7·4274$ (12), $b = 9·1782$ (16), $c = 11·8979$ (9) Å, $\alpha = 121·180$ (17), $\beta = 104·194$ (18), $\gamma = 92·689$ (13)° (20 ± 1 °C), $D_m = 1·48$ g cm^{-3}, $D_x = 1·48$ g cm^{-3} ($Z = 2$). The hydrobromide salt was prepared by the method of Heffter [*Ber. dtsch. chem. Ges.* (1898). **31**, 1193–1199] from mescaline sulfate dihydrate supplied by the L. Light Co. Crystals were grown from aqueous n-butanol.

Introduction. Cell parameters were determined by least-squares refinement from 22 reflections measured on a four-circle Syntex $P\bar{1}$ diffractometer using graphite monochromated Mo $K\alpha$ radiation (0·710688 Å) (Ernst, 1973). A small acicular crystal (elongated along

Table 1. *Atomic parameters in fractional coordinates and thermal parameters with e.s.d.'s* ($\times 10^4$)

Temperature factor: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br$^-$	−2340 (2)	−2810 (2)	8801 (1)	211 (3)	168 (2)	70 (1)	16 (2)	44 (2)	65 (2)
C(1)	3188 (14)	339 (14)	7018 (12)	88 (20)	136 (21)	80 (15)	35 (16)	23 (14)	75 (15)
C(2)	2874 (15)	−523 (13)	5605 (12)	114 (21)	86 (17)	57 (13)	26 (15)	25 (14)	34 (13)
C(3)	2348 (15)	285 (15)	4933 (11)	120 (22)	136 (21)	39 (13)	16 (17)	34 (13)	42 (14)
C(4)	2143 (15)	2081 (15)	5687 (12)	109 (22)	156 (22)	76 (15)	50 (17)	33 (15)	95 (16)
C(5)	2359 (14)	2873 (12)	7061 (11)	122 (21)	45 (15)	61 (13)	22 (14)	48 (14)	19 (12)
C(6)	2921 (14)	2054 (14)	7777 (12)	104 (21)	123 (20)	60 (14)	24 (16)	35 (14)	58 (14)
C(7)	3766 (17)	−544 (16)	7787 (14)	154 (25)	157 (23)	89 (17)	52 (20)	18 (16)	88 (17)
C(8)	2058 (19)	−1780 (17)	7625 (14)	213 (31)	156 (24)	84 (17)	53 (22)	42 (18)	73 (17)
C(9)	2250 (19)	−2190 (15)	2750 (14)	218 (31)	104 (21)	74 (16)	46 (21)	60 (18)	4 (15)
C(10)	3175 (21)	3958 (18)	5095 (16)	253 (36)	176 (27)	145 (23)	−3 (24)	76 (23)	129 (22)
C(11)	2380 (21)	5482 (17)	9153 (13)	290 (38)	149 (24)	45 (15)	78 (24)	44 (19)	36 (16)
O(3)	2030 (11)	−415 (10)	3544 (8)	152 (18)	138 (15)	44 (9)	32 (13)	38 (10)	27 (10)
O(4)	1585 (11)	2833 (10)	4969 (8)	176 (18)	138 (15)	55 (10)	20 (13)	39 (11)	69 (11)
O(5)	2034 (11)	4526 (10)	7673 (8)	169 (18)	109 (14)	50 (9)	36 (13)	34 (10)	44 (10)
N	553 (14)	−803 (13)	8072 (11)	163 (22)	142 (19)	73 (13)	31 (16)	52 (14)	60 (13)