The Crystal Structure of KMnCl₃,2H₂O

STIG JORGO JENSEN

Department of Technology, The Royal Dental College, Aarhus C, Denmark

The crystal structure of $KMnCl_3,2H_2O$ has been determined by three-dimensional Patterson and Fourier methods and the parameters refined by least-squares computations. $KMnCl_3,2H_2O$ is triclinic, space group $P\bar{1}$ with $a = 6.49$ Å, $b = 6.91$ Å, $c = 9.91$ Å, $\alpha = 96.8°$, $\beta = 114.1°$, $\gamma = 112.6°$. There are two formula units per unit cell. $KMnCl_3,2H_2O$ is isostructural with $\beta\text{-}RbMnCl_3,2H_2O$. The manganese atom is octahedrally coordinated to four chlorine atoms and to two water molecules. The water molecules occupy trans-positions. $KMnCl_3, 2H_2O$ contains discrete groups $[Mn_2Cl_6,4H_2O]^{2-}$.

The system $KCl\text{-}MnCl_2\text{-}H_2O$ was investigated by Süss.[1] He prepared the following double salts: $KMnCl_3,2H_2O$, $K_2MnCl_4,2H_2O$, and K_4MnCl_6. Axial ratios and angles in $KMnCl_3,2H_2O$ were reported by Mügge.[2] A crystal structure analysis of K_4MnCl_6 was carried out by Bellanca[3] and corrected by Bergerhoff and Schmitz-Dumont.[4] This paper presents a structure determination of $KMnCl_3,2H_2O$. A structure analysis of $K_2MnCl_4,2H_2O$ will be published subsequently. The present investigation has been undertaken as part of a study of the structures of hydrated halides containing manganese and alkali metals.[5-7] A preliminary account of the work on $KMnCl_3,2H_2O$ has been published.[8]

EXPERIMENTAL

$KMnCl_3,2H_2O$ was prepared from an aqueous solution containing KCl and $MnCl_2$, $4H_2O$ in equimolar ratio and slow evaporation at 20°C. The crystals formed pink prisms frequently twinned. Chemical analysis gave the following results: Mn 23.55; Cl 44.89; H_2O 15.20; K 16.36. Calc.: Mn 23.24; Cl 44.99; H_2O 15.24; K 16.53. Mn was determined by complexometric titration with EDTA, Cl by potentiometric titration using $AgNO_3$, and the water gravimetrically by heating to 110°C. K was calculated as the balance. $KMnCl_3,2H_2O$ gives off the water at 76°C. The density was 2.20 g/cm³ (20°C) as measured by flotation in a mixture of acetylene tetrabromide and carbon tetrachloride.

Unit cell dimensions were determined at room temperature from Guinier powder diagrams using potassium chloride as reference ($a_{KCl} = 6.2905$ Å). $FeK\alpha$-radiation ($FeK\alpha = 1.9360$ Å) was employed. The cell was chosen to bring out the similarity in structure between $KMnCl_3,2H_2O$ and $\beta\text{-}RbMnCl_3,2H_2O$.[7] In Table 1 the cell constants first listed are in accordance with this choice. The dimensions of the Dirichlet reduced cell (Balashov and Ursell[9]) are listed next. Table 2 gives a comparison between the

goniometric data of Mügge [2] and this X-ray work. The goniometric data have been transformed to the X-ray cell by the matrix [100/010/212].

Intensities were recorded by multiple film and multiple exposure technique on an integrating Nonius Weissenberg camera using $MoK\alpha$-radiation and were measured by a Joyce-Loebl double-beam densitometer. 773 independent reflections with $\sin \theta/\lambda < 0.72$ were recorded. Two levels around [001] and five levels around [110] were recorded and scaled together. An irregularly shaped single crystal with maximum dimension 0.200 mm was used. The intensities were corrected for Lorentz- and polarization factors but not for absorption (absorption coefficient: 46 cm^{-1} for $MoK\alpha$-radiation). The crystals showed no piezo-electric effect.

STRUCTURE DETERMINATION

Although the cell dimensions of $KMnCl_3,2H_2O$ differ from those of β-$RbMnCl_3,2H_2O$ a three dimensional Patterson function revealed that $KMnCl_3,2H_2O$ is probably isostructural with β-$RbMnCl_3,2H_2O$. Therefore a three dimensional Fourier synthesis was calculated in the space group $P\bar{1}$ using signs based on the positions of the potassium and manganese atoms from the Patterson synthesis. In the Fourier maps all atoms except hydrogens appeared clearly. A program written by Lauesen [10] was used for the Fourier computations. The atomic scattering factors were taken from Vol. III of *International Tables of Crystallography* [11] and their parameters calculated according to the Bassi [12] interpolation formula.

The refinement was carried out with ALGOL-programs developed at the University of Aarhus. First the program D 45, written by Danielsen,[13] based on the Bhuiya-Stanley [14] method, was used. This program, working with

Table 1. Crystal data.

Crystal system	: triclinic		
Space group	: $P\bar{1} - C_i^1$		
Formula units per unit cell	: 2		
Unit cell	:	This work	Dirichlet cell
		$a = \ \ \ 6.49 \pm 0.01$ Å	$a = \ \ 6.49$ Å
		$b = \ \ \ 6.91 \pm 0.01$ Å	$b = \ \ 6.91$ Å
		$c = \ \ \ 9.91 \pm 0.01$ Å	$c = \ \ 9.21$ Å
		$\alpha = \ \ 96.8 \ \ \pm 0.1°$	$\alpha = \ \ 69.4°$
		$\beta = 114.1 \ \ \pm 0.1°$	$\beta = \ \ 88.7°$
		$\gamma = 112.6 \ \ \pm 0.1°$	$\gamma = \ \ 67.4°$

Density, calculated (20°C)   : 2.22 g/cm^3
Density, measured (20°C)   : 2.20 g/cm^3
Absorption coefficient ($MoK\alpha$)   : 46 cm^{-1}
Residual factor, R : 6.5 %
including all observed reflections with $\sin \theta/\lambda < 0.72$.

Table 2. Comparison between axial ratios and angles from the paper of Mügge [2] and from this work. The goniometric data have been transformed to the X-ray cell.

	a		b		c	α	β	γ
Mügge	0.6549	:	0.6956	:	1	96.2°	114.5°	112.7°
This work	0.6544	:	0.6968	:	1	96.8°	114.1°	112.6°

Table 3. Final atomic coordinates and temperature factors. The temperature factor, B, is from the last cycle in which the atoms were isotropic. The anisotropic temperature factors are in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)$. Anisotropic temperature factors and standard deviations (in brackets) have been multiplied by 10^4.

Atom	x/a	y/b	z/c	B Å²
O_I	0.7739 (19)	0.7853 (16)	0.5111 (10)	2.5
O_{II}	0.6989 (17)	0.4026 (15)	0.1663 (9)	2.3
Cl_I	0.2504 (7)	0.7112 (5)	0.4984 (3)	1.9
Cl_{II}	0.6501 (7)	0.8929 (5)	0.1877 (3)	2.2
Cl_{III}	0.1725 (7)	0.3353 (6)	0.1686 (4)	2.5
Mn	0.9517 (4)	0.2972 (3)	0.3254 (2)	1.3
K	0.1394 (7)	0.8468 (6)	0.1963 (4)	2.8

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O_I	207 (46)	163 (29)	100 (13)	181 (69)	144 (40)	160 (33)
O_{II}	100 (39)	136 (27)	79 (11)	82 (62)	84 (33)	38 (29)
Cl_I	166 (14)	135 (9)	65 (3)	122 (21)	150 (11)	50 (9)
Cl_{II}	208 (16)	117 (9)	73 (3)	112 (23)	138 (12)	31 (9)
Cl_{III}	214 (17)	219 (11)	88 (4)	203 (27)	216 (13)	111 (11)
Mn	110 (8)	90 (5)	45 (2)	89 (12)	92 (6)	39 (5)
K	301 (16)	293 (12)	95 (4)	413 (27)	220 (13)	187 (11)

Table 4. Interatomic distances and, in brackets, standard deviations $\times$ 10³ Å. Hydrogen bonds are indicated with h.

Within octahedra

Mn —	Cl_I	2.594 (3)	Cl_{II} —	Cl_{III}	3.681 (5)
Mn —	Cl_I	2.570 (5)	Cl_I —	O_I	3.368 (15)
Mn —	Cl_{II}	2.490 (3)	Cl_I —	O_I	3.360 (12)
Mn —	Cl_{III}	2.482 (5)	Cl_I —	O_{II}	3.320 (7)
Mn —	O_I	2.182 (12)	Cl_I —	O_{II}	3.419 (11)
Mn —	O_{II}	2.187 (11)	Cl_{II} —	O_I	3.277 (8)
Cl_I —	Cl_I	3.447 (5)	Cl_{II} —	O_{II}	3.451 (12)
Cl_I —	Cl_{II}	3.542 (5)	Cl_{III} —	O_I	3.293 (11)
Cl_I —	Cl_{III}	3.647 (6)	Cl_{III} —	O_{II}	3.270 (14)

Between neighbouring octahedra

Mn —	Mn	3.845 (3)	Cl_{III} —	O_I	3.708 (7)
Cl_{II} —	Cl_{III}	3.826 (5)	Cl_{III} —	O_{II}	3.274 (13) h
Cl_I —	O_I	3.179 (14) h	Cl_{III} —	O_{II}	4.186 (11)
Cl_I —	O_I	3.551 (13)	O_I —	O_I	3.381 (15)
Cl_{II} —	O_I	3.223 (11) h	O_I —	O_I	4.074 (14)
Cl_{II} —	O_{II}	3.510 (13)	O_I —	O_{II}	3.795 (16)
Cl_{II} —	O_{II}	3.140 (8) h			

From the potassium-atom

K —	Cl_I	3.128 (5)	K —	Cl_{III}	3.349 (6)
K —	Cl_I	3.587 (4)	K —	Cl_{III}	3.121 (4)
K —	Cl_{II}	3.241 (7)	K —	O_I	3.316 (12)
K —	Cl_{II}	3.277 (7)	K —	O_{II}	3.164 (10)
K —	Cl_{II}	4.855 (6)	K —	[O_{II}	4.294 (11)
K —	Cl_{III}	3.606 (7)	K —	O_{II}	4.469 (13)

Table 5. Observed and calculated structure factors. F_{obs} and F_{calc} have been multiplied by 10.

h	k	l	Fobs	Fcalc
0	0	2	481	-495
0	0	3	813	-767
0	0	6	713	747
0	0	7	217	-241
0	0	8	233	-254
0	0	9	108	-86
0	0	10	136	149
0	0	12	114	145

(Table 5 continues as a large multi-column listing of h, k, l, Fobs, Fcalc structure-factor data.)

Table 5. Continued.

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h   k   l   Fobs Fcalc   h  k   l  Fobs Fcalc   h  k   l  Fobs Fcalc   h  k   l  Fobs Fcalc   h  k   l  Fobs Fcalc   h  k   l  Fobs Fcalc
4  -2  -6  100  -93     5  -8  -2  112  -98    5  -3  -4  213 -173   6  -5  -8  175  183   7  -8  -4  114  124   
4  -2  -5  290  263     5  -8  -1  288  278    5  -3  -1  222 -218   6  -5  -7  169  172   7  -8   1  163 -180
4  -2  -4  215  206     5  -8   3   86  -90    5  -3   0  202  206   6  -5  -5  438 -447   7  -7  -5  125  141
4  -2  -2  851 -873     5  -8   5  272  243    5  -3   2  144 -137   6  -5  -4  174  163   7  -7  -4  199 -212
4  -2  -1  326  335     5  -7  -7  155 -154    5  -3   4   92   89   6  -5  -3  114  107   7  -7   3  140 -132
4  -2   0  226  230     5  -7  -5  183  196    5  -3   5  160 -154   6  -5  -2  132  130   7  -6  -9  123  134
4  -2   1  268  257     5  -7  -1  169 -146    5  -2 -13  100  101   6  -5   1  272 -293   7  -6  -8   91  -93
4  -2   2   90  -56     5  -7  -5  240  238    5  -2 -11  201 -218   6  -5   2  181  200   7  -6  -4  256 -250
4  -2   3  116 -102     5  -6  -7  162 -201    5  -2 -10  109  121   6  -4 -11  164  154   7  -6  -3  124  114
4  -2   4  435 -435     5  -6  -6  218  235    5  -2  -9  101  -66   6  -4 -10  120  -93   7  -6   2  209 -221
4  -2   5  265  257     5  -6  -5  102  -81    5  -2  -8   80  -54   6  -4  -9  106  -80   7  -5 -10  171  157
4  -2   6  175  170     5  -6  -4  126  134    5  -2  -7  160  147   6  -4  -8  118  109   7  -5  -8  138 -113
4  -1 -12  249 -259     5  -6  -2  107 -112    5  -2  -6  183  159   6  -4  -7  130  116   7  -5  -5  120  -97
4  -1  -9  187  144     5  -6  -1  272 -305    5  -2  -4  325 -325   6  -4  -6  302 -270   7  -5  -4  188  191
4  -1  -8  395  392     5  -6   0  298  316    5  -2  -2  331  338   6  -4  -5  107  106   7  -5  -2  176 -183
4  -1  -6  648 -658     5  -6   4   87  -94    5  -2  -2  123 -129   6  -4  -2  159  157   7  -4 -10  132  121
4  -1  -4  258  235     5  -6   5  154 -167    5  -2  -1  172  153   6  -4   0  382 -398   7  -4  -9  234 -225
4  -1  -3  143  144     5  -6   6  209  219    5  -2   0  176  177   6  -4   2   66  103   7  -4  -8  121  113
4  -1  -2  185  195     5  -5  -7  186  199    5  -2   1  278 -270   6  -3 -12  193  208   7  -4  -5   89   65
4  -1  -1   77  -65     5  -5  -6  117 -136    5  -1 -12  235 -250   6  -3 -11  193  176   7  -4  -4  185  192
4  -1   0  420 -494     5  -5  -5  170 -189    5  -1  -8  144  127   6  -3 -10  305 -305   7  -4  -3  237 -240
4  -1   1  206  194     5  -5  -4  125  142    5  -1  -7  141  124   6  -3  -9  100  -81   7  -4   2  150  132
4  -1   2  197  191     5  -5  -1  161  164    5  -1  -6  423 -444   6  -3  -8  128 -120   7  -4   3  151 -154
4  -1   3  110  -90     5  -5   0   88 -110    5  -1  -5  152  131   6  -3  -7  167  136   7  -3 -10  236 -223
4  -1   5  113   74     5  -5   1  162 -174    5  -1  -4   97   95   6  -3  -5  356  327   7  -3  -5  103   91
4  -1   6  113 -113     5  -5   2  160  172    5  -1  -1  172  174   6  -3  -4  160  145   7  -3  -4  233 -241
4   0 -13  173 -163     5  -5   4  116 -119    5  -1   0  288 -319   6  -3  -3  560 -539   7  -3  -2  114   98
4   0 -12  141  145     5  -4 -11  132  142    5  -1   1  147  122   6  -3  -2   92   90   7  -3   2  119 -111
4   0 -11  161 -160     5  -4 -10  102  -99    5  -1   6  126 -135   6  -3  -1  131  130   8  -7  -5  139  117
4   0  -9  148  145     5  -4  -8  105  101    6  -9   0  191  159   6  -3   0  115   99   8  -7  -3  246 -249
4   0  -8  331  319     5  -4  -6  342 -349    6  -8  -4  124  144   6  -3   2  305 -304   8  -6  -7  118 -128
4   0  -7  539 -540     5  -4  -5  234  229    6  -8  -3   86 -100   6  -3   3  116   92   8  -6  -4  129 -113
4   0  -5  157 -153     5  -4  -4  116  -85    6  -8  -1   97   97   6  -2 -11  194 -176   8  -6   0  119   77
4   0  -4  213  241     5  -4  -3  100   75    6  -7  -6  172 -204   6  -2 -10  169  176   8  -5  -9  234  211
4   0  -3  205  250     5  -4  -2  161  146    6  -7  -5  193  215   6  -2  -9  109  -97   8  -5  -8  232 -222
4   0  -2  227  288     5  -4   0  387 -415    6  -7  -1   59 -107   6  -2  -8  322  315   8  -5  -6  122 -112
4   0  -1  656 -788     5  -4   1  176  178    6  -7   0  130 -143   6  -2  -5  343 -362   8  -5  -4  178  167
4   0   1  136  131     5  -4   6  254 -196    6  -7   1  215  244   6  -2  -3   96  -90   8  -5  -2  177  168
4   0   2  225  237     5  -4   7   93   99    6  -6  -3  136  154   6  -2  -2  135  122   8  -5  -2  261 -282
4   0   5  315 -350     5  -3 -12  158  157    6  -6  -1  213 -232   6  -2   0  240  238   8  -4  -9  142 -136
5  -9   0  191  182     5  -3  -7  255 -225    6  -6   0  145  149   6  -2   1  325 -365   8  -4  -8  132  130
5  -8  -3  117 -118     5  -3  -6  320  297    6  -6   5  126 -128   7  -8  -4  109   93   8  -4  -1  193  181
                                               6  -6   6  103  124   7  -8  -5  143 -150   8  -4  -3  174 -154
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individual isotropic temperature factors, brought the R-value down to 8.5 % after five cycles of refinement $(R = \sum||F_o| - |F_c||/\sum|F_o|)$. Next a block-diagonal least-squares program, G 3, written by Grønbæk [15], with anisotropic temperature factors was employed. The R-index was 6.5 % omitting un-observed reflections after five cycles of calculation with this program. A difference Fourier synthesis was calculated, but did not give the positions of the hydrogen atoms.

CRYSTAL DATA

The crystal data are given in Table 1. The coordinates found, the temperature factors and standard deviations are given in Table 3, the interatomic distances in Table 4, and observed and calculated structure factors in Table 5.

DISCUSSION

The main points of interest are the arrangement of the water molecules in relation to the manganese atom and the hydrogen bonding scheme. $KMnCl_3$, $2H_2O$ has the same structure as $\beta\text{-}RbMnCl_3,2H_2O$;[7] thus four chlorine atoms and two water molecules surround the manganese atom in octahedral coordination. The water molecules occupy *trans*-positions in the octahedra. The octahedra are joined in pairs by sharing edges, forming discrete groups $[Mn_2Cl_6, 4H_2O]^{2-}$.

The main difference between the unit cell of $KMnCl_3,2H_2O$ and of $\beta\text{-}RbMnCl_3,2H_2O$ is, that the c-axis in $KMnCl_3,2H_2O$ makes a larger angle with the normal to the (001)-plane. This distortion of the cell makes the c-axis longer, as the volume of $KMnCl_3,2H_2O$ is smaller than that of $\beta\text{-}RbMnCl_3$,

$2H_2O$ (353 $\mathring{A}^3$ and 358 $\mathring{A}^3$). The distortion causes only minor changes in the bond lengths within the Mn-octahedra. The Mn—O distances in the potassium compound are 2.18 Å and 2.19 Å compared with 2.20 Å and 2.23 Å in the rubidium compound. Two of the four Mn—Cl bonds are rather long, 2.59 Å and 2.57 Å (compared with 2.62 Å and 2.54 Å in β-$RbMnCl_3,2H_2O$), the two other bonds are rather short, 2.48 Å and 2.49 Å (2.49 Å and 2.50 Å in β-$RbMnCl_3,2H_2O$).

Larger differences between the two structures can be seen in the distances from the oxygen to the chlorine atoms outside of the coordination polyhedron of the manganese atom. As in the rubidium compound each oxygen atom has four Cl-atoms as neighbours, two of these are placed in distances varying from 3.51 Å to 4.19 Å and the two others in distances varying from 3.14 Å to 3.27 Å. But a short and a long Cl—O distance have been interchanged; the Cl_{II}—O_{II} bond is 3.14 Å in $KMnCl_3,2H_2O$ and 3.78 Å in β-$RbMnCl_3,2H_2O$, whereas the Cl_{III}—O_{II} bond is 4.19 Å in $KMnCl_3,2H_2O$ and 3.18 Å in β-$RbMnCl_3,2H_2O$. As the short Cl—O distances probably correspond to hydrogen bonds, it is suggested, that the positions of the hydrogen atoms in the two compounds are not quite the same. The Cl—O—Cl angles in $KMnCl_3,2H_2O$ corresponding to this suggestion are 96.2° and 87.5°; both values are smaller than the normal H—O—H angle 109.5°, so the hydrogen atoms must be positioned a little away from the Cl—O vectors.

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