

The Crystal Structure of $K_2MnCl_4 \cdot 2H_2O$

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The crystal structure of $K_2MnCl_4 \cdot 2H_2O$ has been determined by three-dimensional Fourier methods and the parameters refined by least-squares computations. $K_2MnCl_4 \cdot 2H_2O$ is tetragonal, space group $I4/mmm$ with $a = 7.415 \text{ \AA}$ and $c = 8.220 \text{ \AA}$ and with two formula units per unit cell. Each manganese atom is octahedrally coordinated to four chlorine atoms and to two water molecules forming discrete groups $[MnCl_4 \cdot 2H_2O]^{2-}$. The water molecules occupy *trans*-positions.

As part of a study of hydrated halides containing manganese and alkali metals¹⁻⁴ the crystal structure of $K_2MnCl_4 \cdot 2H_2O$ has been determined. $K_2MnCl_4 \cdot 2H_2O$ was first prepared by Süß.⁵ The crystal structure of the related hydrate $(NH_4)_2MnCl_4 \cdot 2H_2O$ was investigated by Greenberg and Walden.⁶ They reported, that $(NH_4)_2MnCl_4 \cdot 2H_2O$ was isostructural with $(NH_4)_2CuCl_4 \cdot 2H_2O$ (Hendricks and Dickenson⁷). It was assumed that the crystal structure of $K_2MnCl_4 \cdot 2H_2O$ would be similar to the structure of these compounds.

EXPERIMENTAL

$K_2MnCl_4 \cdot 2H_2O$ was prepared from an aqueous solution containing $MnCl_2 \cdot 4H_2O$ and KCl (molar ratio, $MnCl_2 \cdot KCl = 1.2:1$) and slow evaporation at $45^\circ C$. (Süß⁵ reported, that $K_2MnCl_4 \cdot 2H_2O$ must be prepared above $28.2^\circ C$). The crystals formed pale pink tetragonal bipyramids. The formation interval in the system $MnCl_2 - KCl - H_2O$ is quite narrow at $45^\circ C$, a bigger molar ratio (1.4:1) gives $KMnCl_3 \cdot 2H_2O$, a smaller (1.1:1) gives KCl.

Chemical analysis gave the following results: Mn 17.80; Cl 45.50; K 25.89; H_2O 11.69. Calc.: Mn 17.67; Cl 45.60; K 25.15; H_2O 11.58. Manganese was determined by complexometric titration with EDTA, chlorine by potentiometric titration using $AgNO_3$, potassium gravimetrically as K_2SO_4 and the water from the loss in weight after heating to $110^\circ C$. $K_2MnCl_4 \cdot 2H_2O$ gives off the water at $85^\circ C$. The density is 2.28 g/cm^3 as measured by flotation in a mixture of acetylene tetrabromide and carbon tetrachloride.

Unit cell dimensions were determined at $25^\circ C$ from Guinier powder diagrams using potassium chloride as reference ($a_{KCl} = 6.2905 \text{ \AA}$). $FeK\alpha$ -radiation ($FeK\alpha = 1.9360 \text{ \AA}$) was employed. Intensities were recorded by multiple film and multiple exposure technique on an integrating Nonius Weissenberg camera ($MoK\alpha$ -radiation) and were measured by means of a Joyce-Loebl double beam densitometer. An octahedrally shaped crystal with dimensions $0.150 \times 0.150 \times 0.150 \text{ mm}$ was oriented along the a -axis, and the levels $0kl - 7kl$ were recorded. The reflexions were scaled together setting $F(hkl)$ equal to $F(khl)$.

192 independent reflexions with $h \leq k$ were used for the structure determination. Corrections for Lorentz- and polarization factors were computed. No corrections for absorption were applied (absorption coefficient = 35 cm^{-1} for $\text{MoK}\alpha$ -radiation).

STRUCTURE DETERMINATION

Guinier powder photographs of $\text{K}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ show, that these compounds are probably isostructural. The unit cell contains two formula units. The condition limiting reflexions are $hkl: h+k+l = 2n$, thus indicating a body centered space group and not $P4_2/mnm$, as proposed for $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ by Greenberg and Walden.⁶ Since $F(\bar{h}\bar{k}\bar{l}) = F(h\bar{k}l) = F(hk\bar{l}) = F(hkl)$ and no piezo-electric effect could be observed the space group $I4/mmm$ is the most probable. The only difference between $P4_2/mnm$ and $I4/mmm$ is in this case, that the positions of the chlorine atoms are not identical; in $P4_2/mnm$ four Cl-atoms must be placed in the fourfold position $x,x,0$ and four Cl-atoms in the other fourfold position $x,-x,0$, whereas all eight Cl-atoms must be placed in the same eightfold position $x,x,0$ in $I4/mmm$.

Structure factors were calculated using coordinates of the atoms from $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, and a three dimensional Fourier synthesis was evaluated using signs obtained from this calculation. Although the Fourier maps indicated, that the potassium atom showed a marked anisotropic thermal motion, the refinement began with the program D45 (Danielsen⁸), based on the Bhuiya-Stanley⁹ method with isotropic temperature factors. The starting values for the coordinates were taken from the Fourier and the individual temperature factors from the work on $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$.⁴ The reliability index ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was reduced from 25 % to 9.6 % during six cycles of refinement. Atomic scattering factors were taken from Vol. III of *International Tables of Crystallography*¹⁰ and their parameters calculated according to the interpolation formula of Bassi.¹¹ A Fourier program written by Lauesen¹² was used.

The refinement was continued by means of the block-diagonal least-squares program G3 (Grønbaek¹³), with anisotropic temperature factors. After four cycles the R -index was 3.8 % excluding the strongest reflexion, 220, which probably was affected by extinction.

In a subsequent difference Fourier peaks of electron density could be seen between the oxygen and chlorine atoms. As the peaks appeared in reasonable distances from the oxygen atoms, they were probably due to hydrogen atoms.

In space group $I4/mmm$ the eight hydrogen atoms had to be placed in the position x,x,z , which is sixteen-fold. Therefore a statistical distribution of the hydrogen atoms had to be accepted. In the next cycles of refinement the hydrogen atoms were included in the structure factor calculations by isotropic, half atoms placed in the 16-fold position. The R -value stopped at 3.41 % after three cycles. Finally a refinement in the acentric space group $I\bar{4}2m$ was attempted. In this space group the four-fold rotation axis is replaced by a four-fold inversion axis, and the hydrogen position x,x,z is 8-fold, so an ordered structure can be obtained. Another difference is, that the Cl-position $x,x,0$ in $I4/mmm$ is changed to x,x,z in $I\bar{4}2m$. This refinement gave $R = 3.39 \%$ and

the alteration of the z -coordinate of the Cl-atom was only equal to one standard deviation of this parameter. According to Hamilton's significance test,¹⁴ the hypothesis that $I4/mmm$ is the correct space group cannot be rejected at the 50 % significance level.

CRYSTAL DATA

$K_2MnCl_4 \cdot 2H_2O$ is tetragonal. The cell contains two formula units and has the dimensions $a = 7.415 \pm 0.005$ Å, $c = 8.220 \pm 0.005$ Å, $a:c = 1:1.109$. The axial ratio can be compared with $a:c = 1:1.152$ reported by Süss⁵ (after transformation by the matrix $[110/1\bar{1}0/001]$). Probable space group: $I4/mmm-D_{4h}^{17}$. Density, calculated: 2.284 g/cm³. Density, measured: 2.28 g/cm³. Absorption coefficient for MoK α -radiation: 35 cm⁻¹. Residual factor $R = 3.4$ % including observed reflexions with $\sin \theta/\lambda < 0.72$. The coordinates, the temperature factors, and standard deviations are given in Table 1, the interatomic distances in Table 2, and observed and calculated structure factors in Table 3.

Table 1. Final atomic coordinates and temperature factors. Hydrogen temperature factor B is isotropic. Anisotropic temperature factors are in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)$ with $b_{11} = b_{22}$ and $b_{13} = b_{23} = 0$ for non hydrogen atoms. Anisotropic temperature factors and standard deviations (in brackets) have been multiplied by 10⁴.

Atom	x/a	y/b	z/c	$b_{11} = b_{22}$	b_{33}	b_{12}	B
H	0.0634 (71)	0.0634 (71)	0.3134 (99)	—	—	—	3 (2)
O	0.0000 (0)	0.0000 (0)	0.2647 (5)	145 (5)	66 (5)	0 (0)	—
Cl	0.2414 (2)	0.2414 (2)	0.0000 (0)	135 (2)	130 (2)	-73 (3)	—
Mn	0.0000 (0)	0.0000 (0)	0.0000 (0)	74 (2)	53 (1)	0 (0)	—
K	0.0000 (0)	0.5000 (0)	0.2500 (0)	282 (5)	96 (2)	0 (0)	—

THERMAL MOTION

The large drop in the R -value in the refinement process going from isotropic to anisotropic temperature factors (9.6 % and 3.8 %) shows, that a considerable anisotropic thermal motion could be expected. Table 4 gives the magnitudes of the principal axes of the vibration ellipsoids as the root mean square displacements, and the angles in degrees between the principal axes and the unit cell edges. The calculations were made according to the method of Rollett and Davies.¹⁵ From the table it can be seen, that the motion of the manganese atom is almost isotropic. For the chlorine and oxygen atoms the principal axis, along which the r.m.s. displacement is least, is parallel to the corresponding Mn—Cl or Mn—O vector. The r.m.s. displacement along this axis is in each case very close in magnitude to the isotropic displacements of the manganese atom. The larger displacements of the Cl- and O-atoms are perpendicular to the Mn—Cl and Mn—O vectors. Probably the motion of chlorine and oxygen is a librational motion about the manganese atom in combination with a translational motion of the manganese atom.

Table 2. Interatomic distances under 4.0 Å and, in brackets, standard deviations $\times 10^3$ Å. Hydrogen atom distances are not included. Distances corrected for thermal motion are indicated with c, the hydrogen bond is indicated with h.

Within octahedron				Outside octahedron				
Mn	—	Cl	2.531 (1)	2.542 c	K	—	Cl	3.332 (1)
Mn	—	O	2.175 (4)	2.184 c	K	—	O	3.709 (0)
Cl	—	Cl	3.579 (2)		Cl	—	Cl	3.836 (2)
Cl	—	O	3.337 (3)		Cl	—	O	3.332 (3) h
					O	—	O	3.870 (6)

Table 3. Observed and calculated structure factors. F_{obs} and F_{calc} have been multiplied by 10.

h	k	l	F _{obs}	F _{calc}	0	8	0	394	423	1	7	4	108	107	2	7	1	252	251	4	4	4	653	649
0	0	2	682	635	0	8	2	236	244	1	7	6	453	452	2	7	2	244	237	4	4	6	259	230
0	0	4	1563	1614	0	8	4	323	340	1	7	8	84	86	2	7	5	184	172	4	4	8	342	327
0	0	6	306	298	0	8	6	154	158	1	8	1	141	137	2	7	7	150	153	4	4	10	104	100
0	0	8	605	653	0	9	1	174	179	1	8	3	133	134	2	8	2	148	-145	4	5	1	293	277
0	0	10	113	118	0	9	3	101	104	1	5	10	105	97	2	8	6	74	-75	4	5	3	240	266
0	1	1	514	469	0	9	5	111	128	1	8	7	85	97	2	10	0	202	206	4	5	5	188	185
0	1	3	508	499	0	10	2	72	-58	1	9	0	79	86	2	10	2	136	141	4	5	7	175	169
0	1	5	236	229	1	1	2	661	678	1	9	2	95	94	3	3	2	361	378	4	5	9	78	90
0	1	7	252	255	1	1	4	74	69	1	9	4	70	73	3	5	4	87	94	4	6	2	236	-222
0	1	9	102	103	1	1	6	342	393	1	9	6	72	73	3	3	6	252	245	4	6	6	158	-122
0	1	11	120	119	1	1	10	184	183	1	10	1	72	66	3	3	10	133	127	4	8	0	318	315
0	2	0	158	158	1	2	1	320	304	2	2	2	520	505	3	4	1	148	145	4	8	2	194	196
0	2	2	1263	-1253	1	2	3	344	351	2	2	4	1157	1218	3	4	3	181	182	4	8	4	260	254
0	2	4	179	182	1	2	5	167	165	2	2	6	295	284	3	4	5	91	99	4	8	6	125	130
0	2	6	476	-479	1	2	7	198	202	2	2	8	524	531	3	4	7	121	116	4	9	1	152	149
0	2	8	107	103	1	2	9	86	78	2	2	10	116	116	3	5	0	154	164	4	9	3	142	141
0	2	10	157	-151	1	2	11	106	103	2	3	1	420	413	3	5	2	274	281	5	5	2	158	152
0	3	1	190	193	1	3	0	160	152	2	3	3	401	403	3	5	4	123	128	5	5	4	80	78
0	3	3	261	243	1	3	2	507	520	2	3	5	231	238	3	5	6	195	190	5	5	6	119	112
0	3	5	106	112	1	3	4	102	105	2	3	7	237	232	3	5	8	74	70	5	7	0	117	125
0	3	7	182	158	1	3	6	317	319	2	3	9	99	107	3	6	1	254	227	5	7	2	136	137
0	3	9	81	37	1	3	10	159	155	2	3	11	116	112	3	6	3	220	219	5	7	4	96	104
0	3	11	95	89	1	4	1	326	310	2	4	0	89	85	3	6	5	160	155	5	7	6	103	100
0	4	0	1355	1375	1	4	3	305	310	2	4	2	577	-587	3	6	7	139	144	5	8	1	148	144
0	4	2	464	469	1	4	5	191	185	2	4	4	78	77	3	6	9	84	78	5	8	3	140	138
0	4	4	941	962	1	4	7	184	190	2	4	6	305	-296	3	7	0	98	84	5	8	5	107	104
0	4	6	271	267	1	4	9	87	86	2	4	8	70	60	3	7	2	136	133	6	0	6	365	366
0	4	8	419	449	1	5	0	156	152	2	4	10	102	-90	3	7	4	75	79	6	6	2	219	219
0	4	10	113	111	1	5	2	307	309	2	5	1	86	93	3	7	6	100	99	6	6	4	297	294
0	5	1	353	366	1	5	4	100	104	2	5	3	115	111	3	8	1	78	82	6	6	6	148	144
0	5	3	340	346	1	5	6	291	286	2	5	5	64	57	3	8	3	72	68	6	7	1	176	166
0	5	5	219	230	1	5	10	105	110	2	5	7	98	90	3	9	0	110	101	6	7	3	169	159
0	5	7	211	211	1	6	1	167	165	2	6	0	659	700	3	9	2	103	101	6	7	5	122	119
0	5	9	92	106	1	6	3	160	154	2	6	2	343	354	3	9	4	89	86	6	8	2	70	-58
0	6	2	331	-343	1	6	5	115	106	2	6	4	519	545	3	10	1	102	97	7	7	0	64	59
0	6	4	186	-190	1	6	7	104	117	2	6	6	209	210	4	4	0	817	853	7	7	2	61	58
0	7	2	65	52	1	7	0	127	130	2	6	8	275	281	4	4	2	370	368	7	7	4	53	54
0	7	7	66	56	1	7	2	186	188															

Table 4. Magnitudes and orientations of the principal axes of the vibration ellipsoids. The magnitudes are given as the root mean square displacements. The angles (in degrees) refer to the axes of the unit cell.

Atom	R.m.s. displacement (Å)	Angle to axis		
		a	b	c
O	0.202	0	90	90
	0.202	90	0	90
	0.151	90	90	0
Cl	0.218	135	45	0
	0.211	90	90	0
	0.166	45	-45	0
Mn	0.143	0	90	90
	0.143	90	0	90
	0.135	90	90	0
K	0.279	0	90	90
	0.279	90	0	90
	0.182	90	90	0

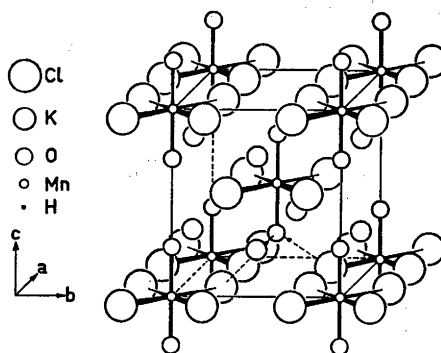


Fig. 1. Atomic arrangement of $K_2MnCl_4 \cdot 2H_2O$. Only one pair of hydrogen atoms is shown.

According to this assumption the Mn—Cl and Mn—O bond lengths can be corrected for thermal motion by means of the "riding motion" method (Busing and Levy¹⁶). The correction to be added to the Mn—Cl bond is 0.011 Å, and the correction to be added to the Mn—O bond is 0.009 Å.

The difference in the r.m.s. displacements of the potassium atom seems reasonable in view of the packing around this atom. The potassium atom is surrounded by eight chlorine atoms in a CsCl arrangement. The K—K distances in the direction of the *c*-axis are 4.11 Å, whereas the K—K distances perpendicular to this axis are 5.24 Å.

DISCUSSION

The manganese atom is surrounded by four chlorine atoms and two water molecules forming discrete octahedra $[MnCl_4 \cdot 2H_2O]^{2-}$. The water molecules occupy *trans*-positions (Fig. 1). The distances from manganese to chlorine and oxygen are nearly the same as the corresponding distances in other three-dimensionally refined structures containing Mn-octahedra. No significant difference can be detected between these distances in structures with the water molecules in *trans*-positions (β -RbMnCl₃·2H₂O,³ KMnCl₃·2H₂O,⁴ K₂MnCl₄·2H₂O and MnCl₂·2H₂O¹⁷), with the water molecules in *cis*-positions (α -RbMnCl₃·2H₂O³) and with the chlorine atoms in *cis*-positions (MnCl₂·4H₂O¹⁸).

Each oxygen atom has four chlorine atoms as nearest neighbours outside of the coordination polyhedron of the manganese atom. The distances to these chlorine atoms are identical, 3.33 Å. The hydrogen atoms are placed near to these Cl—O bonds at a distance of 0.8 Å from the oxygen atom. The two hydrogen atoms belonging to the same oxygen must be placed in *x,x,z* and $-x,-x,z$ or *x,-x,z* and $-x,x,z$, as the corresponding Cl—O—Cl angle is 109.4°. A statistical distribution between the two possibilities for the hydrogen positions is the most probable. In the corresponding Cu-compound, K₂CuCl₄·2H₂O (Hendricks and Dickenson,⁷ Crobak¹⁹), with a structure very similar to that of K₂MnCl₄·2H₂O, two of the oxygen-chlorine distances are shorter than the two others. The reason for this is, that two sorts of Cu—Cl bonds with unequal lengths exist in K₂CuCl₄·2H₂O, and this compound there-

fore belongs to the space group $P4_2/mnm$. Due to the different Cl—O distances the hydrogen atoms in $K_2CuCl_4 \cdot 2H_2O$ probably have ordered positions.

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