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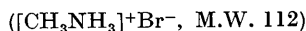
**The crystal structure of methyl ammonium bromide.** By E. J. GABE\*, *Pure Physics Division, National Research Council, Ottawa, Canada*

(Received 30 June 1961)

The crystal structures of the methyl ammonium halides were first investigated by Hendricks (1928), and the structure of the chloride was later redetermined by Hughes & Lipscomb (1946). The present investigation was undertaken at the suggestion of Prof. C. Sandorfy of the University of Montreal, who is working on the infra-red spectra of these substances, with particular interest in a hydrogen bond of the type  $N^+-H \cdots Br^-$ .

### Crystal data

The crystals of methyl ammonium bromide



are extremely thin, irregularly shaped, soft plates, tabular on (001). The space group ( $P4/nmm$ ) and axial lengths ( $a=4.81$ ,  $c=8.74$  Å) were determined from precession photographs. The observed density is  $1.78 \text{ g.cm.}^{-3}$ ; the density calculated for  $Z=2$  is  $1.84 \text{ g.cm.}^{-3}$ . Hendricks found  $a=5.09$  and  $c=8.75$  Å.

### Structure determination

With  $Z=2$  the molecules must be in special positions, but the only systematic absences were those characteristic of the space group. Hence the molecules must occupy positions,  $0, \frac{1}{2}, z$  and  $\frac{1}{2}, 0, \bar{z}$  and only the  $z$  parameters remain undetermined.

The  $0kl$  intensity data were collected from Weissenberg photographs; 51 reflections of a possible 60 within the Cu circle were recorded. The Br coordinate was determined as 0.810 from the  $00l$  Patterson synthesis (Hendricks gives a value of 0.815), and bromine structure factors were calculated with an assumed  $B=4.5$  Å<sup>2</sup>. The  $F_o$  data were placed on an approximately absolute scale by comparison with  $F_{c(Br)}$  and a correction of  $\Delta B = +0.3$  Å<sup>2</sup> was also derived from this comparison.  $R_{0kl}$  was 23.1% at this stage. The  $0kl$  Fourier map gave the positions of the two light atoms, though it was not possible to distinguish between them. Two cycles of Fourier and difference map refinement brought the  $R$  value down to 8.9%. It was still not possible to resolve the ambiguity of the light atom positions and it seems unlikely that this could be done even with three-dimensional data, both because of the dominance of the Br atom and the poor shape of the crystals for accurate data collection.

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**Cell dimensions and space group of magnesium nitrate hexahydrate.** By R. L. MOZZI and W. R. BEKEBÉDE, *Research Division, Raytheon Company, Waltham, Massachusetts, U.S.A.*

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Precession camera data were obtained on single crystals of  $Mg(NO_3)_2 \cdot 6H_2O$  grown from aqueous solution and encapsulated in thin-walled glass capillaries to prevent

The fractional coordinates are

	$x$	$y$	$z$
Br	0	0.500	0.817
C	0	0.500	0.196
N	0	0.500	0.365

The light-atom positions were assigned on the basis of a slight difference of peak height in the final Fourier map.

### Discussion

With these parameters  $N-C=1.48$  Å, the distance from the C atom to the Br at  $0, \frac{1}{2}, -0.193$  is 3.31 Å and to the Br at  $\frac{1}{2}, 0, 0.193$  is 3.40 Å. The distance from the N atom to the Br at  $0, \frac{1}{2}, 0.817$  is 3.95 Å. If we consider the ionic radius of  $Br^-$  to be 1.95 Å and use the values for the van der Waal radius of the methyl group (2.0 Å) and the ionic radius of the  $NH_4^+(CH_3-NH_3^+)$  group (1.4 Å), as given by Hughes & Lipscomb (1946),  $N-Br^- = 3.35$  Å and  $C-Br^- = 3.95$  Å. Therefore it seems likely that the C and N parameters as given above need to be interchanged. The observed non-bonded distances then agree very well with the calculated values and the results are in good agreement with those for the chloride. It is also of interest to note that when this is done the N, H and Br atoms are almost in a straight line if we assume a tetrahedral C-H-N angle.

The light atoms occupy the same pair of special positions as they do in the chloride, which has the same space group but is not isomorphous. Hence the remarks in the earlier paper about the rotation of the  $CH_3$  and  $NH_3^+$  groups also apply here, but no attempt has been made to allow for this rotation. However, some photographs were taken at approximately  $-120$  °C. but no change in the diffraction pattern could be detected. The crystals tended to shatter at this temperature and because of their poor quality no structure work was attempted.

I wish to thank Prof. C. Sandorfy for suggesting the problem and supplying the crystals, Dr W. H. Barnes and Dr A. W. Hanson for their interest in the work, and the referee for some helpful suggestions.

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Table 1. *Interplanar spacings for Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O*

<i>hkl</i>	<i>d<sub>c</sub></i> (Å)	<i>d<sub>o</sub></i> (Å)	<i>I<sub>rel.</sub></i>	<i>hkl</i>	<i>d<sub>c</sub></i> (Å)	<i>d<sub>o</sub></i> (Å)	<i>I<sub>rel.</sub></i>	<i>hkl</i>	<i>d<sub>c</sub></i> (Å)	<i>d<sub>o</sub></i> (Å)	<i>I<sub>rel.</sub></i>
100	6.186	6.176	6*	150	2.351	2.349	1	21 $\bar{3}$	1.818	1.818	3
011	5.851	5.840	45*	202	2.316	2.317	10*	242	1.808		
110	5.562	5.556	3*	042	2.287	2.290	3	043	1.807	1.807	5
021	4.574	4.573	6*	151	2.200			33 $\bar{1}$	1.807		
120	4.432	4.433	55*	202	2.199	2.201	10	062	1.782	1.782	1
11 $\bar{1}$	4.352	4.349	25*	22 $\bar{2}$	2.176			22 $\bar{3}$	1.765		
111	4.156	4.154	35*	14 $\bar{2}$	2.171	2.172	3	331	1.763	1.764	4
12 $\bar{1}$	3.743	3.743	1	212	2.166			213	1.732		
031	3.563	3.562	20*	013	2.165			340	1.730		
002	3.295	3.295	100*	24 $\bar{1}$	2.125	2.118	15	16 $\bar{2}$	1.725	1.725	4
012	3.190	3.190	35*	142	2.120	2.118	15	32 $\bar{2}$	1.723		
13 $\bar{1}$	3.126	3.124	4*	060	2.118			25 $\bar{2}$	1.712	1.710	1
200	3.093	3.092	5*	222	2.078			302	1.708		
131	3.051	3.051	8*	241	2.077	2.077	30	312	1.693		
10 $\bar{2}$	2.973	2.972	1	11 $\bar{3}$	2.077			34 $\bar{1}$	1.691		
022	2.925	2.925	75*	023	2.076			17 $\bar{1}$	1.690	1.690 $b$	3
11 $\bar{2}$	2.895	2.896	4	310	2.035	2.036	4	223	1.686		
041	2.862	2.848	25	23 $\bar{2}$	2.032			23 $\bar{3}$	1.685		
102	2.847			061	2.016			171	1.678	1.678	2
21 $\bar{1}$	2.788			052	2.012			261	1.677		
220	2.781	2.781	15	113	2.011	2.009 $b$	6	252	1.663	1.663	1
112	2.779			160	2.004			053	1.662		
12 $\bar{2}$	2.693	2.688	35	12 $\bar{3}$	1.998			322	1.650		
211	2.683			311	1.974	1.976	1	332	1.649	1.649	5
14 $\bar{1}$	2.620	2.620	10*	250	1.964	1.964	2	004	1.648		
141	2.575	2.576	6*	320	1.961			014	1.634	1.635	1
221	2.520	2.520	2*	311	1.917	1.918	5	153	1.621	1.621	<1
13 $\bar{2}$	2.434	2.435	1*	13 $\bar{3}$	1.885	1.885	4				
051	2.371			24 $\bar{2}$	1.872	1.866	5				
23 $\bar{1}$	2.369	2.368	20	251	1.865						
132	2.363			133	1.836	1.839	1				

\* indicates an observation that was used in the least-squares refinement of the cell parameters.  
*b* indicates a broad line.

for *l* odd uniquely determined the space group as  $P2_1/c$ .

A 20 mil. thick powder sample was prepared from Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, supplied by the Fisher Scientific Company, and covered with a 10 mil. thick strip of beryllium. The beryllium served to isolate the powder from the atmosphere in addition to providing a well-defined flat surface for samples which otherwise tended to shrink and warp. Powder patterns were obtained on a Norelco diffractometer using Ni-filtered Cu  $K\alpha$  radiation and Geiger counter detection. A fixed count, step-scanning device was employed in recording the patterns, with steps of 0.02°–0.04° in  $2\theta$  and 6400 counts per point. The *d*-values were calibrated with a silicon standard sample. All of the powder lines could be indexed consistent with the approximate parameters and space group assignment determined from the precession photographs. Final parameters were derived from a least-squares refinement of the powder data, using an IBM 704 program (Mozzi & Newell, 1961). The resulting cell dimensions are:

$$a = 6.194 \pm 0.002, \quad b = 12.707 \pm 0.003, \\ c = 6.600 \pm 0.002 \text{ \AA}; \quad \beta = 92.99 \pm 0.02^\circ.$$

The density, calculated on the basis of two molecules of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O per unit cell, is 1.64 g.cm.<sup>-3</sup>, in satisfactory agreement with the pycnometric value of 1.58 g.cm.<sup>-3</sup>. A comparison of observed and calculated interplanar spacings is presented in Table 1. Also included are the relative integrated intensities measured on a powder pattern scanned continuously at  $\frac{1}{8}^\circ$  per minute, with the protective beryllium strip removed. The intensities have not been corrected for Geiger counter dead-time losses nor possible preferred orientation effects.

Morphological measurements on Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (*Dana's System of Mineralogy*, 1951) yielded axial ratios of  $a:b:c = 0.9698:1:0.5191$  and  $\beta = 92.93^\circ$  compared with our values of  $a:b:c = 0.4874:1:0.5194$  and  $\beta = 92.99^\circ$ . The precession photographs, including a cone axis photograph indicating the spacing between  $b^*c^*$  reciprocal lattice planes, showed no reflections which required a doubling of the *a* axis, and the discrepancy is felt to be due to an incorrect choice of the parametral plane in the morphological measurements. The proper parametral plane is not always apparent and factor-of-two errors in morphological axial ratios are not uncommon (Phillips, 1956).

A final verification of the crystal data presented above was obtained by single crystal measurements on a General Electric single-crystal goniostat. These provided parameters which are within 0.01 Å of the refined powder data values.

The authors are indebted to Mr Robert Bierig and Miss Barbara Healy for providing the crystals.

## References

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