

## The Crystal Structure of $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$

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The crystal structure of  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  has been determined by three-dimensional Patterson and Fourier methods and the parameters refined by least-squares computations.  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  is triclinic, space group  $P\bar{1}$  with  $a = 6.49 \text{ \AA}$ ,  $b = 6.91 \text{ \AA}$ ,  $c = 9.91 \text{ \AA}$ ,  $\alpha = 96.8^\circ$ ,  $\beta = 114.1^\circ$ ,  $\gamma = 112.6^\circ$ . There are two formula units per unit cell.  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  is isostructural with  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ . The manganese atom is octahedrally coordinated to four chlorine atoms and to two water molecules. The water molecules occupy *trans*-positions.  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  contains discrete groups  $[\text{Mn}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}]^{2-}$ .

The system  $\text{KCl-MnCl}_2\text{-H}_2\text{O}$  was investigated by Süß.<sup>1</sup> He prepared the following double salts:  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{K}_4\text{MnCl}_6$ . Axial ratios and angles in  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  were reported by Mügge.<sup>2</sup> A crystal structure analysis of  $\text{K}_4\text{MnCl}_6$  was carried out by Bellanca<sup>3</sup> and corrected by Bergerhoff and Schmitz-Dumont.<sup>4</sup> This paper presents a structure determination of  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ . A structure analysis of  $\text{K}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$  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.<sup>5-7</sup> A preliminary account of the work on  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  has been published.<sup>8</sup>

### EXPERIMENTAL

$\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  was prepared from an aqueous solution containing  $\text{KCl}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in equimolar ratio and slow evaporation at  $20^\circ\text{C}$ . The crystals formed pink prisms frequently twinned. Chemical analysis gave the following results: Mn 23.55; Cl 44.89;  $\text{H}_2\text{O}$  15.20; K 16.36. Calc.: Mn 23.24; Cl 44.99;  $\text{H}_2\text{O}$  15.24; K 16.53. Mn was determined by complexometric titration with EDTA, Cl by potentiometric titration using  $\text{AgNO}_3$ , and the water gravimetrically by heating to  $110^\circ\text{C}$ . K was calculated as the balance.  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  gives off the water at  $76^\circ\text{C}$ . The density was  $2.20 \text{ g/cm}^3$  ( $20^\circ\text{C}$ ) 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 ( $a_{\text{KCl}} = 6.2905 \text{ \AA}$ ).  $\text{FeK}\alpha$ -radiation ( $\text{FeK}\alpha = 1.9360 \text{ \AA}$ ) was employed. The cell was chosen to bring out the similarity in structure between  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  and  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ .<sup>7</sup> In Table 1 the cell constants first listed are in accordance with this choice. The dimensions of the Dirichlet reduced cell (Balashov and Ursell<sup>9</sup>) are listed next. Table 2 gives a comparison between the

goniometric data of Mügge<sup>2</sup> 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<sup>-1</sup> for MoK $\alpha$ -radiation). The crystals showed no piezo-electric effect.

### STRUCTURE DETERMINATION

Although the cell dimensions of KMnCl<sub>3</sub>·2H<sub>2</sub>O differ from those of  $\beta$ -RbMnCl<sub>3</sub>·2H<sub>2</sub>O a three dimensional Patterson function revealed that KMnCl<sub>3</sub>·2H<sub>2</sub>O is probably isostructural with  $\beta$ -RbMnCl<sub>3</sub>·2H<sub>2</sub>O. 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<sup>10</sup> was used for the Fourier computations. The atomic scattering factors were taken from Vol. III of *International Tables of Crystallography*<sup>11</sup> and their parameters calculated according to the Bassi<sup>12</sup> interpolation formula.

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

Table 1. Crystal data.

Crystal system	: triclinic		
Space group	: $P\bar{1} - C_1^1$		
Formula units per unit cell	: 2		
Unit cell	:	This work	Dirichlet cell
		$a = 6.49 \pm 0.01 \text{ \AA}$	$a = 6.49 \text{ \AA}$
		$b = 6.91 \pm 0.01 \text{ \AA}$	$b = 6.91 \text{ \AA}$
		$c = 9.91 \pm 0.01 \text{ \AA}$	$c = 9.21 \text{ \AA}$
		$\alpha = 96.8 \pm 0.1^\circ$	$\alpha = 69.4^\circ$
		$\beta = 114.1 \pm 0.1^\circ$	$\beta = 88.7^\circ$
		$\gamma = 112.6 \pm 0.1^\circ$	$\gamma = 67.4^\circ$
Density, calculated (20°C)	: 2.22 g/cm <sup>3</sup>		
Density, measured (20°C)	: 2.20 g/cm <sup>3</sup>		
Absorption coefficient (MoK $\alpha$ )	: 46 cm <sup>-1</sup>		
Residual factor, <i>R</i>	: 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<sup>2</sup> and from this work. The goniometric data have been transformed to the X-ray cell.

	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$
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	$x/a$	$y/b$	$z/c$	$B \text{ \AA}^2$
O <sub>I</sub>	0.7739 (19)	0.7853 (16)	0.5111 (10)	2.5
O <sub>II</sub>	0.6989 (17)	0.4026 (15)	0.1663 (9)	2.3
Cl <sub>I</sub>	0.2504 (7)	0.7112 (5)	0.4984 (3)	1.9
Cl <sub>II</sub>	0.6501 (7)	0.8929 (5)	0.1877 (3)	2.2
Cl <sub>III</sub>	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 <sub>I</sub>	207 (46)	163 (29)	100 (13)	181 (69)	144 (40)	160 (33)
O <sub>II</sub>	100 (39)	136 (27)	79 (11)	82 (62)	84 (33)	38 (29)
Cl <sub>I</sub>	166 (14)	135 (9)	65 (3)	122 (21)	150 (11)	50 (9)
Cl <sub>II</sub>	208 (16)	117 (9)	73 (3)	112 (23)	138 (12)	31 (9)
Cl <sub>III</sub>	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  $\times 10^3 \text{ \AA}$ . Hydrogen bonds are indicated with h.

Within octahedra					
Mn — Cl <sub>I</sub>	2.594 (3)	Cl <sub>II</sub> — Cl <sub>III</sub>	3.681 (5)		
Mn — Cl <sub>I</sub>	2.570 (5)	Cl <sub>I</sub> — O <sub>I</sub>	3.368 (15)		
Mn — Cl <sub>II</sub>	2.490 (3)	Cl <sub>I</sub> — O <sub>I</sub>	3.360 (12)		
Mn — Cl <sub>III</sub>	2.482 (5)	Cl <sub>I</sub> — O <sub>II</sub>	3.320 (7)		
Mn — O <sub>I</sub>	2.182 (12)	Cl <sub>I</sub> — O <sub>II</sub>	3.419 (11)		
Mn — O <sub>II</sub>	2.187 (11)	Cl <sub>II</sub> — O <sub>I</sub>	3.277 (8)		
Cl <sub>I</sub> — Cl <sub>I</sub>	3.447 (5)	Cl <sub>II</sub> — O <sub>II</sub>	3.451 (12)		
Cl <sub>I</sub> — Cl <sub>II</sub>	3.542 (5)	Cl <sub>III</sub> — O <sub>I</sub>	3.293 (11)		
Cl <sub>I</sub> — Cl <sub>III</sub>	3.647 (6)	Cl <sub>III</sub> — O <sub>II</sub>	3.270 (14)		
Between neighbouring octahedra					
Mn — Mn	3.845 (3)	Cl <sub>III</sub> — O <sub>I</sub>	3.708 (7)		
Cl <sub>II</sub> — Cl <sub>III</sub>	3.826 (5)	Cl <sub>III</sub> — O <sub>II</sub>	3.274 (13) h		
Cl <sub>I</sub> — O <sub>I</sub>	3.179 (14) h	Cl <sub>III</sub> — O <sub>II</sub>	4.186 (11)		
Cl <sub>I</sub> — O <sub>I</sub>	3.551 (13)	O <sub>I</sub> — O <sub>I</sub>	3.381 (15)		
Cl <sub>II</sub> — O <sub>I</sub>	3.223 (11) h	O <sub>I</sub> — O <sub>I</sub>	4.074 (14)		
Cl <sub>II</sub> — O <sub>II</sub>	3.510 (13)	O <sub>I</sub> — O <sub>II</sub>	3.795 (16)		
Cl <sub>II</sub> — O <sub>II</sub>	3.140 (8) h				
From the potassium-atom					
K — Cl <sub>I</sub>	3.128 (5)	K — Cl <sub>III</sub>	3.349 (6)		
K — Cl <sub>I</sub>	3.587 (4)	K — Cl <sub>III</sub>	3.121 (4)		
K — Cl <sub>II</sub>	3.241 (7)	K — O <sub>I</sub>	3.316 (12)		
K — Cl <sub>II</sub>	3.277 (7)	K — O <sub>II</sub>	3.164 (10)		
K — Cl <sub>III</sub>	4.855 (6)	K — O <sub>II</sub>	4.294 (11)		
K — Cl <sub>III</sub>	3.606 (7)	K — O <sub>II</sub>	4.469 (13)		

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

h	k	l	F <sub>obs</sub>	F <sub>calc</sub>	1	-6	-3	134	-135	1	2	-5	418	439	2	-2	-1	633	-584	3	-3	0	236	257	
0	0	2	481	-495	1	-6	-1	187	186	1	2	-4	153	170	2	-2	0	470	-476	3	-3	2	249	-255	
0	0	3	813	-767	1	-6	0	285	285	1	2	-1	75	-79	2	-2	1	436	-420	3	-3	3	274	252	
0	0	4	713	747	1	-6	1	478	-489	1	2	0	555	-546	2	-2	2	1175	1198	3	-3	8	126	-146	
0	0	7	217	-241	1	-6	4	747	161	1	2	1	548	523	2	-2	3	77	72	3	-3	9	115	137	
0	0	8	233	-254	1	-6	5	131	122	1	2	2	177	154	2	-2	4	205	-215	3	-3	-12	84	-69	
0	0	9	108	-86	1	-6	6	181	178	1	2	3	182	-122	2	-2	5	340	-330	3	-3	-10	84	92	
0	0	10	136	149	1	-6	7	389	-401	1	2	4	256	-231	2	-2	6	366	390	3	-3	-9	97	-62	
0	0	12	114	145	1	-5	-6	130	-133	1	2	7	180	173	2	-2	10	132	-133	3	-3	-8	247	-255	
0	1	-12	168	-175	1	-5	-5	116	122	1	3	-12	114	120	2	-1	-12	124	118	3	-3	-7	257	277	
0	1	-10	87	-63	1	-5	-4	305	73	1	3	-10	302	-328	2	-1	-11	128	98	3	-3	-6	146	-133	
0	1	-9	169	182	1	-5	-3	484	-174	1	3	-9	148	149	2	-1	-10	229	-257	3	-3	-4	246	246	
0	1	-8	67	68	1	-5	-1	202	166	1	3	-8	129	117	2	-1	-9	251	-279	3	-3	-2	535	-534	
0	1	-7	49	-61	1	-5	0	225	-218	1	3	-7	135	132	2	-1	-8	278	311	3	-3	-1	358	352	
0	1	-6	328	-350	1	-5	3	104	110	1	3	-4	503	-496	2	-1	-7	175	176	3	-3	2	164	167	
0	1	-5	36	-44	1	-5	3	177	-200	1	3	-3	304	293	2	-1	-4	490	-476	3	-3	3	89	-65	
0	1	-4	512	527	1	-5	3	124	101	1	3	-2	195	180	2	-1	-3	405	-381	3	-3	2	189	204	
0	1	-3	236	-252	1	-5	3	234	241	1	3	-1	101	-122	2	-1	-2	789	781	3	-3	1	89	204	
0	1	-2	478	-491	1	-5	6	218	-201	1	3	0	63	63	2	-1	-1	136	128	3	-3	6	91	95	
0	1	1	139	-138	1	-5	7	132	-118	1	3	1	128	121	2	-1	0	311	-326	3	-3	-9	280	-284	
0	1	2	214	210	1	-5	8	113	75	1	3	2	115	-150	2	-1	1	60	58	3	-3	-8	215	210	
0	1	3	236	-252	1	-4	-10	108	107	1	3	3	182	160	2	-1	2	56	55	3	-3	-1	442	-434	
0	1	4	261	-259	1	-4	-11	119	-105	1	3	4	98	89	2	-1	3	199	-197	3	-3	-2	445	464	
0	1	5	449	448	1	-4	-7	89	-88	1	3	7	110	103	2	-1	4	274	276	3	-3	0	186	-171	
0	1	6	126	121	1	-4	-5	399	387	1	3	8	138	-132	2	-1	5	119	-99	3	-3	1	104	106	
0	1	7	206	-229	1	-4	-4	285	-280	1	4	-7	141	156	2	-1	6	171	-179	3	-3	1	113	104	
0	1	8	186	-172	1	-4	-2	233	-204	1	4	-6	105	-100	98	0	-12	100	98	3	-3	3	350	-342	
0	2	-12	190	-184	1	-4	-1	107	-108	1	4	-5	586	-605	2	0	-10	355	-359	3	-3	4	215	210	
0	2	-11	180	-174	1	-4	0	118	118	1	4	-4	7	177	170	2	0	-9	218	210	3	0	-13	134	-118
0	2	-9	233	215	1	-4	1	690	704	1	4	-3	169	157	2	0	-7	364	346	3	0	-12	120	108	
0	2	-7	248	-242	1	-4	2	438	-443	1	4	-2	190	172	2	0	-6	530	527	3	0	-10	130	-97	
0	2	-6	612	-632	1	-4	3	173	-169	1	4	0	102	84	2	0	-5	120	-126	3	0	-9	330	-354	
0	2	-5	668	698	1	-4	4	121	-116	1	4	1	509	-524	2	0	-4	1185	-1151	3	0	-7	253	-205	
0	2	-4	279	265	1	-4	6	98	85	1	4	2	159	158	2	0	-3	759	790	3	0	-6	250	194	
0	2	-3	363	349	1	-4	7	340	346	1	4	3	170	165	2	0	0	360	-356	3	0	-5	69	69	
0	2	-2	483	-497	1	-4	8	284	-270	1	4	4	215	-200	2	0	1	315	-304	3	0	-4	330	-354	
0	2	-1	544	-519	1	-4	9	131	-113	1	5	-9	506	-297	2	0	2	784	-768	3	0	-3	280	331	
0	2	0	179	-759	1	-3	-6	222	213	1	5	-7	109	120	2	0	3	712	721	3	0	-2	175	199	
0	2	1	1207	1242	1	-3	-5	296	-289	1	5	-5	136	146	2	0	4	289	289	3	0	-1	235	184	
0	2	2	205	180	1	-3	-4	205	180	1	5	-3	336	-339	2	0	5	277	284	3	0	0	90	84	
0	2	3	147	-157	1	-3	-2	182	-168	1	5	-1	172	173	2	0	-9	152	-167	3	0	2	235	-256	
0	2	4	383	-371	1	-3	-1	82	-88	1	5	3	191	-160	2	0	-8	396	-415	3	0	3	195	182	
0	2	5	169	-168	1	-3	0	419	417	1	5	4	175	179	2	0	-7	125	121	3	0	4	116	106	
0	2	6	415	417	1	-3	1	304	-302	1	6	-10	188	-208	2	0	-6	275	272	3	0	5	138	-139	
0	2	7	137	-143	1	-3	3	171	157	1	6	-5	258	267	2	0	-4	259	251	3	0	-11	112	95	
0	2	8	138	-152	1	-3	4	185	-180	1	6	-4	393	-409	2	0	1	251	259	3	0	-10	162	160	
0	2	9	110	-133	1	-3	5	184	-182	1	6	-3	166	153	2	0	2	344	-324	3	0	-9	447	-503	
0	2	10	110	-133	1	-3	6	376	381	1	6	1	179	169	2	0	3	489	66	3	0	-7	179	157	
0	2	11	102	-105	1	-3	7	143	-121	1	6	2	301	-302	2	0	4	85	108	3	0	-6	127	114	
0	2	12	131	133	1	-3	8	143	-143	1	7	-10	117	126	2	0	-3	126	-118	3	0	-5	135	134	
0	2	13	140	147	1	-3	9	184	182	1	7	-9	132	122	2	0	-4	140	146	3	0	-4	10	135	134
0	2	14	212	212	1	-2	-10	199	183	1	7	-8	128	-143	2	0	-5	166	165	3	0	-3	154	154	
0	2	15	225	-233	1	-2	-9	133	-120	1	7	-7	87	-113	2	0	-6	148	-453	3	0	-2	276	-285	
0	2	16	164	-167	1	-2	-8	205	-191	1	7	-6	150	-156	2	0	-7	125	121	3	0	-1	162	157	
0	2	17	301	-327	1	-2	-5	160	-161	1	7	0	129	129	2	0	-8	125	-112	3	0	0	157	-147	
0	2	18	137	133	1	-2	-4	510	525	1	8	-4	231	244	2	0	-9	283	283	3	0	-1	152	131	
0	2	19	497	-509	1	-2	-3	196	-202	1	8	-3	161	-155	2	0	-10	257	279	3	0	0	155	-122	
0	2	20	289	291	1	-2	-2	351	351	1	8	-2	6	176	124	2	0	-11	340	344	3	0	-1	330	-320
0	2	21	111	116	1	-2	1	250	-254	1	8	-1	182	164	3	0	-12	164	-166	3	0	0	172	-160	
0	2	22	311	-311	1	-2	2	801	786	1	8	-2	182	162	3	0	-13	116	92	3	0	1	209	188	
0	2	23	243	237	1	-2	3	180	-186	1	8	-1	251	-275	3	0	-14	192	177	3	0	2	156	156	
0	2	24	140	140	1	-2	4	180	-186	1	8	0	166	153	2	0	-15	205	-183	3	0	3	122	111	
0	2	25	235	-240	1	-2	6	87	-96	1	8	2	140	-116	3	0	-16	151	116	3	0	4	188	-184	
0	2	26	152	145	1	-2	7	80	-77	1	8	3	115	99	3	0	-17	175	-165	3	0	5	205	206	
0	2	27	485	487	1	-2	8	265	272	1	8	4	167	156	3	0	-18	147	123	3	0	6	366	366	
0	2	28	611	-651	1	-2	10	116	-117	1	8	5	262	-251	3	0	-19	141	-114	3	0	7	160	-175	
0	2	29	250	235	1	-1	-11	178	192	1	8	6	120	105	3	0	-20	149	-132	3	0	8	338	339	
0	2	30	244	231	1	-1	-10	136	-117	1	8	7	181	-130	3	0	-21	130	438	3	0	9	446	-466	
0	2	31	259	265	1	-1	-9	113	-112	1	8	8	115	-113	3	0	-22	117	-103	3	0	10	153	-187	
0	2	32	140	140	1	-1	-6	144	-114	1	8	9													

Table 5. Continued.

h	k	l	Fobs	Fcalc	5	-8	-2	112	-98	5	-3	-4	213	-173	6	-5	-8	175	183	7	-8	-4	114	124
h	-2	-6	100	-93	5	-8	-1	288	278	5	-3	-1	222	-218	6	-5	-7	169	172	7	-8	-1	163	-180
h	-2	-5	290	263	5	-8	3	86	-80	5	-3	0	202	206	6	-5	-5	438	-447	7	-7	-5	125	141
h	-2	-4	215	206	5	-8	5	272	243	5	-3	2	144	-137	6	-5	-4	174	163	7	-7	-3	199	-212
h	-2	-2	851	-873	5	-7	-7	155	-154	5	-3	4	92	89	6	-5	-3	114	107	7	-7	3	140	-132
h	-2	-1	326	335	5	-7	-5	183	196	5	-3	5	160	-154	6	-5	-2	132	130	7	-6	-9	123	134
h	-2	0	226	230	5	-7	-1	189	-146	5	-2	-13	100	101	6	-5	-1	272	-293	7	-6	-8	91	-93
h	-2	1	268	227	5	-7	1	240	238	5	-2	-11	201	-218	6	-5	2	181	200	7	-6	-4	256	-258
h	-2	2	90	-56	5	-6	-7	162	-201	5	-2	-10	109	121	6	-4	-11	164	154	7	-6	-3	124	116
h	-2	3	116	-102	5	-6	-6	218	235	5	-2	-9	101	-66	6	-4	-10	120	-93	7	-6	-2	209	-221
h	-2	4	435	-435	5	-6	-5	102	-81	5	-2	-8	80	-54	6	-4	-9	100	-80	7	-5	-10	171	157
h	-2	5	265	257	5	-6	-4	126	134	5	-2	-7	160	147	6	-4	-8	116	108	7	-5	-8	158	-113
h	-2	6	175	170	5	-6	-2	107	-112	5	-2	-6	183	159	6	-4	-7	130	116	7	-5	-5	120	-97
h	-1	-12	249	-259	5	-6	-1	272	-305	5	-2	-5	325	-325	6	-4	-6	302	-270	7	-5	-4	188	191
h	-1	-9	187	144	5	-6	0	292	316	5	-2	-4	131	158	6	-4	-5	107	106	7	-5	-2	176	-183
h	-1	-8	395	392	5	-6	4	87	-94	5	-2	-2	123	-129	6	-4	-2	159	157	7	-4	-10	132	121
h	-1	-6	648	-658	5	-6	5	154	-167	5	-2	-1	172	153	6	-4	0	382	-398	7	-4	-9	234	-225
h	-1	-4	258	235	5	-6	6	209	219	5	-2	0	176	177	6	-4	-2	86	103	7	-4	-8	121	113
h	-1	-3	143	144	5	-6	7	186	199	5	-2	1	278	-270	6	-3	-12	193	208	7	-4	-5	89	65
h	-1	-2	185	195	5	-5	-6	117	-136	5	-1	-12	235	-250	6	-3	-11	193	176	7	-4	-4	185	192
h	-1	-1	77	-63	5	-5	-5	170	-189	5	-1	-8	144	127	6	-3	-10	305	-305	7	-4	-3	237	-240
h	-1	0	420	-494	5	-5	-4	125	142	5	-1	-7	141	124	6	-3	-9	100	-81	7	-4	-2	150	132
h	-1	1	206	194	5	-5	-1	161	164	5	-1	-6	423	-444	6	-3	-8	128	-120	7	-4	-1	151	-154
h	-1	2	197	191	5	-5	0	88	-110	5	-1	-5	152	131	6	-3	-7	167	136	7	-3	-10	236	-223
h	-1	3	110	-90	5	-5	1	162	-174	5	-1	-4	97	95	6	-3	-6	356	327	7	-3	-5	103	91
h	-1	5	113	74	5	-5	2	160	172	5	-1	-1	172	174	6	-3	-5	160	145	7	-3	-4	235	-241
h	-1	6	113	-113	5	-5	4	116	-119	5	-1	0	288	-319	6	-3	-4	500	-539	7	-3	-2	114	98
h	0	-13	173	-163	5	-4	-11	132	142	5	-1	5	147	122	6	-3	-2	92	80	7	-3	-2	119	-111
h	0	-12	141	143	5	-4	-10	102	-99	5	-1	1	278	-135	6	-3	-1	131	130	8	-2	-3	139	117
h	0	-11	161	-160	5	-4	-9	90	78	6	-9	0	191	159	6	-3	0	115	99	8	-2	-3	246	-248
h	0	-9	148	143	5	-4	-8	105	101	6	-8	-4	124	144	6	-3	2	305	-304	8	-6	-7	118	-128
h	0	-8	331	319	5	-4	-6	342	-349	6	-8	-3	86	-100	6	-3	4	116	92	8	-6	-4	129	-113
h	0	-7	330	-340	5	-4	-5	229	229	6	-8	-1	97	97	6	-2	-11	194	-176	8	-6	-0	119	77
h	0	-5	157	-153	5	-4	-4	116	-85	6	-7	-6	172	-204	6	-2	-10	189	178	8	-5	-9	234	211
h	0	-4	213	241	5	-4	-3	100	75	6	-7	-5	193	215	6	-2	-9	109	-97	8	-5	-8	232	-222
h	0	-3	205	200	5	-4	-2	161	146	6	-7	-1	39	-107	6	-2	-8	322	315	8	-5	-6	122	-112
h	0	-2	227	288	5	-4	0	387	-415	6	-7	0	130	-143	6	-2	-5	343	-362	8	-5	-4	178	167
h	0	-1	656	-788	5	-4	1	176	-178	6	-7	1	215	244	6	-2	-3	96	-90	8	-5	-3	177	168
h	0	1	136	131	5	-4	6	234	-196	6	-6	-3	136	154	6	-2	-1	135	122	8	-5	-2	261	-282
h	0	2	225	237	5	-4	7	93	98	6	-6	-1	213	-232	6	-2	0	240	238	8	-4	-9	142	-136
h	0	5	315	-350	5	-3	-12	158	157	6	-6	0	145	149	6	-2	1	325	-365	8	-4	-8	132	130
h	-9	0	191	182	5	-3	-7	253	-225	6	-6	5	126	-128	6	-2	4	109	93	8	-4	-4	193	181
h	-8	-3	117	-118	5	-3	-6	320	297	6	-6	6	103	124	7	-8	-5	143	-150	8	-4	-3	174	-154

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 Grønbaek<sup>15</sup>, with anisotropic temperature factors was employed. The  $R$ -index was 6.5 % omitting unobserved 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.  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  has the same structure as  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ ;<sup>7</sup> 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  $[\text{Mn}_2\text{Cl}_6, 4\text{H}_2\text{O}]^{2-}$ .

The main difference between the unit cell of  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  and of  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$  is, that the  $c$ -axis in  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  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  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  is smaller than that of  $\beta\text{-RbMnCl}_3$ ,

$2\text{H}_2\text{O}$  ( $353 \text{ \AA}^3$  and  $358 \text{ \AA}^3$ ). The distortion causes only minor changes in the bond lengths within the Mn-octahedra. The Mn—O distances in the potassium compound are  $2.18 \text{ \AA}$  and  $2.19 \text{ \AA}$  compared with  $2.20 \text{ \AA}$  and  $2.23 \text{ \AA}$  in the rubidium compound. Two of the four Mn—Cl bonds are rather long,  $2.59 \text{ \AA}$  and  $2.57 \text{ \AA}$  (compared with  $2.62 \text{ \AA}$  and  $2.54 \text{ \AA}$  in  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ ), the two other bonds are rather short,  $2.48 \text{ \AA}$  and  $2.49 \text{ \AA}$  ( $2.49 \text{ \AA}$  and  $2.50 \text{ \AA}$  in  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ ).

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  $3.51 \text{ \AA}$  to  $4.19 \text{ \AA}$  and the two others in distances varying from  $3.14 \text{ \AA}$  to  $3.27 \text{ \AA}$ . But a short and a long Cl—O distance have been interchanged; the  $\text{Cl}_{\text{II}}\text{—O}_{\text{II}}$  bond is  $3.14 \text{ \AA}$  in  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  and  $3.78 \text{ \AA}$  in  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ , whereas the  $\text{Cl}_{\text{III}}\text{—O}_{\text{II}}$  bond is  $4.19 \text{ \AA}$  in  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  and  $3.18 \text{ \AA}$  in  $\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$ . 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  $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$  corresponding to this suggestion are  $96.2^\circ$  and  $87.5^\circ$ ; both values are smaller than the normal H—O—H angle  $109.5^\circ$ , so the hydrogen atoms must be positioned a little away from the Cl—O vectors.

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