

Fig. 4. Drawing of NTP showing the thermal ellipsoids as viewed along the *b* axis.

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The Crystal Structure of NaMnCl₃

BY C. J. J. VAN LOON AND G. C. VERSCHOOR

Gorlaeus Laboratories, Sections of Solid State Chemistry and of X-ray and Electron Diffraction, University of Leiden, P.O. Box 75, Leiden, The Netherlands

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Crystals of NaMnCl₃ are rhombohedral, $R\bar{3}$, with hexagonal cell dimensions $a = 6.591$ (3) and $c = 18.627$ (9) Å and $Z = 6$. NaMnCl₃ adopts the same structure as FeTiO₃ (ilmenite). A second isostructural halide is NaCdCl₃. Up to now no other halides isostructural with ilmenite have been reported.

Introduction

The crystal structure determination of NaMnCl₃ is part of an investigation of ABX₃ halides. B represents a first-row transition or an alkaline earth metal and X = Cl, Br or I. The choice of the monovalent metal A depends on the size of the anions. Since the authors are especially interested in ABX₃ compounds that do not have a perovskite-like structure, A = Li or Na when X = Cl. The purpose of this investigation is to advance our understanding of the structures and the structural relations of these compounds. The first author is engaged in a systematic derivation of ABX₃ structures with both A and B octahedrally coordinated,

the results of which will be published elsewhere. The phase diagram of the NaCl–MnCl₂ system was constructed by Ehrlich, Koknat & Seifert (1965). The crystal structure of Na₂MnCl₄ was determined by Goodyear, Ali & Steigmann (1971). This compound is isostructural with Sr₂PbO₄ (Trömel, 1965). Kestigian & Croft (1969) reported single crystals of NaMnCl₃ to have hexagonal symmetry with cell dimensions $a = 26.65$ (6) and $c = 6.19$ (8) Å.

Experimental

According to the phase diagram of NaCl–MnCl₂ the compound NaMnCl₃ melts congruently at 428°C.

NaCl was dried *in vacuo* at 400°C and MnCl₂ was obtained by dehydration of MnCl₂·4H₂O at 350–400°C in a stream of dry HCl gas. Single crystals were obtained from a molten, stoichiometric mixture of NaCl and MnCl₂ in an evacuated sealed high-melting ('Supremax') glass tube by gently lowering the temperature from 440 to 400°C. [Analysis: * Mn 30.25% (29.81%), Cl: 56.54% (57.71%)]. The material was unstable in the presence of water vapour and, prior to X-ray examination, selected crystals had to be quickly encapsulated in sealed glass tubes of diameter 0.3 mm.

Unit cell and space group

The crystal symmetry and approximate cell parameters were determined from zero- and upper-level Weissenberg photographs. Systematically absent reflexions were of the type $-h+k+l \neq 3n$, indicating a rhombohedral symmetry; the Laue group appeared to be $\bar{3}$ leaving two possible space groups: $R\bar{3}$ and $R3$. The consistency of the final results justified the choice of the space group $R\bar{3}$.

The precise unit-cell parameters were determined on a single-crystal diffractometer at 20°C, using Mo $K\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$). The parameters of the hexagonal cell were $a=6.591(3)$ and $c=18.627(9) \text{ \AA}$.

The cell dimensions agree with a structure model, in which the anions form a hexagonal close-packed (h.c.p.) lattice (Wessel & IJdo, 1957). Representing

* Element analysis was carried out under the supervision of W. J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry T.N.O., Utrecht, the Netherlands.

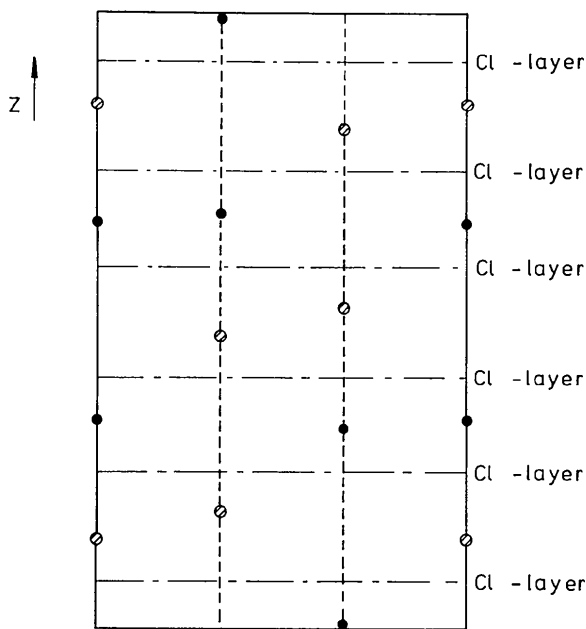


Fig. 1. [110] section in the hexagonal cell. In all figures the manganese ions are represented by small, black circles while the sodium ions are represented by hatched circles.

the radius of the chlorine ion by r , the respective a and c axes correspond with $2r/3$ and $4r/6$ (Ahrens, 1952; Shannon & Prewitt, 1969). Consequently the unit cell had to contain six layers of three anions each, resulting in six formula units per unit cell. The calculated density was 2.62 g cm^{-3} .

Collection and reduction of X-ray diffraction data

A single crystal of irregular shape and a maximum thickness of 0.2 mm was mounted along its a axis on an Enraf-Nonius three-circle single-crystal diffractometer. Intensities were recorded by the $\theta-2\theta$ scan method for all reflexions with θ between 3 and 35° and negative h . Monochromatic (graphite) Mo $K\alpha$ radiation was used for measuring the intensities. Background intensities were determined at $\theta \pm \frac{1}{2}\Delta$ with $\Delta=0.8+0.7 \tan \theta$. The mean counting time was 25 sec for each background and 50 sec for the scan. 2209 reflexions were measured. The standard deviations $\sigma(I)$ were calculated from counting statistics.

Table 1. Observed and calculated structure factors ($\times 10$)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	1137	1137	0	0	0	1137	1137	0	0	0	1137	1137
0	0	1	931	931	0	0	1	931	931	0	0	1	931	931
0	0	2	755	755	0	0	2	755	755	0	0	2	755	755
0	0	3	611	611	0	0	3	611	611	0	0	3	611	611
0	0	4	495	495	0	0	4	495	495	0	0	4	495	495
0	0	5	403	403	0	0	5	403	403	0	0	5	403	403
0	0	6	331	331	0	0	6	331	331	0	0	6	331	331
0	0	7	277	277	0	0	7	277	277	0	0	7	277	277
0	0	8	237	237	0	0	8	237	237	0	0	8	237	237
0	0	9	207	207	0	0	9	207	207	0	0	9	207	207
0	0	10	183	183	0	0	10	183	183	0	0	10	183	183
0	0	11	161	161	0	0	11	161	161	0	0	11	161	161
0	0	12	141	141	0	0	12	141	141	0	0	12	141	141
0	0	13	123	123	0	0	13	123	123	0	0	13	123	123
0	0	14	107	107	0	0	14	107	107	0	0	14	107	107
0	0	15	93	93	0	0	15	93	93	0	0	15	93	93
0	0	16	81	81	0	0	16	81	81	0	0	16	81	81
0	0	17	71	71	0	0	17	71	71	0	0	17	71	71
0	0	18	63	63	0	0	18	63	63	0	0	18	63	63
0	0	19	57	57	0	0	19	57	57	0	0	19	57	57
0	0	20	53	53	0	0	20	53	53	0	0	20	53	53
0	0	21	51	51	0	0	21	51	51	0	0	21	51	51
0	0	22	51	51	0	0	22	51	51	0	0	22	51	51
0	0	23	53	53	0	0	23	53	53	0	0	23	53	53
0	0	24	57	57	0	0	24	57	57	0	0	24	57	57
0	0	25	63	63	0	0	25	63	63	0	0	25	63	63
0	0	26	71	71	0	0	26	71	71	0	0	26	71	71
0	0	27	81	81	0	0	27	81	81	0	0	27	81	81
0	0	28	93	93	0	0	28	93	93	0	0	28	93	93
0	0	29	107	107	0	0	29	107	107	0	0	29	107	107
0	0	30	123	123	0	0	30	123	123	0	0	30	123	123
0	0	31	141	141	0	0	31	141	141	0	0	31	141	141
0	0	32	161	161	0	0	32	161	161	0	0	32	161	161
0	0	33	183	183	0	0	33	183	183	0	0	33	183	183
0	0	34	207	207	0	0	34	207	207	0	0	34	207	207
0	0	35	237	237	0	0	35	237	237	0	0	35	237	237
0	0	36	277	277	0	0	36	277	277	0	0	36	277	277
0	0	37	331	331	0	0	37	331	331	0	0	37	331	331
0	0	38	403	403	0	0	38	403	403	0	0	38	403	403
0	0	39	495	495	0	0	39	495	495	0	0	39	495	495
0	0	40	611	611	0	0	40	611	611	0	0	40	611	611
0	0	41	755	755	0	0	41	755	755	0	0	41	755	755
0	0	42	931	931	0	0	42	931	931	0	0	42	931	931
0	0	43	1137	1137	0	0	43	1137	1137	0	0	43	1137	1137
0	1	0	1000	1000	0	1	0	1000	1000	0	1	0	1000	1000
0	1	1	850	850	0	1	1	850	850	0	1	1	850	850
0	1	2	720	720	0	1	2	720	720	0	1	2	720	720
0	1	3	610	610	0	1	3	610	610	0	1	3	610	610
0	1	4	510	510	0	1	4	510	510	0	1	4	510	510
0	1	5	420	420	0	1	5	420	420	0	1	5	420	420
0	1	6	340	340	0	1	6	340	340	0	1	6	340	340
0	1	7	270	270	0	1	7	270	270	0	1	7	270	270
0	1	8	210	210	0	1	8	210	210	0	1	8	210	210
0	1	9	160	160	0	1	9	160	160	0	1	9	160	160
0	1	10	120	120	0	1	10	120	120	0	1	10	120	120
0	1	11	90	90	0	1	11	90	90	0	1	11	90	90
0	1	12	70	70	0	1	12	70	70	0	1	12	70	70
0	1	13	55	55	0	1	13	55	55	0	1	13	55	55
0	1	14	45	45	0	1	14	45	45	0	1	14	45	45
0	1	15	39	39	0	1	15	39	39	0	1	15	39	39
0	1	16	35	35	0	1	16	35	35	0	1	16	35	35
0	1	17	33	33	0	1	17	33	33	0	1	17	33	33
0	1	18	33	33	0	1	18	33	33	0	1	18	33	33
0	1	19	35	35	0	1	19	35	35	0	1	19	35	35
0	1	20	39	39	0	1	20	39	39	0	1	20	39	39
0	1	21	45	45	0	1	21	45	45	0	1	21	45	45
0	1	22	55	55	0	1	22	55	55	0	1	22	55	55
0	1	23	70	70	0	1	23	70	70	0	1	23	70	70
0	1	24	90	90	0	1	24	90	90	0	1	24	90	90
0	1	25	120	120	0	1	25	120	120	0	1	25	120	120
0	1	26	160	160	0	1	26	160	160	0	1	26	160	160
0	1	27	210	210	0	1	27	210	210	0	1	27	210	210
0	1	28	270	270	0	1	28	270	270	0	1	28	270	270
0	1	29	340	340	0	1	29	340	340	0	1	29	340	340
0	1	30	420	420	0	1	30	420	420	0	1	30	420	420
0	1	31	510	510	0	1	31	510	510	0	1	31	510	510
0	1	32	610	610	0	1	32	610	610	0	1	32	610	610
0	1	33	720	720	0	1	33	720	720	0	1	33	720	720
0	1	34	850	850	0	1	34	850	850	0	1	34	850	850
0	1	35	1000	1000	0	1	35	1000	1000	0	1	35	1000	1000
0	1	36	1137	1137	0	1	36	1137	1137	0	1	36	1137	1137
0	1	37	1300	1300	0	1	37	1300	1300	0	1	37	1300	1300
0	1	38	1480	1480	0	1	38	1480	1480	0	1	38	1480	1480
0	1	39	1680	1680	0	1	39	1680	1680	0	1	39	1680	1680
0	1	40	1900	1900	0	1	40	1900	1900	0	1	40	1900	1900
0	1	41	2150	2150	0	1	41	2150	2150	0	1	41	2150	2150
0	1	42	2450	2450	0	1	42	2450	2450	0	1	42	2450	2450
0	1	43	2800	2800	0	1	43	2800	2800	0	1	43	2800	2800
0	1	44	3200	3200	0	1	44	3200	3200	0	1	44	3200	3200
0	1	45	3650	3650	0	1	45	3650	3650	0	1	45	3650	3650
0	1	46	4150	4150	0	1	46	4150	4150	0	1	46	4150	4150
0	1	47	4700	4700	0	1	47	4700	4700	0	1	47	4700	4700
0	1	48	5300	5300	0	1	48	5300	5300	0	1	48	5300	5300
0	1	49	5950	5950	0	1	49	5950	5950	0	1	49	5950	5950
0	1	50	6650	6650	0	1	50	6650	6650	0	1	50	6650	6650
0	1	51	7400	7400	0	1	51	7400	7400	0	1	51	7400	7400
0	1	52	8200	8200	0	1	52	8200	8200	0	1	52	8200	8200
0	1	53	9050	9050	0	1	53	9050	9050	0	1	53	9050	

Reflexions with intensity less than twice the standard deviation were considered non-significant. Absorption corrections were applied using a computer program written by de Graaff (1973). The transmission factors ranged between 0.40 and 0.58 ($\mu = 45.4 \text{ cm}^{-1}$). Together with the absorption corrections new standard deviations $\sigma(I)$ were computed, taking into account the inaccuracy of the absorption correction and the attenuation factors.

The equivalent reflexions were then averaged, leaving 694 non-equivalent reflexions, 637 of which were significant. After reduction of the intensities to F values, a Wilson (1942) plot was calculated, yielding approximate values for the scale factor and the initial overall isotropic thermal parameter B .

Structure determination and refinement

All crystallographic calculations were carried out on the Leiden University IBM 360/65 computer, using a set of computer programs written or modified by Rutten-Keulemans and de Graaff. Scattering factors for the sodium, manganese and chlorine ions were taken from Cromer & Waber (1965) and used after correction for the real part of the anomalous dispersion $\Delta f'$.

The function minimized during the least-squares refinement process was $\sum w_F (|F_o| - |F_c|)^2$, using the weighting scheme $w_F = 1/\sigma_F^2$. Starting from the idea of a hexagonal close-packed (h.c.p.) lattice of anions we obtained three different structure models with space-group $R\bar{3}$, in which both sodium and manganese had an octahedral environment.

1a: Na	3(a)	0	0	0
Na	3(b)	0	0	$\frac{1}{2}$
Mn	6(c)	0	0	$\approx \frac{1}{3}$
Cl	18(f)	$\approx \frac{1}{3}$	≈ 0	$\approx \frac{1}{12}$
1b: Mn	3(a)	0	0	0
Mn	3(b)	0	0	$\frac{1}{2}$
Na	6(c)	0	0	$\approx \frac{1}{3}$
Cl	18(f)	$\approx \frac{1}{3}$	≈ 0	$\approx \frac{1}{12}$
2: Na	6(c)	0	0	$\approx \frac{1}{6}$
Mn	6(c)	0	0	$\approx \frac{1}{3}$
Cl	18(f)	$\approx \frac{1}{3}$	≈ 0	$\approx \frac{1}{12}$

The difference between models 1 and 2 is in the way cations are distributed over the octahedral interstices. Unoccupied octahedral interstices will be referred to as vacancies and indicated by \square .

In model 1a the layers of octahedral interstices are alternately of composition (1A+2B) and (1A+2 \square). In model 1b the compositions of these layers are (1B+2A) and (1B+2 \square). In structure model 2, layers of composition (2A+ \square) and (2B+ \square) are alternating. Models 1a and 1b can be derived from the Cr_2S_3 structure (Jellinek, 1957) while model 2 has been realized in FeTiO_3 (ilmenite; Barth & Posnjak, 1934) and

many other oxides (Wyckoff, 1964). A three-dimensional Patterson synthesis proved model 2 to be the correct model. A few cycles of full-matrix refinement of positional parameters and individual anisotropic thermal parameters for all ions led to convergence at $R_F = \sum ||F_o| - |F_c|| / \sum F_o(H) = 0.0382$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w(H) F_o^2(H)]^{1/2} = 0.0522$.

A difference Fourier synthesis revealed some insignificant negative peaks at the positions of the ions. At the origin, however, a positive peak indicated broadly three electrons per \AA^{-3} . This peak was attributed to Mn, since the sample analysis had indicated a small excess of manganese. This excess is probably due to traces of MnO in the starting material MnCl_2 . Least-squares refinement led to an occupation number of 0.014 for the manganese at the origin and to reliability values

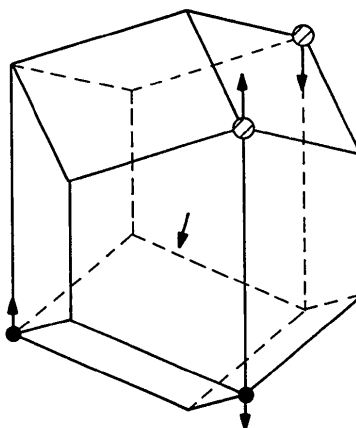


Fig. 2. Space-filling polyhedron of an anion in an ideal h.c.p. lattice. The arrows indicate the displacements. The cations are represented as in Fig. 1.

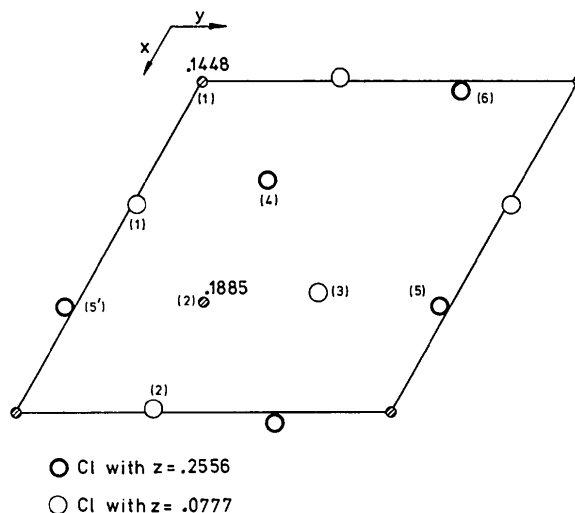


Fig. 3. Projection along the c axis of a sodium layer and its nearest chlorine layers. The cations are represented as in Fig. 1.

$R_F=0.0329$ and $R_{wF}=0.0465$. A final difference Fourier synthesis no longer contained the positive peak at the origin. The negative peaks, however, had remained almost unchanged. These peaks may be due to errors in the absorption correction. Since the shape of the single crystal was very irregular, the absorption correction had to be carried out for an imaginary crystal form that corresponded with the measured transmission curve for the head reflexions $\bar{2}10$, $\bar{4}20$ and $\bar{6}30$. Observed and calculated structure factors are given in Table 1. Positional parameters are listed in Table 2 and anisotropic thermal parameters in Table 3.

Table 2. Positional parameters ($\times 10^4$)

	Position	x/a	y/b	z/c
Mn	6(c)	0	0	3407 (4)
Na	6(c)	0	0	1449 (15)
Cl	18(f)	3713 (5)	105 (4)	777 (4)

Table 3. Anisotropic temperature factors ($\text{\AA}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Mn	171 (2)	171 (2)	179 (2)	171 (2)	0	0
Na	297 (4)	297 (4)	281 (6)	297 (4)	0	0
Cl	232 (2)	174 (2)	200 (2)	153 (3)	-28 (2)	124 (2)

Discussion of the structure

Interionic distances and bond angles, both with their estimated standard deviations (e.s.d.'s), are presented in Tables 4 and 5.

The structure can be regarded as a trigonally distorted h.c.p. lattice of chlorine ions. Layers of composition $(2\text{Na} + \square)$ and $(2\text{Mn} + \square)$ alternate between the anion layers. The sodium and manganese ions are

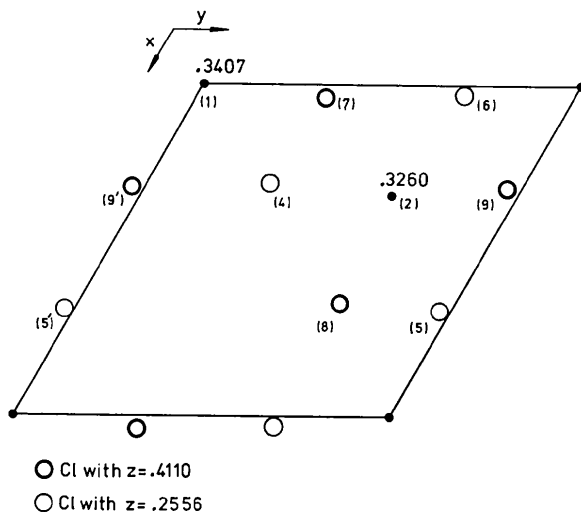


Fig. 4. Projection along the c axis of a manganese layer and its nearest chlorine layers. The cations are represented as in Fig. 1.

Table 4. Interionic distances (\AA) and their estimated standard deviations

The e.s.d.'s in the interionic distances and in the bond angles (Table 5) include the e.s.d.'s in the cell parameters.

Mn(1)—Cl(7)	2.520 (1)
Mn(1)—Cl(4)	2.585 (1)
Na(1)—Cl(1)	2.719 (1)
Na(1)—Cl(4)	2.903 (2)
Mn(1)—Na(1)	3.646 (2)
Mn(1)—Mn(2)	3.815 (2)
Na(1)—Na(2)	3.891 (2)
Cl(7)—Cl(9)	3.539 (2)
Cl(7)—Cl(9')	3.728 (2)
Cl(8)—Cl(9')	4.180 (2)
Cl(4)—Cl(7)*	3.393 (1)
Cl(4)—Cl(8)*	3.769 (1)
Cl(4)—Cl(3)*	3.952 (2)
Cl(4)—Cl(1)*	4.062 (2)

* These distances are between anions in different layers.

Table 5. Bond angles and their estimated standard deviations

Cl(4)—Mn(2)—Cl(7)	83.30 (5) $^\circ$
Cl(4)—Mn(2)—Cl(8)	95.15 (5)
Cl(4)—Mn(2)—Cl(9)	169.45 (2)
Cl(4)—Mn(2)—Cl(5)	95.40 (4)
Cl(7)—Mn(2)—Cl(8)	86.39 (6)
Cl(1)—Na(2)—Cl(4)	92.47 (4)
Cl(4)—Na(2)—Cl(3)	89.26 (3)
Cl(2)—Na(2)—Cl(4)	161.99 (5)
Cl(1)—Na(2)—Cl(2)	75.11 (6)
Cl(4)—Na(2)—Cl(5')	100.49 (4)
Mn(1)—Cl(4)—Mn(2)	96.70 (4)
Na(1)—Cl(4)—Na(2)	87.53 (3)
Mn(1)—Cl(4)—Na(1)	83.05 (4)
Mn(2)—Cl(4)—Na(1)	139.23 (3)
Mn(1)—Cl(4)—Na(2)	126.94 (3)
Mn(2)—Cl(4)—Na(2)	122.22 (2)

surrounded by six chlorine ions on the corners of a distorted octahedron. The chlorine ions are surrounded by two sodium and two manganese ions.

Fig. 1 shows the cations in a $[110]$ section. In Fig. 2 the space-filling polyhedron (S.F.P.) of anions in an ideal h.c.p. lattice is depicted (Gorter, 1970), the arrows indicating the displacements. A projection of a cation layer, sandwiched between two anion layers is given for sodium and manganese in Figs. 3 and 4. Up to now no halides isostructural with FeTiO_3 have been reported. In addition to NaMnCl_3 another compound isostructural with ilmenite was found, *viz.* NaCdCl_3 . The compound Na_2CdCl_4 adopts the same structure as Na_2MnCl_4 . The cell parameters obtained by Kestigian & Croft (1969) are erroneous: their powder pattern contains reflexions of both NaMnCl_3 and Na_2MnCl_4 .

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The Crystal Structure of *p*-Dimethylaminobenzaldehyde Hydrobromide

BY J. K. DATTA GUPTA AND N. N. SAHA

Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Calcutta-9, India

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p-Dimethylaminobenzaldehyde hydrobromide ($C_9H_{11}NO \cdot HBr$) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The cell dimensions are $a = 12.65 \pm 0.02$, $b = 10.20 \pm 0.02$, $c = 7.42 \pm 0.03$ Å, $\beta = 90^\circ 30' \pm 20'$. The structure was solved by heavy-atom methods using three-dimensional X-ray data. The positions of hydrogen atoms were located from a difference Fourier synthesis. The structure was refined by three-dimensional full-matrix least squares method leading to a final *R* value of 10.8%. The intra- and intermolecular features of the structure are discussed in detail. The amino nitrogen atom has been found to assume a tetrahedral configuration. The planar benzene ring is almost coplanar with the aldehyde group. The partial double-bond character of the exocyclic C–C bond has been attributed to a number of resonance forms. The only hydrogen bond (between the amino nitrogen and the bromine atom) is of the type $N^+ - H \cdots Br^-$ with a length of 3.127 ± 0.018 Å. The molecules are held together by van der Waals forces.

Introduction

The determination of the crystal and molecular structure of *p*-dimethylaminobenzaldehyde ($C_9H_{11}NO$) in the form of its hydrohalides has been undertaken by us in an attempt to correlate their structural features and biological functions. This compound plays an important role in differentiating between serum eruptions and true scarlet fever. From the chemical point of view also, *p*-dimethylaminobenzaldehyde is an interesting compound. The three isomers exist with aldehyde and dimethylamino groups in the *p*, *m* and *o* positions with respect to each other. If structural studies of all three isomers, *i.e.* *p*-, *m*-, and *o*-, could be made, they might furnish useful information. Thus, both from structural and functional points of view the study of this compound is indeed significant. The present communication deals with the complete solution of the crystal and molecular structure of *p*-dimethylaminobenzaldehyde hydrobromide. A preliminary account of the structure of this compound has already been published (Dattagupta & Saha, 1970) and was also pre-

sented at the Fourth All India Symposium in Biophysics (Saha & Dattagupta, 1969).

Experimental

The compound was prepared by treating *p*-dimethylaminobenzaldehyde with 30% hydrobromic acid and single crystals were grown by allowing the solution to evaporate at about 35–40°C. The transparent needle shaped crystals thus grown belong to the monoclinic system, *c* being the needle axis. As the crystal was unstable under normal atmospheric conditions, it was sealed in a thin glass capillary tube for taking X-ray photographs. The unit cell dimensions, as determined from rotation, oscillation and Weissenberg photographs are: $a = 12.65 \pm 0.02$, $b = 10.20 \pm 0.02$, $c = 7.42 \pm 0.03$ Å, $\beta = 90^\circ 30' \pm 20'$.

Systematic absences, $0k0$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, indicate that the space group is $P2_1/c$. The density of the crystals, as measured by the method of flotation, has been found to be 1.54 g cm^{-3} , while that calculated for four formula units ($C_9H_{11}NO \cdot HBr$) per unit cell is