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Neutron Diffraction Study of $KMnCl_3.2H_2O$

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The coordinates of the hydrogen atoms in $KMnCl_3.2H_2O$ have been determined by neutron diffraction technique. The hydrogen bonding schemes in $KMnCl_3.2H_2O$ and β-$RbMnCl_3.2H_2O$ are not identical. In β-$RbMnCl_3.2H_2O$ H_{III} takes part in a hydrogen bond to Cl_{III}, whereas H_{III} in $KMnCl_3.2H_2O$ takes part in a bond to Cl_{II}. The reason for the difference is probably the different coordination around O_{II}, in β-$RbMnCl_3.2H_2O$ this coordination is threefold planar, in $KMnCl_3.2H_2O$ the coordination is tetrahedral.

The crystal structure of $KMnCl_3.2H_2O$ has previously been determined by X-ray diffraction.[1] The unit cell dimensions are $a = 6.49$ Å, $b = 6.91$ Å, $c = 9.91$ Å, $\alpha = 96.8°$, $\beta = 114.1°$, and $\gamma = 112.6°$. The space group is $P\bar{1}$. In the paper it was pointed out, that $KMnCl_3.2H_2O$ and β-$RbMnCl_3.2H_2O$ were isostructural, but it was suggested, that the hydrogen bonding schemes in the two compounds were not identical. The hydrogen atom positions in β-$RbMnCl_3.2H_2O$ have been determined by neutron diffraction.[2] The present investigation has been undertaken to clarify the hydrogen bonding scheme in $KMnCl_3.2H_2O$. NMR studies[3] and specific heat measurements[4] have been performed on $KMnCl_3.2H_2O$.

EXPERIMENTAL AND STRUCTURE DETERMINATION

$KMnCl_3.2H_2O$ was prepared from an aqueous solution containing KCl and $MnCl_2.4H_2O$ in equimolar ratio and slow evaporation at 20°C. A crystal with dimensions 10 mm × 4 mm × 1 mm was used for data collection. The neutron diffraction data were collected on an automatic Hilger-Ferranti four-cicle diffractometer located at the Atomic Energy Commission Research Establishment, Risø. The wavelength of the monochromatic neutron beam was 1.025 Å, and the neutron flux at the crystal was 10^6 n/(cm² sec). The reflexions were recorded in the A-setting position with the ω-scan technique. A standard reflexion, 003, was measured at intervals of 15. The diffractometer data were reduced to structure factors using an ALGOL-program DRAM.[5] The crystal was twinned and about 5 % of the reflexions were affected by overlapping. Because of the stepscanning technique used, it was possible to correct several of these reflexions. A plot of the integrated intensity as a function of the peak intensity within intervals of $\sin\theta/\lambda$ gave a linear relationship. The curves were used to calculate the integrated intensity for

reflexions with separated peaks. Reflexions with unresolved peaks were neglected. 1012 observed independent reflexions were obtained. A reflexion was defined to be observed, when the intensity was greater than three times its standard deviation. No correction for absorption and extinction was applied, $\mu = 1.40$ cm^{-1}.

Structure factors were calculated using the coordinates and isotropic temperature factors of the non-hydrogen atoms from the X-ray work. Nuclear scattering lengths applied were the following: $b_K = 0.37$, $b_{Mn} = -0.36$, $b_{Cl} = 0.96$, $b_O = 0.588$ and $b_H = -0.372$ (10^{-12} cm). The scattering lengths were taken from the Neutron Diffraction Commission [6] (K, Mn, Cl, and H) and Brown and Chidambaram [7] (O). Three-dimensional Fourier and difference Fourier syntheses were calculated using signs from the structure factor calculation. In the maps all H-atoms appeared clearly. With the ALGOL-program D445 [8] the parameters of the H-atoms and isotropic temperature factors of all atoms were refined to a conventional R-value of 11 %. The refinement was continued with the block-diagonal least-squares program G403 [9] with anisotropic temperature factors. Eight cycles with this program gave $R = 5.3$ %.

CRYSTAL DATA

The atomic coordinates and temperature factors are given in Table 1. The non-hydrogen atom positions are within standard deviation in agreement with the X-ray coordinates. Probably due to absorption errors in the X-ray data, the agreement between the temperature factors in the X-ray and neutron investigations are rather poor. El Saffar [10] has calculated the coordinates of the hydrogen atoms in $KMnCl_3.2H_2O$ by means of Baur's least electrostatic

Table 1. Final atomic coordinates and temperature factors. The temperature factors are in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)$. Temperature factors and standard deviations (in brackets) have been multiplied by 10^4.

Atom	x/a	y/b	z/c
H_I	0.6034 (10)	0.7246 (10)	0.4934 (7)
H_{II}	0.7642 (10)	0.8193 (9)	0.4203 (6)
H_{III}	0.5989 (10)	0.3092 (8)	0.0618 (5)
H_{IV}	0.5736 (11)	0.4217 (11)	0.1901 (6)
O_I	0.7707 (4)	0.7828 (4)	0.5097 (3)
O_{II}	0.6963 (4)	0.4025 (4)	0.1673 (3)
Cl_I	0.2502 (2)	0.7120 (2)	0.4983 (1)
Cl_{II}	0.6500 (3)	0.8918 (2)	0.1878 (2)
Cl_{III}	0.1712 (3)	0.3355 (2)	0.1686 (2)
Mn	0.9516 (6)	0.2967 (5)	0.3254 (3)
K	0.1388 (9)	0.8457 (8)	0.1959 (5)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
H_I	280 (18)	367 (18)	204 (9)	354 (31)	200 (22)	236 (22)
H_{II}	382 (21)	340 (16)	135 (6)	400 (31)	232 (20)	230 (18)
H_{III}	339 (19)	269 (14)	106 (6)	316 (27)	140 (18)	68 (15)
H_{IV}	433 (23)	439 (21)	148 (8)	640 (39)	268 (22)	156 (20)
O_I	199 (9)	217 (7)	101 (3)	250 (14)	144 (9)	162 (8)
O_{II}	218 (9)	186 (7)	78 (3)	266 (13)	108 (9)	72 (7)
Cl_I	177 (5)	113 (3)	64 (2)	108 (7)	122 (5)	36 (4)
Cl_{II}	194 (5)	115 (3)	74 (2)	96 (7)	108 (5)	28 (4)
Cl_{III}	229 (5)	208 (4)	86 (2)	202 (8)	186 (6)	98 (5)
Mn	153 (11)	83 (7)	50 (4)	116 (16)	90 (11)	46 (9)
K	338 (18)	273 (13)	97 (5)	402 (26)	196 (16)	154 (14)

Table 2. Observed and calculated structure factors.

h	k	l	Fobs	Fcalc
0	0	-10	82	72
0	0	-9	150	-155
0	0	-8	17	14
0	0	-7	62	-62
0	0	-6	237	239
0	0	-5	52	48
0	0	-4	67	64
0	0	-3	329	-338
0	0	-2	50	-49
0	0	-1	10	7
0	1	-10	14	10
0	1	-9	91	91
0	1	-7	93	-86
0	1	-6	86	-82
0	1	-4	51	-47
0	1	-3	53	55
0	1	-2	48	-51
0	1	0	33	30
0	1	1	44	43
0	1	2	48	-42
0	1	3	45	-41
0	1	4	102	109
0	1	6	72	56
0	1	7	40	-42
0	1	8	102	-110
0	1	9	19	-16
0	2	-11	33	31
0	2	-10	34	31
0	2	-9	119	121
0	2	-8	148	-151
0	2	-7	42	-46
0	2	-6	156	-161
0	2	-5	178	181
0	2	-4	94	87
0	2	-3	223	224
0	2	-2	227	-234
0	2	-1	80	-76
0	2	0	57	-53
0	2	1	201	206
0	2	2	111	104
0	2	4	258	-254
0	2	5	63	-59
0	2	7	150	144
0	2	8	27	-28
0	2	9	22	21
0	3	-11	56	-56
0	3	-9	25	-29
0	3	-8	65	68
0	3	-6	13	-16
0	3	-4	63	62
0	3	-3	51	-47
0	3	-1	64	-63
0	3	0	19	16
0	3	3	110	-105
0	3	4	91	-92
0	3	6	74	72
0	3	7	44	49
0	4	-9	17	19
0	4	-8	147	151
0	4	-7	46	-48
0	4	-6	46	-46
0	4	-5	177	-175
0	4	-4	34	31
0	4	-3	19	18
0	4	-2	202	198
0	4	-1	122	-127
0	4	0	96	-95
0	4	1	83	-87
0	4	2	95	94
0	4	3	86	87
0	4	4	89	98
0	4	5	87	-91
0	4	6	45	-46
0	5	-10	51	-53
0	5	-9	29	33
0	5	-8	41	-42
0	5	-5	35	-34
0	5	-3	94	92
0	5	0	55	-53
0	5	1	32	33
0	5	2	15	11
0	5	3	112	111
0	5	4	49	-51
0	5	5	53	-57
0	6	-9	33	-37
0	6	-6	33	34
0	6	-4	59	-58
0	6	-1	106	110
0	6	1	79	-75
0	6	2	37	-41
0	7	-6	22	18
0	7	-5	21	-19
0	7	-4	42	-44
0	7	-3	53	-53
0	7	-2	66	66
0	7	-1	19	16
0	7	1	64	-63
1	-8	3	198	185
1	-8	4	52	-53
1	-7	-1	39	37
1	-7	1	21	21
1	-7	2	42	41
1	-7	3	17	16
1	-7	4	27	-28
1	-7	5	16	-16
1	-7	6	24	-29
1	-7	7	14	12
1	-6	-9	89	-93
1	-6	-4	39	-39
1	-6	-3	89	-89
1	-6	-2	185	192
1	-6	-1	40	32
1	-6	1	176	-173
1	-6	2	38	-36
1	-6	4	205	211
1	-6	5	37	-31
1	-6	7	138	-135
1	-5	-5	22	21
1	-5	-4	40	-40
1	-5	-3	42	43
1	-5	-2	42	-46
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1	-5	2	48	-37
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1	-5	4	52	52
1	-5	6	40	-34
1	-5	7	32	-26
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1	-5	9	92	97
1	-4	-8	136	-139
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1	-4	-4	93	-94
1	-4	-2	177	-166
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1	-4	0	67	69
1	-4	1	124	113
1	-4	2	78	-68
1	-4	4	132	-123
1	-4	5	155	158
1	-4	7	46	51
1	-4	8	79	-85
1	-3	-9	48	-41
1	-3	-8	44	30
1	-3	-7	41	-40
1	-3	-6	34	30
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1	-3	-3	88	-94
1	-3	-2	102	96
1	-3	-1	14	-10
1	-3	0	92	91
1	-3	2	37	-38
1	-3	3	120	-121
1	-3	5	54	58
1	-3	7	46	-52
1	-3	8	39	-45
1	-3	9	78	-82
1	-3	10	73	75
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1	-2	-5	27	-16
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1	-2	-1	147	-141
1	-2	0	11	-11
1	-2	1	22	20
1	-2	3	13	9
1	-2	4	18	-16
1	-2	5	67	-71
1	-2	6	40	46
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1	-1	4	109	-123
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1	-1	8	15	-18
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1	0	-6	35	-36
1	0	-5	37	38
1	0	-4	21	19
1	0	-2	23	20
1	0	-1	57	50
1	0	0	49	47
1	0	1	12	-13
1	0	2	79	80
1	0	3	107	-116
1	0	4	27	30
1	0	5	42	-42
1	0	6	14	12
1	0	7	25	-27
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1	1	-11	94	-93
1	1	-9	42	42
1	1	-8	147	150
1	1	-7	27	-29
1	1	-6	45	-48
1	1	-5	66	-73
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1	1	-3	98	95
1	1	-2	154	150
1	1	-1	162	-161
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1	5	3	27	-25
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1	6	-5	79	88
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2	-7	-4	34	-34
2	-7	-3	29	-31
2	-7	-2	88	-93
2	-7	-1	80	82
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2	0	-2	71	66
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2	0	0	258	-264
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2	1	-2	21	-16
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2	1	0	53	53
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2	2	-3	251	-252
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2	2	0	263	259
2	2	2	94	-93
2	2	3	165	-168
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2	2	5	22	18
2	2	6	124	126
2	3	-10	63	62
2	3	-9	63	60
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2	3	0	28	-19
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2	3	5	70	73
2	4	-11	102	93
2	4	-9	59	55
2	4	-7	52	-49
2	4	-6	113	-112
2	4	-3	54	54
2	4	-2	151	-153
2	4	0	41	-31
2	4	1	178	177
2	4	3	32	-30
2	4	4	86	-77
2	5	-8	22	25
2	5	-4	31	31
2	5	-3	29	24
2	5	-1	80	-76
2	5	0	57	60
2	5	1	15	12
2	5	2	30	26
2	6	-8	47	49
2	6	-6	25	-28
2	6	-5	65	-76
2	6	-4	53	59
2	6	-3	29	29
2	6	-1	56	-56
3	-8	-2	54	-59
3	-8	-1	126	-129
3	-8	0	121	126
3	-8	1	47	48
3	-8	2	101	105
3	-8	3	96	-98
3	-8	4	36	-39
3	-7	-5	51	-53
3	-7	-3	16	14
3	-7	-2	45	47
3	-7	-1	23	25
3	-7	0	23	18
3	-7	1	68	-70
3	-7	2	40	37
3	-7	3	35	-35
3	-7	6	23	23
3	-6	-6	162	-165
3	-6	-5	60	53
3	-6	-3	159	162
3	-6	-1	60	-63
3	-6	0	214	-221
3	-6	1	70	66
3	-6	2	44	44
3	-6	3	132	137
3	-6	4	83	-83
3	-6	5	37	-36
3	-6	6	133	-139
3	-6	7	91	100
3	-5	-6	47	55
3	-5	-5	20	-21
3	-5	-4	62	-57
3	-5	-3	34	-43
3	-5	0	26	25
3	-5	1	54	52
3	-5	2	63	-56
3	-5	3	56	55
3	-5	4	16	-20
3	-5	7	48	49
3	-5	8	12	-3
3	-4	-9	68	-75
3	-4	-8	96	98
3	-4	-6	61	64
3	-4	-5	210	-205
3	-4	-2	164	168
3	-4	-1	66	67
3	-4	1	168	-160
3	-4	2	14	10
3	-4	3	49	45
3	-4	4	106	106
3	-4	5	28	-36
3	-4	7	120	-130
3	-4	8	25	25
3	-3	-7	28	28
3	-3	-5	69	62
3	-3	-1	41	33
3	-3	0	54	-54
3	-3	1	36	-37
3	-3	4	37	41
3	-3	6	33	-38
3	-3	7	25	-25
3	-3	8	30	29
3	-2	-11	94	82
3	-2	-10	58	-53
3	-2	-9	14	-7
3	-2	-8	55	-50
3	-2	-7	68	54
3	-2	-6	21	19
3	-2	-5	77	75
3	-2	-4	149	-159
3	-2	-3	35	-32
3	-2	-2	37	-36
3	-2	-1	33	28
3	-2	0	33	29
3	-2	2	68	-53
3	-2	4	72	65
3	-2	5	50	40
3	-2	7	39	19
3	-2	8	63	-41
3	-1	-10	33	23
3	-1	-9	53	-55

Table 2. Continued.

energy method.[11] His results are in accordance with the coordinates in this work.

Observed and calculated structure factors are given in Table 2. Table 3 gives the root-mean-square displacements and the orientations of the principal axes of the thermal parameter ellipsoids. Distances and angles concerning the hydrogen bonds and the oxygen coordination spheres are given in Tables 4 and 5. The O – H bond lengths in parenthesis in Table 4 are corrected for ther-

Table 3. Magnitudes and orientations of the principal axes of the vibration ellipsoids. The magnitudes are given as the root mean square displacements. The angles (in degress) refer to the axes of the unit cell.

Atom	R.m.s.d. Å	Angle to axis *a*	*b*	*c*	Atom	R.m.s.d. Å	Angle to axis *a*	*b*	*c*
H_I	0.185	27	112	88	Cl_I	0.082	144	38	65
	0.246	98	147	58		0.158	109	83	133
	0.297	116	66	32		0.169	120	127	53
H_{II}	0.192	79	131	40	Cl_{II}	0.141	84	46	77
	0.227	164	83	61		0.172	36	93	149
	0.260	102	41	64		0.182	125	44	117
H_{III}	0.195	82	82	44	Cl_{III}	0.145	144	89	32
	0.209	34	146	100		0.188	119	84	121
	0.244	123	122	48		0.198	109	6	94
H_{IV}	0.175	20	132	110	Mn	0.120	107	8	95
	0.234	92	83	151		0.134	68	87	174
	0.298	70	42	109		0.145	28	98	94
O_I	0.147	43	130	72	K	0.171	63	136	56
	0.171	52	65	137		0.187	38	112	146
	0.216	106	51	52		0.234	66	54	93
O_{II}	0.143	33	140	89					
	0.171	81	107	145					
	0.200	121	126	55					

Table 4. Geometry of the hydrogen bonds. Distances in paranthesis are O – H bond lengths corrected for thermal motion. Standard deviations of O – Cl distances are 0.004 Å, of H – Cl and O – H distances about 0.008 Å. Standard deviations of Cl – O – Cl angles are 0.1°, of O – H – Cl and H – O – H angles 0.6°.

Hydrogen bonds	Distances (Å)			Angles (degrees)		
	O – Cl	H – Cl	O – H	O – H – Cl	Cl – O – Cl	H – O – H
O_I H_I — Cl_I	3.174	2.282	0.934 (0.972)	159.5	96.4	106.3
O_I H_{II} — Cl_{II}	3.215	2.297	0.938 (0.964)	166.2		
O_{II} H_{III} — Cl_{II}	3.147	2.203	0.947 (0.969)	174.6	87.7	104.8
O_{II} H_{IV} — Cl_{III}	3.264	2.354	0.961 (1.001)	157.8		

Table 5. Distances (Å) and angles (degrees) in the coordination spheres of the oxygen atoms.

O_I – Mn	2.188 (5)	Mn – O_I – H_I	120.6 (5)
O_I – H_I	0.934 (8)	Mn – O_I – H_{II}	128.3 (5)
O_I – H_{II}	0.938 (8)	H_I – O_I – H_{II}	106.3 (6)
O_{II} – Mn	2.195 (5)	Mn – O_{II} – K	96.2 (2)
O_{II} – K	3.174 (5)	Mn – O_{II} – H_{III}	113.9 (5)
O_{II} – H_{III}	0.947 (5)	Mn – O_{II} – H_{IV}	118.9 (5)
O_{II} – H_{IV}	0.961 (9)	K – O_{II} – H_{III}	108.0 (4)
		K – O_{II} – H_{IV}	114.9 (5)
		H_{III} – O_{II} – H_{IV}	104.8 (6)

mal motion on the assumption that the hydrogen atoms "ride" the oxygen atoms (Busing and Levy [12]). R.m.s. displacements and O – H corrections have been performed by the program ORFFE in the program-system X-Ray-63 (Stewart [13]).

DISCUSSION

The crystal structure analyses of β-$RbMnCl_3.2H_2O$[14] and of $KMnCl_3.2H_2O$[1] investigated by X-ray diffraction show that these compounds are isostructural except for the hydrogen atoms. This work and the neutron diffraction investigation of β-$RbMnCl_3.2H_2O$[2] show that the hydrogen bonding schemes are not identical. The H_I-atom in β-$RbMnCl_3.2H_2O$ forms a bifurcated bond to Cl_I- and Cl_{III}-atoms, whereas H_I in the potassium compound forms a normal hydrogen bond to Cl_I. Further H_{III} in β-$RbMnCl_3.2H_2O$ is bonded to a Cl_{III}-atom and H_{III} in $KMnCl_3.2H_2O$ is bonded to Cl_{II}. The differences in the hydrogen bonding schemes are probably connected to different lone pair coordination of the water molecules. In β-$RbMnCl_3.2H_2O$ both water molecules are of the type D (Chidambaram *et al.*[15]), in which the bisector of the lone pairs points toward one bivalent ion (Mn^{2+}). In $KMnCl_3.2H_2O$ the water molecule containing O_I is of D-type, whereas one of the lone pairs points toward Mn^{2+}, the other toward K^+ in the water molecule corresponding to O_{II}. This type of coordination is not included in the classification of Chidambaram *et al.* The distances and angles in the coordination spheres of the oxygen atoms in $KMnCl_3.2H_2O$ can be seen in Table 5. The sum of angles about O_I is 355.2° thus indicating a nearly planar configuration. The six angles about O_{II} have values not deviating essentially from the tetrahedral angle 109.5°, thus indicating tetrahedral coordination around this oxygen atom. The main reason for the different coordination about O_{II} in the rubidium and potassium compounds is probably, that the smaller radius and the bigger hydration energy of the potassium ion make a K – O bond more possible than an Rb – O bond. It is suggested, that in hydrated halides containing both alkali metal and divalent metal, the water molecules mainly will be of D-type if the alkali metal is Rb or Cs, whereas the water oxygen will have a bond to the alkali metal if this is K, Na, or Li. Thus $CsMnCl_3.2H_2O$,[16] $Cs_2MnCl_4.2H_2O$,[17] α-$RbMnCl_3.2H_2O$,[14] and $Rb_2MnCl_4.2H_2O$ [17] contain D-type molecules and $KZnCl_3.2H_2O$[18] has tetrahedrally coordinated oxygen with a K – O bond.[19]

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