Acta Cryst. (1971). B**27**, 1672

The Crystal Structure of Na_2MnCl_4

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(*Received* 7 *December* 1970)

The crystal structure of Na_2MnCl_4, determined from Weissenberg data, is orthorhombic with a= 6·93 (1), b=11·86 (2) and c=3·86 (2) Å. The space group is *Pbam* and Z=2. Mn ions are surrounded octahedrally by chlorine ions and the octahedra share opposite edges to form infinite chains parallel to c. The chains are held together by the sodium ions; each Na^+ is surrounded by six chlorine ions at the corners of a trigonal prism.

Introduction

The material examined in this work was prepared in this Department by Dr I. S. Robertson for infrared phosphorescent study. A mixture, comprising appropriate amounts of NaCl and $MnCl_2$ with some excess $MnCl_2$, was heated in a sealed silica tube to melting point and was then allowed to cool to room temperature for several days. Red-coloured crystals were formed, some of which were needle-shaped and of approximately square cross-section with dimensions suitable for Weissenberg examination; the subsequent structure analysis showed that the composition of the material was Na_2MnCl_4.

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 Lindemann glass tubes of diameter 0·3 mm. The experimental density was determined by measuring the loss of weight of a fairly large crystal when immersed in toluene.

X-ray data

Two crystals, each elongated parallel to **c**, were used to collect X-ray intensity data. Three layer lines were recorded on equi-inclination Weissenberg photographs taken about the c axis of one crystal with Cu $K\alpha$ radiation. Mo $K\alpha$ intensity data were also obtained from four layer lines using a second crystal, because the first crystal partially decomposed owing to a crack that developed in the capillary tube enclosing it.

Table 1. *Crystal data*

Formula, Na_2MnCl_4; F.W. 242·75
Orthorhombic; a=6·93 (1), b=11·86 (2), c=3·86 (2) Å
Z=2; D_o=2·53, D_x=2·54 g.cm^{-3}.

	Crystal 1	Crystal 2
Mean r (mm)	0·068	0·092
μ(cm^{-1})	331 (λ=1·5418 Å)	38·1 (λ=0·7107 Å)

Diffraction data indicated an orthorhombic cell whose parameters, determined from the Cu $K\alpha$ photographs, are given with other crystal data in Table 1. Assuming the chemical formula Na_2MnCl_4 and two molecules per cell, good agreement between measured and calculated densities was obtained.

A total of 182 Cu $K\alpha$ and 107 Mo $K\alpha$ reflexions was observed and intensities were measured from multiple-film exposures using a Joyce–Loebl flying-spot microdensitometer; intensities of weak reflexions were estimated visually against a calibrated scale. The intensity data were corrected for the Lorentz–polarization factor and for spot shape on upper layer lines (Phillips, 1954). Absorption corrections given by Bond (1959) were applied by assuming each crystal to be cylindrical in shape.

The systematically absent reflexions were of the type $0kl$ with k odd and $h0l$ with h odd, consistent with space groups *Pba*2 (No. 32) and *Pbam* (No. 55).

Structure determination

Packing considerations suggested that the eight chlorine atoms in the cell must be situated at equipoints 4(h) and 4(g) in space group *Pbam* or in two sets at 4(c) in *Pba*2; a sensible distribution of metal atoms was then possible with Mn at 2a in either space group, and Na at 4h in *Pbam* or at 4c in *Pba*2. The only difference between the two arrangements is that z takes the special value of 0 or $\frac{1}{2}$ in *Pbam*. It seemed most likely, at the outset, that for each atom, z would not be very different from 0 or $\frac{1}{2}$; so it was decided to try and solve the structure in the centro-symmetrical space group, *Pbam*.

With Mn at the origin, a Patterson projection along the c axis using the Cu $K\alpha$ data revealed directly the positions of the chlorine atoms. Although a small peak, possibly due to the Mn–Na vector, was discernible in the projection, it was decided to establish the position of the sodium atom by two-dimensional Fourier synthesis using the Cu $K\alpha$ data and phases calculated from positions of the Mn and Cl atoms. The electron-density projection along c clearly indicated the positions of all atoms. Atomic coordinates were then improved by a two-dimensional least-squares refinement, in which an initial individual temperature factor of 3·16 Å^2 was assumed for each atom. After a few cycles of refinement the reliability index, $\sum||F_o|-|F_c||/\sum|F_o|$, decreased from 0·35 to 0·24, indicating the correctness of the structure in projection.

Mo $K\alpha$ data were then used in a final three-dimensional refinement using individual isotropic temperature factors. A total of 74 structure factors obtained from intensity measurements with Cu $K\alpha$, but not with Mo $K\alpha$, were also used in the refinement. After several cycles the reliability index reduced to 0·104, at which stage the shift in each parameter was less than $\frac{1}{60}$ of the standard deviation. Finally, an attempt at further refinement in the non-centred space group, *Pba*2, was tried with initial z parameters of 0·5050 and 0·4950 for Na and Cl(2) respectively; the position of Mn was held at $z=0$. With the limited intensity data available, there were no systematic shifts in the z parameters to suggest that the structure might be other than centrosymmetrical. Atomic scattering factors for Mn^{2+}, Na^+ and Cl^- used in the calculations were taken from *International Tables for X-ray Crystallography* (1962) and the least-squares program was that of Daly, Wheatley & Stephens (1963) written for the Elliot 803B computer.

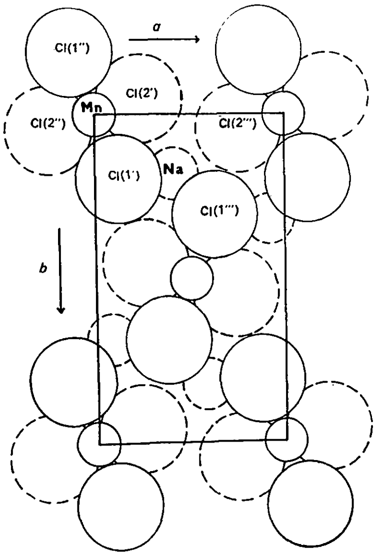

Fig. 1. Structure of Na_2MnCl projected along the c axis. Full circles represent Cl(1) and Mn atoms at $z=0$. Broken circles represent Cl(2) and Na atoms at $z=\frac{1}{2}$. In each case the smaller circle is the cation.

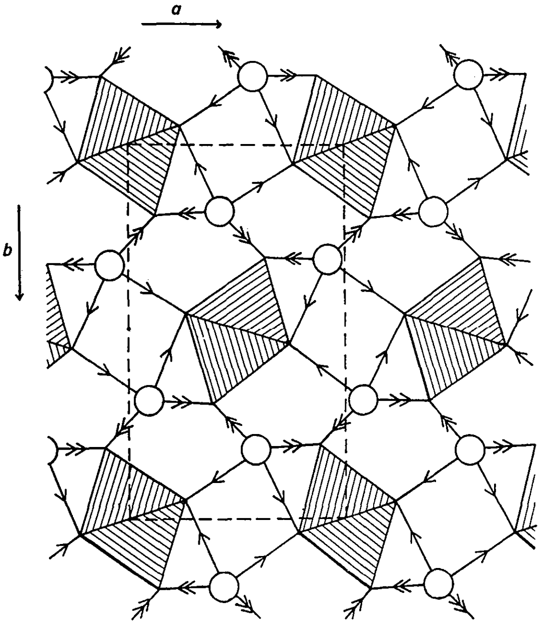

Fig. 2. Chains of Mn–Cl octahedra (viewed along the chain direction) linked together by Na ions (circles). Each double arrow represents two Na–Cl(1) bonds superimposed in the projection; a single arrow represents an Na–Cl(2) bond parallel to the plane of the diagram.

Final atomic parameters are given in Table 2. Calculated and observed structure factors are compared in Table 3. Data for 83 unobserved reflexions were not included in the refinement, and in each case $|F_c|$ was less than the minimum observable value.

Table 2. *Final atomic parameters*

Origin is at centre 2/*m*. Standard deviations are given in parentheses.

	x	y	z	B(Å^2)
Mn	0	0	0	2·28 (12)
Na	0·4186 (18)	0·1818 (11)	$\frac{1}{2}$	3·28 (25)
Cl(1)	0·1215 (9)	0·1952 (6)	0	1·88 (11)
Cl(2)	0·2399 (9)	−0·0449 (6)	$\frac{1}{2}$	2·19 (12)

Table 3. *Observed and calculated structure factors* (2 × *absolute*)

Asterisks indicate Cu $K\alpha$ data.

H	K	F_o	F_c
L=0			
0	2	50*	47
0	4	133	129
0	6	122	129
0	8	72	-75
0	10	52	46
0	12	26*	-22
1	1	102*	100
1	2	34*	-16
1	3	72	72
1	4	168	181
1	5	82	86
1	7	32	25
1	8	54	51
1	9	58	53
1	10	34*	32
1	11	32*	27
1	12	30*	-35
2	1	38	-46
2	2	28*	-35
2	3	38	42
2	4	32*	28
2	6	78	81
2	8	64	55
2	9	36*	34
2	10	76	74
2	11	28*	-30
2	12	64	54
3	1	26	32
3	2	100	-120
3	3	84	96
3	4	44	36
3	6	102	-111
3	7	70	68
3	9	56	37
4	0	30	31
4	1	22	25
4	2	148	163
4	3	20*	-18
4	4	52	60
4	8	48	54
4	9	6*	-13
4	10	32*	-43
5	1	46	54
5	2	36	33
5	3	50	59
5	6	66	55
5	7	46	42
6	0	52	-34
6	1	60	46
6	7	36*	37
6	8	50	52
6	9	18*	-24
6	10	26*	30
7	1	26*	23
7	3	24*	-16
7	4	62	-56
7	5	56	45
7	8	24*	-23
8	0	68	63
8	2	22*	15
8	4	36*	31
L=1			
0	2	70*	-50
0	4	64	56
0	6	56	58
0	8	58	55
0	10	118	100
0	12	26*	28
0	14	20*	37
1	1	124*	121
1	2	96*	-74
1	3	38	-40
1	4	44	-44
1	5	148	147
1	6	96	-91
1	9	34*	25
1	11	64	59
1	14	24*	34
2	0	132	135
2	1	130	-135
2	2	144	156
2		42	47
2	4	92	94
2	5	20*	22
2	6	28*	26
2	7	66	-74
2	9	52	56
2	11	28*	-29
3	1	56	57
3	2	52	38
3	3	92	100
3	4	56	60
3	6	32	32
3	7	52	56
3	8	44	51
4	0	58	-50
4	1	44	-32
4	2	34	35
4	3	18*	21
4	5	24*	26
4	6	24*	28
4	7	20*	-13
4	8	78	80
5	3	80	78
5	4	74	-77
5	5	22*	-19
5	7	60	52
5	8	24*	-30
5	9	26*	34
6	0	92	80
6	1	36*	33
6	2	54	50
6	3	36*	-30
6	4	36*	37
6	5	20*	-17
6	6	32*	28
6	9	28*	-32
7	1	42*	37
7	2	24*	28
7	3	26*	24
7	5	32*	30
7	6	42*	41
8	0	30*	27
8	2	28*	-26
L=2			
0	2	36*	30
0	4	96	82
0	6	86	87
0	8	60	-57
0	10	30	34
1	1	66*	61
1	3	72*	50
1	4	116	112
1	5	60	60
1	8	40	40
1	9	40	38
1	10	22*	25
1	11	20*	23
1	12	20*	-28
2	1	28*	-26
2	2	18*	-15
2	3	26	27
2	4	24*	20
2	6	62	56
2	8	50	43
2	9	30*	30
2	10	60	58
2	11	36	-25
2	12	42	43
3	2	76	-79
3	3	62	67
3	4	16*	23
3	6	86	-83
3	7	56	51
3	9	24*	28
4	0	18*	22
4	1	14*	15
4	2	122	119
4	4	44	44
4	8	42	42
4	10	26*	-36
5	1	38	38
5	2	36	28
5	3	46	48
5	6	50	46
5	7	32*	33
6	0	38*	-26
6	1	46*	38
6	7	32*	30
6	8	40*	40
7	1	16*	17
7	3	20*	-13
7	4	46	-46
7	5	46*	36
L=3			
0	4	26	27
0	10	66	67
1	2	40	-35
1	5	80	74
1	6	54	-56
2	0	64	67
2	1	66	-63
2	2	72	75
2	4	56	49
3	3	64	55

Description of the structure

A projection of the structure along the c axis is shown in Fig. 1. Distances between neighbouring atoms are listed in Table 4. Average values of the Mn–Cl and Na–Cl distances, 2·56 and 2·85 Å, respectively, suggest that the structure is mainly ionic in character.

Table 4. *Bond lengths*

Standard deviations are given in parentheses.
Atoms are identified as shown in Fig. 1.

		Multiplicity
Mn–Cl octahedron:		
Mn——Cl(2)	2·603 (6) Å	4
Mn——Cl(1)	2·463 (5)	2
Cl(2′)—Cl(2′)	3·860 (= *c*)	1
Cl(2″) -Cl(2″)		1
Cl(1′)—Cl(2″)	3·630 (8)	2
Cl(1″) -Cl(2′)		2
Cl(1′)—Cl(2′)	3·537 (8)	2
Cl(1″) -Cl(2″)		2
Cl(2′)—Cl(2″)	3·493 (8)	2
Na–Cl trigonal prism:		
Na——Cl(2′)	2·960 (12)	1
Na——Cl(2‴)	2·871 (12)	1
Na——Cl(1′)	2·825 (12)	2
Na——Cl(1‴)	2·799 (12)	2
Cl(1′)—Cl(1′)	3·860 (= *c*)	1
Cl(1‴)-Cl(1‴)		1
Cl(1‴)-Cl(2‴)	3·761 (8)	2
Cl(2′)—Cl(2‴)	3·759 (8)	1
Cl(1′)—Cl(1‴)	3·701 (7)	2
Cl(1′)—Cl(2′)	3·537 (8)	2

Each Mn^{2+} is surrounded by two $Cl^-(1)$ and four $Cl^-(2)$ situated at the corners of a somewhat distorted octahedron. The interesting feature of the structure is that these octahedra share opposite edges to form infinite chains of composition $(MnCl_4)_n^{2n-}$. All such chains are parallel to **c** and the Cl(1)–Mn–Cl(1) axis of each octahedron is parallel to (001). The chains are oriented in one of two ways as shown in Fig. 2, which views the structure along the chain direction. Those passing through the corners of the unit cells have their Cl(1)–Mn–Cl(1) axes turned anticlockwise at an angle of 20·0° to *b*. Those passing through the centres of the cells are inclined at the same angle to **b** but in the opposite direction.

The chains, which can be regarded as infinite one-dimensional anions, are held together by the sodium ions. Fig. 2. shows that each sodium ion is linked to two $Cl^-(1)$ and one $Cl^-(2)$ from one chain, to two $Cl^-(1)$ from another and to one $Cl^-(2)$ from a third, such that it is surrounded by six Cl^- in trigonal prismatic coordination. Thus each $Cl^-(1)$ is bonded to one Mn^{2+} and four Na^+ and each $Cl^-(2)$ is bonded to two Mn^{2+} and two Na^+, permitting Pauling's electrostatic valency rule to be obeyed.

Table 4 reveals that the shortest side, 3·49 Å, of a Mn–Cl octahedron is the shared edge, Cl(2′)–Cl(2″), between two neighbouring octahedra in a chain; this contraction is presumably due to electrostatic repulsion between adjacent Mn^{2+} ions. The next shortest distance, 3·54 Å, in an octahedron is an edge which is shared with a Na–Cl trigonal prism, and this is the shortest side of the prism. The distortion of an octahedron is mainly due to the shortening of the common octahedral edge, for all the Cl(1)–Mn–Cl(2) octahedral angles are within 1·5° of 90°, whilst the Cl(2)–Mn–Cl(2) angles depart from a right angle by 5·7°.

We thank Dr I. S. Robertson for making the material available to us for analysis and Monsanto Research S. A. for permitting us to use the computer programs of Daly, Stephens & Wheatley. One of us (S.A.D.A.) is indebted to the University of Damascus for the award of a research studentship. Finally, we thank the Scientific Research Council for a grant that enabled us to purchase a flying-spot microdensitometer.

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