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The Crystal Structure of Ammonium Heptabromodialuminate, $NH_4Al_2Br_7$

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Ammonium heptabromodialuminate, $NH_4Al_2Br_7$, is orthorhombic with unit-cell dimensions $a = 12{\cdot}560$ (5), $b = 9{\cdot}501$ (4) and $c = 11{\cdot}423$ (4) Å. The space group is $Pna2_1$ and the calculated density with four formula units in the cell is 3·077 g cm^{-3}. Three-dimensional X-ray intensity data were measured with an on-line Picker automatic diffractometer using Mo $K\alpha$ radiation. The structure was determined by direct methods and refined by full-matrix least-squares methods to an R_1 value of 0·130. The $Al_2Br_7^-$ ion consists of two $AlBr_4$ tetrahedra sharing one corner, in staggered arrangement and with a bent Al–Br–Al bridge (107·7°). The symmetry of $Al_2Br_7^-$ is close to C_2.

The compound $NH_4Al_2Br_7$ was prepared by melting together a 1:2·05 mixture of NH_4Br and $AlBr_3$ in a sealed glass tube. Crystallization was performed by reducing the temperature to ~5°C below the melting point and keeping the mixture at this temperature for five days. The $AlBr_3$ used was prepared by reacting HBr with Al at 450°C as described by Rytter, Rytter, Øye & Krogh-Moe (1973) and NH_4Br (purity 99·5%, Hopkin & Williams, England) was dried and purified by crystallization. All operations were carried out in a dry box filled with N_2 or under vacuum.

The crystal used in the structure determination had a somewhat irregular form, but may be described as a rectangular prism of dimensions 0·15 × 0·26 × 0·37 mm. This crystal was kept in a capillary tube which was sealed. The Weissenberg photographs showed well formed reflexions. Intensity data were collected with a Picker FACS-1 automatic diffractometer and Mo $K\alpha$ radiation, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7093$ Å. The X-ray reflexions were measured at 1319 different reciprocal lattice points ($\theta_{\max} = 25°$).

The 1231 reflexions with intensities larger than zero were used in the calculations. The standard deviation of the intensity $\sigma(I)$ is defined as $\sqrt{[\sigma_N^2 + (0{\cdot}01N)^2]}$ where the last term accounts for a 1% instrumental instability and N is the sum of peak and background counts. Corrections of the measured intensities for Lorentz and polarization effects and absorption were performed. The linear absorption coefficient is 219·0 cm^{-1}.

The observed systematic extinctions, $0kl$ for $k+l$ odd and $h0l$ for h odd, were consistent with the space groups $Pnma$ and $Pna2_1$. A statistical test of the normalized structure factors, $|E_h|$, using the computer program *SCALER* (Hjortås, 1970), gave a clear indication that the crystal had no centre of symmetry, the space group thus being $Pna2_1$ (No. 33).

Phases of the largest structure factors were determined by the symbolic addition method with the aid of the computer program *MULTAN* (Main, Woolfson & Germain, 1971). An E map based on 127 reflexions revealed the bromine positions quite clearly and the aluminum atoms were placed in the centra of two Br_4 tetrahedra. After a preliminary refinement of the structure, a difference Fourier map revealed several relatively weak peaks. The largest of these, with a density of 3 e $Å^{-3}$, was assigned to the ammonium ion. In contrast to the other peaks larger than 1·5 e $Å^{-3}$, this assignment was consistent with the space requirement of the NH_4^+ ion.

Unit weights were employed during the refinement of the structure by the full-matrix least-squares computer program of the X-RAY program system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The program minimizes $\sum w(|F_o| - |F_c|)^2$. The X-RAY system also was used for the calculation of Fourier maps. The atomic scattering factors of Al and Br were taken from Cromer & Mann (1968) and the scattering factors of a spherically symmetric ammonium ion from Davis & Whitaker (1966). Values of $\Delta f'$ and $\Delta f''$ used for anomalous dispersion corrections for the bromine atoms, were found in *International Tables for X-ray Crystallography* (1962). The refinement, with anisotropic temperature factors for bromine, converged at $R_1 = 0{\cdot}130$ ($R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$). A final difference Fourier map revealed no peak larger than 2 e $Å^{-3}$. The largest peaks were found in the vicinity of the bromine atoms.

Introduction of weighting of the reflexions by the reciprocal of the square of the standard deviation increased R_1 as well as $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. An explanation of this observation is that the largest structure factors have the largest deviations between observed and calculated values. However, both posi-

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tive and negative $|F_o|-|F_c|$ values were frequent for these reflexions and no extinction correction seemed to be applicable.

A decrease of R_1 was found when the linear absorption coefficient was reduced. This is equivalent to a reduction in the size of the crystal. An explanation may be that the crystal size, which was difficult to measure through the walls of the capillary, has been over-

Table 1. *Observed and calculated structure factors*

0,0,L		
4	3541	3688
6	2334	2452
8	1266	1256
10	940	1054
12	378	413
0,1,L		
13	212	227
11	764	746
9	469	404
7	735	689
5	953	952
3	1792	2073
1	829	1115
0,2,L		
0	505	741
2	921	1327
4	969	1150
6	1440	1635
8	881	913
10	404	392
12	370	348
0,3,L		
13	404	385
11	449	456
9	810	909
7	347	363
5	2037	2747
3	1232	1654
1	1609	2508
0,4,L		
0	597	907
2	432	546
4	1271	1696
6	566	746
8	695	891
10	226	287
12	388	480
0,5,L		
11	265	294
9	366	521
7	705	900
5	401	514
3	1191	1683
1	244	378
0,6,L		
0	473	672
2	803	1023
4	267	320
6	487	642
8	328	442
10	247	261
0,7,L		
9	595	818
5	311	374
3	610	862
1	438	599
0,8,L		
0	371	395
2	685	860
4	620	740
6	403	568
8	491	594
0,9,L		
7	202	141
5	330	445
3	144	170
1	298	368
0,10,L		
0	320	326
2	405	428
4	280	311
6	258	237
0,11,L		
3	317	218
1	442	474
1,11,L		
0	71	82
1	302	279
2	191	107
1,10,L		
6	228	102
5	108	71
4	143	104
3	161	228
2	89	203
1	78	108
0	35	41
1,9,L		
0	129	197
1	362	431
2	222	279
3	257	279
4	311	363
5	208	224
6	154	225
7	168	191
1,8,L		
9	207	256
8	152	164
7	251	299
6	312	344
5	334	369
4	146	67
3	195	229
2	513	640
1	418	545
0	77	62
1,7,L		
0	38	57
1	379	487
2	350	487
3	264	302
4	348	422
5	92	102
6	244	246
7	302	369
8	101	142
9	145	97
10	121	208
1,6,L		
11	190	168
10	241	237
9	311	388
8	275	389
7	333	394
6	79	202
5	762	887
4	777	966
3	247	231
2	226	320
1	1032	1356
0	883	1236
1,5,L		
0	149	229
1	370	467
2	934	1193
3	367	445
4	768	889
5	325	429
6	230	241
7	141	194
8	614	695
9	340	360
11	280	302
12	113	120
1,4,L		
12	332	277
11	323	347
10	90	105
9	636	716
8	262	276
7	272	302
6	491	569
5	391	428
4	357	361
3	1405	1682
2	885	1108
1	117	238
0	733	940
1,3,L		
0	2624	3480
1	838	966
2	363	397
3	315	361
4	1124	1161
5	1124	1238
6	1434	1508
7	454	434
8	298	295
9	732	804
10	407	395
11	301	286
12	420	370
13	369	321
1,2,L		
13	215	122
12	362	277
11	402	329
10	352	341
9	569	485
8	137	22
7	447	374
6	752	715
5	1292	1253
4	608	558
3	1788	1741
2	1379	1451
1	459	473
0	603	695
1,1,L		
0	280	246
1	1214	980
2	1352	1064
3	1667	1326
4	1356	1093
5	979	783
6	537	416
7	1825	1725
8	921	869
9	491	468
10	328	303
11	651	634
12	110	162
13	357	339
2,0,L		
0	466	467
1	1250	1199
2	318	301
3	594	516
4	2018	2017
5	1008	1106
6	1594	1600
7	392	389
8	1543	1586
9	562	644
10	158	196
11	347	421
12	155	221
13	95	245
2,1,L		
13	348	362
12	168	77
11	203	108
10	177	204
9	876	860
8	400	425
7	1081	987
6	407	379
5	752	694
4	833	732
3	3145	2939
2	931	790
1	501	378
0	1113	882
2,2,L		
0	1276	1102
1	125	82
2	4609	4462
3	941	756
4	1178	961
5	255	195
6	1594	1246
7	671	559
8	1249	1100
9	442	394
10	680	611
11	412	365
12	448	398
13	184	137
2,3,L		
12	98	160
11	113	75
10	242	171
9	771	696
8	297	298
7	571	505
6	505	462
5	876	782
4	549	548
3	798	713
2	480	453
1	635	599
0	599	703
2,4,L		
0	1095	1140
1	595	677
2	1035	1058
3	1118	1195
4	945	960
5	621	640
6	324	290
7	598	610
8	413	342
9	270	231
10	277	234
11	387	431
12	221	183
2,5,L		
12	210	29
11	675	655
10	203	215
9	265	228
8	398	427
7	1318	1363
6	435	493
5	876	926
4	160	143
3	965	990
2	954	1033
1	1698	1928
0	375	479
2,6,L		
0	1026	1239
1	251	267
2	531	553
3	273	334
4	144	176
5	260	274
6	1161	1175
7	147	176
9	101	88
10	437	426
11	60	19
2,7,L		
10	139	125
9	26	60
8	239	244
7	207	238
6	342	382
5	565	595
3	638	687
2	512	566
1	243	234
0	312	400
2,8,L		
0	682	751
1	178	171
2	270	261
3	402	461
4	467	488
5	322	429
6	387	445
7	116	62
8	318	257
9	175	110
2,9,L		
8	115	163
7	348	394
6	133	138
5	275	346
4	147	101
3	262	308
2	152	119
1	445	515
0	278	335
2,10,L		
0	227	232
1	194	100
2	290	221
3	134	124
4	300	330
5	42	22
6	122	205
2,11,L		
2	72	33
0	228	215
3,11,L		
0	212	240
1	211	113
3,10,L		
5	286	87
4	312	361
3	417	387
2	271	196
1	335	373
0	271	271
3,9,L		
0	209	64
1	128	137
2	116	127
3	176	185
4	145	124
5	306	348
6	241	242
7	183	35
3,8,L		
9	93	141
7	444	439
6	225	189
5	268	252
4	135	92
3	306	294
2	194	215
1	549	582
3,7,L		
0	169	193
1	431	449
2	714	742
3	263	248
4	901	960
5	306	275
6	393	355
7	124	193
8	214	217
9	183	190
10	356	299
3,6,L		
11	350	374
10	162	233
9	367	330
8	297	304
7	609	651
6	182	151
5	169	125
4	455	447
3	226	137
2	286	287
1	496	561
0	1054	1119
3,5,L		
0	1415	1360
1	661	687
2	915	869
3	227	249
4	482	425
5	168	113
6	299	264
7	352	344
8	293	271
9	239	45
10	469	433
11	141	179
3,4,L		
12	267	142
11	54	119
10	156	161
9	355	338
8	190	146
7	531	454
6	227	164
5	900	794
4	508	472
3	2221	1991
2	645	604
1	505	535
0	837	838
3,3,L		
0	795	742
1	598	503
2	135	201
3	324	305
4	1494	1200
5	990	851
6	1680	1435
7	665	590
8	844	699
9	607	539
10	461	402
11	159	179
12	310	229
3,2,L		
13	250	185
11	689	676
10	185	216
9	317	276
8	185	173
7	1083	937
6	675	678
5	1845	1521
4	1186	1013
3	537	360
2	175	165
1	2608	2083
0	612	545
3,1,L		
0	538	469
1	990	904
2	3754	3713
3	560	493
4	417	402
5	1087	1080
6	1224	1108
7	452	425
8	748	771
9	756	792
10	449	393
11	351	353
12	136	122
13	190	262
4,0,L		
0	3332	3690
1	1677	1914
2	1233	1183
3	525	502
4	1637	1682
5	1400	1471
6	1589	1716
7	423	414
8	402	432
9	1183	1282
10	582	660
11	400	486
12	491	578
13	276	330
4,1,L		
13	137	102
12	265	248
11	762	814
10	284	246
9	147	192
8	280	323
7	710	675
6	563	523
5	2187	2056
4	1079	994
3	317	299
2	683	602
1	2210	2085
0	1217	1126
4,2,L		
0	797	596
1	1409	1162
2	395	318
3	336	293
4	681	563
5	1239	1086
6	1314	1125
7	366	305
8	411	385
9	865	845
10	324	311
11	336	344
12	210	250
4,3,L		
12	181	89
11	303	375
10	257	238
9	685	624
8	164	156
7	618	594
6	172	114
5	1152	999
4	1460	1237
3	150	65
2	449	357
1	1794	1518
0	1352	1101
4,4,L		
0	2568	2249
1	554	487
2	1831	1534
3	916	755
4	2046	1705
5	382	343
6	797	661
7	686	621
8	1257	1077
9	242	252
10	578	552
11	305	256
12	293	229
4,5,L		
11	159	118
10	197	230
9	109	152
8	183	207
7	367	345
6	426	374
5	743	639
4	692	613
3	698	571
2	834	758
1	712	674
0	287	293
4,6,L		
0	445	422
1	100	99
2	1004	900
3	509	448
4	587	511
5	651	578
6	211	244
7	261	182
8	399	325
9	228	218
10	223	198
4,7,L		
10	172	204
9	664	580
8	140	68
7	415	334
6	116	97
5	735	618
4	416	424
3	1333	1210
2	345	313
1	687	616
0	495	478
4,8,L		
0	303	286
1	320	309
2	413	393
3	404	361
4	412	371
5	312	323
6	126	141
7	154	195
8	334	251
4,9,L		
7	267	263
6	209	181
4	357	336
3	371	356
2	163	162
1	323	305
0	591	584
4,10,L		
0	181	165
1	196	125
2	195	214
3	139	160
4	303	284
5	199	101
5,10,L		
4	131	216
3	227	134
2	230	197
1	172	104
0	259	206
5,9,L		
0	96	120
1	34	100
2	358	380
4	307	233
6	191	148
5,8,L		
8	271	254
7	215	171
6	279	216
5	431	385
4	299	267
3	223	137
2	542	493
1	466	433
5,7,L		
0	118	160
1	439	402
2	250	239
3	745	662
4	278	277
5	364	344
6	270	211
7	322	260
8	271	245
9	99	191
5,6,L		
10	255	216
9	352	333
8	221	170
7	483	458
6	551	461
5	981	839
4	462	400
3	482	416
2	723	645
1	732	644
0	629	562
5,5,L		
0	397	374
1	980	898
2	411	425
3	701	622
4	837	718
5	504	435
6	716	624
7	630	624
8	842	777
9	309	300
10	172	90
11	290	179
5,4,L		
11	502	477
10	174	202
9	885	824
8	377	356
7	178	124
6	581	537
5	384	352
4	725	668
3	930	809
2	1089	946
1	302	205
0	864	742
5,3,L		
0	3586	3112
1	1188	1026
2	1583	1293
3	1243	1046
4	1173	963
5	635	558
6	614	586
7	642	566
8	184	30
9	341	279
10	268	183
11	249	215
5,2,L		
12	306	296
11	147	194
10	220	213
9	242	137
8	389	387
7	129	157
6	670	642
5	1004	871
4	964	858
3	1748	1554
2	732	651
1	1277	1020
0	888	763
5,1,L		
0	1255	1176
1	287	265
2	726	669
3	610	544
4	2248	2099
5	404	413
6	836	820
7	214	174
8	643	626
9	446	530
10	88	93
11	294	291
6,0,L		
0	2014	2147
1	755	860
2	838	816
3	1962	2102
4	254	291
5	160	190
6	889	948
7	1260	1435
8	478	593
9	386	393
10	363	446
11	641	781
6,1,L		
12	144	89
11	162	66
10	237	239
9	850	910
8	161	112
7	837	874
6	518	515
5	316	340
4	870	832
3	2604	2553
2	556	583
1	977	955
0	252	235
6,2,L		
0	637	530
1	488	421
2	1871	1669
3	1118	1009
4	1248	1109
5	476	481
6	389	313
7	951	943
8	1124	1104
9	559	579
10	294	283
11	480	508
12	220	173
6,3,L		
11	230	106
10	136	172
9	378	278
8	359	367
7	375	344
6	718	696
5	587	510
4	256	179
2	1302	1164
3	279	261
1	745	627
0	388	338
6,4,L		
0	1175	1058
1	579	468
2	1182	1022
3	279	181
4	831	753
5	275	272
6	940	794
7	712	619
8	453	406
9	255	262
10	163	206
11	384	337
6,5,L		
10	259	182
9	503	472
8	408	310
7	284	250
6	376	312
5	798	694
4	277	233
3	416	366
2	1022	894
1	535	420
0	817	679
6,6,L		
0	1256	1061
1	732	681
2	481	390
3	506	403
4	670	583
5	275	207
6	867	777
7	268	224
8	67	95
9	39	98
10	251	272
6,7,L		
9	83	75
7	304	257
6	422	353
5	527	449
4	438	344
3	209	70
2	712	620
1	629	567
0	130	143
6,8,L		
0	343	315
2	110	216
3	331	316
4	236	192
5	342	275
6	284	304
7	276	208
6,9,L		
6	255	239
5	531	435
3	405	353
2	360	304
1	704	628
0	98	142
6,10,L		
1	162	82
2	347	219
3	218	226
7,9,L		
1	371	360
2	87	131
3	97	140
4	254	198
5	217	179
7,8,L		
7	320	251
6	43	61
5	162	187
4	84	190
3	128	130
2	344	309
1	224	257
7,7,L		
0	236	145
1	462	346
2	513	424
3	431	376
4	498	441
5	574	503
6	316	348
7	284	214
8	210	134
7,6,L		
9	274	215
8	227	212
7	577	519
6	479	466
5	430	413
4	386	385
3	509	441
2	322	322
1	702	643
0	191	83
7,5,L		
0	672	533
1	136	121
2	1204	1077
3	216	193
4	198	165
5	247	240
6	147	181
7	335	330
8	329	320
9	274	231
10	279	164
7,4,L		
10	215	332
9	164	111
8	199	133
7	490	459
6	398	348
5	877	765
4	688	633
3	1305	1114
2	331	287
1	601	533
0	185	79
7,3,L		
0	804	710
1	1062	947
2	1090	934
3	460	412
4	296	264
5	290	170
6	1529	1379
7	780	765
8	392	399
9	194	184
10	253	283
11	281	218
7,2,L		
11	344	300
10	231	234
9	645	661
8	433	390
7	165	229
6	405	403
5	255	250
4	922	856
3	1063	971
2	1563	1358
1	480	420
0	656	565
7,1,L		
0	1977	2007
1	1242	1192
2	1422	1408
3	886	829
4	988	963
5	687	655
6	87	167
7	699	687
8	241	253
9	222	122
10	108	111
11	253	281
8,0,L		
0	1278	1284
1	1038	1078
2	998	1020
3	211	256
4	438	109
5	490	518
6	1408	1488
7	1088	1243
8	127	161
9	348	433
10	524	567
11	368	448
8,1,L		
11	388	422
10	371	418
9	207	132
8	109	37
7	302	341
6	203	80
5	1075	1111
4	747	791
3	344	243
2	642	656
1	1172	1222
0	284	272
8,2,L		
0	1850	1749
1	931	935
2	489	438
3	378	432
4	681	663
5	1123	1091
6	529	510
7	245	207
8	257	230
9	592	655
10	231	243
8,3,L		
10	209	196
9	224	226
8	107	68
7	791	746
6	534	482
5	662	543
4	56	42
3	572	520
2	821	718
1	781	709
0	678	613
8,4,L		
0	139	111
1	1118	1037
2	1072	984
3	321	283
4	693	667
5	958	860
6	745	673
7	357	255
8	280	189
9	479	431
10	376	308
8,5,L		
9	384	388
8	530	515
7	210	168
6	417	351
5	481	410
4	1147	1067
3	723	639
2	681	598
1	465	428
0	1134	1084
8,6,L		
0	113	73
1	301	196
2	464	410
3	290	191
4	647	529
5	269	292
7	403	357
8	363	332
8,7,L		
7	321	303
6	210	178
5	57	37
4	599	592
3	656	506
2	373	329
1	364	282
0	718	691
8,8,L		
0	263	285
1	590	517
2	458	385
3	300	273
4	195	178
5	371	283
6	212	154
8,9,L		
3	211	125
2	217	180
1	274	278
0	272	216
9,9,L		
0	220	137
9,8,L		
5	170	136
4	470	381
3	199	59
2	403	367
1	295	285
0	301	262
9,7,L		
0	300	282
1	257	285
2	333	355
3	188	235
4	445	426
5	193	154
6	347	134
9,6,L		
8	182	57
7	476	444
6	288	192
5	157	131
4	164	98
3	602	568
2	378	359
1	542	597
0	558	442
9,5,L		
0	502	382
1	594	610
2	297	281
3	301	298
4	481	470
5	310	270
6	419	348
7	100	112
8	262	169
9	276	267
9,4,L		
9	403	314
8	268	292
7	343	344
6	166	231
4	812	771
3	483	346
2	486	488
1	388	322
0	1025	978
9,3,L		
0	804	715
1	675	606
2	1158	1118
3	222	140
4	146	18
5	438	421
6	377	363
7	549	575
8	377	320
9	371	339
10	106	67
9,2,L		
10	256	235
9	298	231
8	310	324
7	164	156
6	420	353
5	994	970
4	787	814
3	307	311
2	533	528
1	475	533
0	476	500
9,1,L		
0	1023	1087
1	892	1011
2	121	88
3	426	443
4	609	677
5	1068	1141
6	349	257
7	307	249
8	560	593
9	566	640
10	126	117
10,0,L		
0	474	517
1	1030	1196
2	1865	2213
3	916	1020
4	482	551
5	378	395
6	591	709
7	845	939
8	444	560
9	331	347
10	357	314
10,1,L		
10	218	194
9	414	459
8	39	172
7	154	82
6	287	359
5	289	290
4	572	628
3	672	675
2	606	652
1	131	158
10,2,L		
0	810	826
1	631	614
2	233	199
3	330	357
4	1007	1017
5	307	391
6	96	195
7	461	475
8	607	629
9	266	281
10,3,L		
9	172	232
8	141	71
7	780	777
6	458	421
4	588	479
3	1042	1005
2	569	579
1	917	872
0	231	180
10,4,L		
0	248	215
1	212	273
2	454	379
3	137	153
4	514	494
5	514	441
6	401	331
7	216	191
8	220	46
10,5,L		
8	355	309
7	310	305
6	128	90
5	693	650
4	91	124
3	195	207
2	609	617
1	735	712
0	494	452
10,6,L		
0	641	582
1	489	473
2	108	128
3	405	328
4	417	382
5	271	243
6	231	266
7	229	171
10,7,L		
5	123	97
4	380	384
3	121	136
2	440	374
1	185	126
0	224	243
10,8,L		
0	310	314
1	185	120
2	320	302
3	134	160
11,7,L		
0	191	196
1	112	151
3	318	251
11,6,L		
5	164	122
4	255	242
3	180	189
2	719	714
0	656	653
11,5,L		
0	253	257
1	255	298
2	274	247
3	371	411
4	295	301
5	214	228
6	131	162
11,4,L		
7	172	165
6	410	349
5	445	406
4	602	578
3	123	150
2	673	688
1	451	358
0	159	52
11,3,L		
0	223	163
1	694	812
2	204	156
3	1093	1097
4	243	187
5	422	384
6	219	228
7	677	695
8	189	212
11,2,L		
8	450	394
7	202	170
6	427	454
5	279	117
4	353	340
3	386	316
2	284	364
1	207	218
0	772	776
11,1,L		
0	554	575
1	223	223
2	218	211
3	439	414
5	309	364
6	205	265
7	429	506
8	181	97
9	422	434
12,0,L		
0	196	282
1	769	949
2	728	933
3	501	562
5	442	524
6	720	905
7	340	484
8	231	56
12,1,L		
7	293	344
6	392	387
5	475	546
4	470	572
3	109	148
2	515	653
1	347	456
0	382	451
12,2,L		
0	1113	1267
1	421	497
2	261	294
3	432	471
4	812	901
5	334	375
6	268	309
7	168	322
12,3,L		
7	294	370
6	327	285
5	227	345
4	93	174
3	467	462
2	257	111
1	431	399
0	263	374
12,4,L		
0	257	203
1	225	157
2	432	434
3	299	216
4	318	197
5	219	241
6	241	274
12,5,L		
5	505	552
4	330	248
3	420	412
2	370	390
1	634	693
12,6,L		
0	224	231
1	321	331
3	258	300
13,5,L		
0	152	64
1	315	346
2	310	256
13,4,L		
4	457	507
2	205	193
1	293	239
0	413	363
13,3,L		
0	192	194
1	416	479
3	103	78
4	290	262
5	312	253
13,2,L		
6	171	162
5	221	299
4	567	609
3	459	570
2	418	449
1	245	318
0	172	105
13,1,L		
0	543	699
1	482	611
2	277	197
3	176	48
4	232	367
5	495	583
6	229	240
14,0,L		
0	151	41
1	390	527
2	677	851
4	328	329
14,1,L		
4	497	565
3	224	335
2	370	443
1	250	330
0	188	156
14,2,L		
0	271	282
1	250	304
2	231	95
3	120	125
4	386	419
14,3,L		
3	551	536
2	219	164
1	167	279
0	311	298

estimated. However, it is equally probable that the crystal deteriorated. This was indicated by the intensity decrease of the standard reflexions during the data collection.

It should be noted that the present results were obtained by direct methods and that the anion has a plausible configuration (see below). The interatomic distances also are reasonable. The relatively high R_1 value is supposed to be due mainly to an imperfect absorption correction. The observed and calculated structure factors are shown in Table 1 and the final positional and thermal parameters in Table 2.

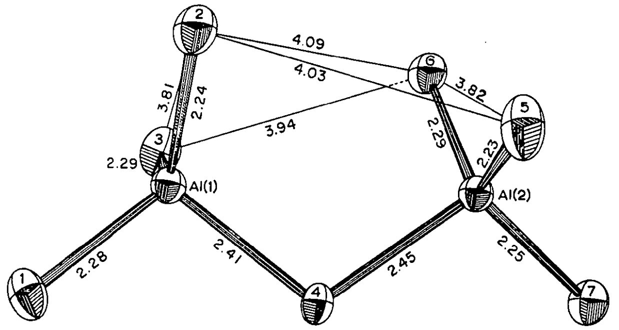

Fig. 1. Bond lengths (Å) of the $Al_2Br_7^-$ ion. The two triangles formed by the atoms Br(2), Br(3) and Br(6) and by Br(2), Br(5) and Br(6) also are shown.

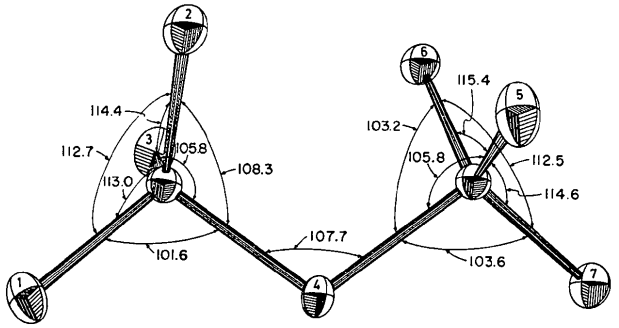

Fig. 2. Bond angles (°) of the $Al_2Br_7^-$ ion.

Discussion

The present investigation was undertaken in a further effort to clarify the structure of $M_2X_7^-$ ions (M = Al, Ga, In; X = halogen) in the solid and liquid state. The possible $M_2X_7^-$ structures have been discussed by Rytter (1974). A linear M–X–M bridge gives the best correspondence with the observed Raman frequencies in molten salts (Rytter, Øye, Cyvin, Cyvin & Klaeboe, 1973; Rytter, 1974), but other configurations cannot be ruled out definitely.

The $NH_4Al_2Br_7$ structure consists of NH_4^+ and $Al_2Br_7^-$ ions (Figs. 1 and 2). The two aluminum atoms of the anion are situated approximately in layers parallel to the *ac* plane. However, the structure cannot be described as a layer structure since no long-range ordering of the bromine atoms is present. No close packing of the bromine atoms is observed. The packing density of these atoms is 48·7 Å^3 per atom which is compatible with 49·8 Å^3 per atom for KAl_2Br_7 (Rytter, Rytter, Øye & Krogh-Moe, 1973). A stereographic view (*ORTEP*, Johnson, 1965) of the structure is given in Fig. 3.

The symmetry of the anion in the present structure is very close to the ideal C_2 symmetry. Thus the missing staggered configuration has been found [see Rytter (1974)]. The bromine bridge is bent and the Al–Br–Al angle (107·7°) is close to the tetrahedral angle (109·5°). The twofold axis is through the bridging bromine atom and perpendicular to a line connecting the aluminum atoms. Figs. 1 and 3 show that the terminal $AlBr_3$ groups are twisted in opposite directions around the Al–Br(4) bonds to minimize halogen–halogen repulsions.

The details of the $Al_2Br_7^-$ structure in $NH_4Al_2Br_7$ are close to those found in KAl_2Br_7 and also close to the details found for $Al_2Cl_7^-$ in $Te_4(Al_2Cl_7)_2$ (Couch, Lokken & Corbett, 1972). Fig. 2 shows that the terminal Al–Br bonds are bent toward the bridging Br(4). This probably is due to a smaller van der Waals radius of a divalent bromine atom. The two Br–Al–Br(4) angles which do not include atoms with bromine–

Table 2. *Final atomic parameters*

Positional parameters are multiplied by 10^4 and thermal parameters by 10^3. Standard deviations are given in parentheses. The isotropic and anisotropic temperature factors are of the forms $\exp[-U8\pi^2(\sin\theta/\lambda)^2]$ and $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$, respectively.

	x/a	y/b	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	109 (5)	1976 (8)	−210†	33 (3)	66 (4)	55 (4)	−13 (3)	−2 (3)	17 (4)
Br(2)	−264 (4)	4683 (7)	3026 (12)	33 (3)	62 (4)	64 (4)	11 (3)	−2 (4)	−14 (4)
Br(3)	2067 (6)	4848 (10)	682 (11)	52 (4)	84 (5)	45 (4)	−6 (4)	−6 (4)	−13 (4)
Br(4)	2541 (4)	7611 (6)	3015 (10)	29 (2)	50 (3)	42 (3)	1 (2)	−6 (3)	−1 (3)
Br(5)	2911 (6)	9548 (10)	193 (10)	39 (4)	103 (7)	47 (4)	−2 (4)	12 (3)	11 (4)
Br(6)	1574 (4)	1305 (7)	2823 (10)	34 (3)	53 (3)	60 (4)	8 (3)	−8 (3)	−3 (4)
Br(7)	182 (5)	8384 (8)	1181 (8)	29 (3)	65 (4)	60 (4)	−16 (3)	−9 (3)	6 (4)
Al(1)	3855 (14)	8805 (19)	4183 (17)	36 (4)					
Al(2)	1760 (14)	9344 (18)	1672 (18)	35 (4)					
NH_4	3774 (68)	3583 (92)	2603 (86)	130 (34)					

† Fixed to define origin.

bromine repulsions across the bridge are generally smaller than the four others.

The interatomic distances (*ORFFE*; Busing, Martin & Levy, 1964) are reasonable. Table 3 shows that the Br–Br distances within the AlBr$_4$ tetrahedra are slightly shorter than twice the van der Waals radius of 3·90 Å (Pauling, 1967). As expected, the bromine atoms next to Br(4) without additional bromine–bromine repulsions across the bridge, *i.e.*, Br(1) and Br(7), occur at the shortest distances. Most of the intermolecular Br–Br distances (Table 4) are longer than the intramolecular ones, although some of the distances in the two sets are comparable. The lengths of the terminal Al–Br bonds average 2·27 Å while the bridging bonds average 2·43 Å. These values indicate that the bridging bonds are weaker than the terminal ones. The distances are close to the corresponding mean values of 2·28 and 2·40 Å found for KAl$_2$Br$_7$. The sum of the covalent radii of aluminum and bromine, corrected for the difference in electronegativity (Pauling, 1967), is 2·32 Å and agrees reasonably well with the terminal distances.

Table 3. *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)	2·28 (2)	Br(1)–Al(1)–Br(2)	112·7 (0·8)
Al(1)–Br(2)	2·24 (2)	Br(1)–Al(1)–Br(3)	113·0 (0·9)
Al(1)–Br(3)	2·29 (2)	Br(1)–Al(1)–Br(4)	101·6 (0·7)
Al(1)–Br(4)	2·41 (2)	Br(2)–Al(1)–Br(3)	114·4 (0·8)
		Br(2)–Al(1)–Br(4)	108·3 (0·9)
		Br(3)–Al(1)–Br(4)	105·8 (0·7)
Al(2)–Br(4)	2·45 (2)	Br(4)–Al(2)–Br(5)	105·8 (0·7)
Al(2)–Br(5)	2·23 (2)	Br(4)–Al(2)–Br(6)	103·2 (0·8)
Al(2)–Br(6)	2·29 (2)	Br(4)–Al(2)–Br(7)	103·6 (0·7)
Al(2)–Br(7)	2·25 (2)	Br(5)–Al(2)–Br(6)	115·4 (0·8)
		Br(5)–Al(2)–Br(7)	114·6 (0·9)
		Br(6)–Al(2)–Br(7)	112·5 (0·8)
		Al(1)–Br(4)–Al(2)	107·7 (0·6)

Non-bonding distances < 6·0 Å

Al(1)–Al(2)	3·93 (3)	Br(2)–Br(4)	3·77 (1)
Al(1)–Br(5)	4·76 (2)	Br(2)–Br(5)	4·03 (1)
Al(1)–Br(6)	4·03 (2)	Br(2)–Br(6)	4·09 (1)
Al(1)–Br(7)	5·76 (2)	Br(3)–Br(4)	3·75 (1)
Al(2)–Br(1)	5·76 (2)	Br(3)–Br(6)	3·94 (2)
Al(2)–Br(2)	4·15 (2)	Br(4)–Br(5)	3·74 (2)
Al(2)–Br(3)	4·84 (2)	Br(4)–Br(6)	3·72 (1)
Br(1)–Br(2)	3·76 (1)	Br(4)–Br(7)	3·70 (1)
Br(1)–Br(3)	3·81 (1)	Br(5)–Br(6)	3·82 (1)
Br(1)–Br(4)	3·63 (1)	Br(5)–Br(7)	3·77 (1)
Br(2)–Br(3)	3·81 (2)	Br(6)–Br(7)	3·78 (1)

Table 4. *Some interatomic distances* (Å)

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

Br(1)–Br(7)	3·77 (1)	Br(2)–Br(6)	3·96 (1)
Br(1)–Br(4)	3·92 (1)	Br(2)–Br(3)	3·97 (1)
Br(1)–Br(6)	3·97 (1)	Br(3)–Br(4)	3·79 (1)
Br(2)–Br(5)	3·86 (1)	Br(4)–Br(5)	3·87 (1)
NH$_4$–Br(3)	3·30 (9)	NH$_4$–Br(5)	3·75 (9)
NH$_4$–Br(2)	3·37 (9)	NH$_4$–Br(4)	4·16 (9)
NH$_4$–Br(6)	3·52 (9)	NH$_4$–Br(7)	4·30 (9)
NH$_4$–Br(6)	3·53 (9)	NH$_4$–Br(1)	4·31 (9)
NH$_4$–Br(1)	3·66 (9)	NH$_4$–Br(5)	4·84 (9)
NH$_4$–Br(7)	3·75 (9)	NH$_4$–Al(2)	4·37 (9)

In summary, the details of the structure of the anion can be explained by:

(i) Minimization of the bromine–bromine repulsions.

(ii) A smaller van der Waals radius of the bridging bromine ion.

(iii) Weaker Al–Br bridging bonds compared to Al–Br terminal bonds.

(iv) Packing perturbations resulting in minor differences in otherwise equivalent parameters.

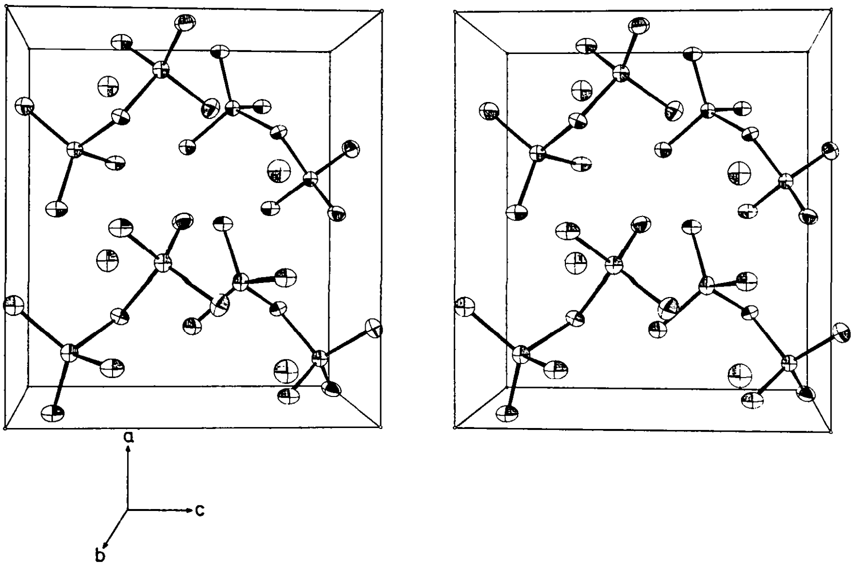

Fig. 3. Stereographic view of the NH$_4$Al$_2$Br$_7$ structure, the *ac* plane being parallel to the paper. Ellipsoids of bromine and spheres of aluminum are scaled to include 45 % probability. The ammonium ions are arbitrarily given a radius of 0·26 Å.

The ammonium ion is surrounded by seven bromine atoms in the range 3·30 to 3·75 Å and three more bromine atoms if the range is extended to 4·31 Å (Table 4). The sum of the crystal radii of ammonium and bromine is 3·43 Å (Pauling, 1967).

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The Crystal and Molecular Structure of Thiazolidine-2,4-dione

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$C_3H_3O_2NS$ is orthorhombic, space group *Pbca*, with a = 7·393 (1), b = 9·416 (1), c = 13·251 (1) Å, Z = 8. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to R = 0·066 for 622 counter reflexions. The predominant tautomer is the thiazolidine form. All the bonds in the molecule show significant multiple character, with the exception of those belonging to the saturated methylene carbon atom, C(5). A series of canonical forms are proposed to interpret the π electron distribution within the molecule. None of the ring atoms shows significant deviation from planarity. The molecules pack in the form of hydrogen-bonded dimers predominantly in the *ab* plane.

Introduction

Thiazolidinones are of physiological and industrial importance. Aravamudan, Krishnan & Udupa (1973) have related the physiological activity of 2-imino-4-oxo-1,3-thiazoline to its coordination chemistry and have shown that the compound forms pseudo-tetrahedral, nitrogen-bonded complexes with Co(II) halides.

Thiazolidine-2,4-dione is an inhibitor of the corrosion of mild steels in acidic solution. The extent of the inhibition, in 0·1 *M* HCl, ranges from 37% at an inhibitor concentration of $0{\cdot}03\times10^{-3}$ *M* to 92% at the solubility limit of the inhibitor, 4×10^{-3} *M* (Donnelly, Downie & Grzeskowiak, unpublished). The compound is also used as a 'brightener' in the electroplating industry. The molecule is potentially ambidentate and a possible explanation of its ability to inhibit metallic corrosion is in terms of its coordination at the metallic surface.

This analysis has been undertaken as part of a programme in which the structure and coordination chemistry of heterocyclic molecules, associated with corrosion inhibition, are being investigated.

Experimental

Crystal data

Single crystals, in the form of cuboid plates, were obtained by evaporation from methanolic solution.

Table 1. *Crystal and experimental data*

$C_3H_3O_2NS$	Systematic absences
F.W. 117·13	$0kl$: $k=2n+1$
a = 7·393 (1) Å	$h0l$: $l=2n+1$
b = 9·416 (1)	$hk0$: $h=2n+1$
c = 13·251 (1)	Space group: *Pbca*
V = 922·44 Å^3	Z = 8
D_c = 1·69 g cm^{-3}	μ(Mo $K\alpha$) = 5·25 cm^{-1}
D_m = 1·68	$F(000)$ = 480