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The Crystal Structures of α- and of β-$RbMnCl_3,2H_2O$

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The crystal structures of α- and of β-$RbMnCl_3,2H_2O$ have been determined by three dimensional Patterson and Fourier methods and the parameters refined by least squares computations. α-$RbMnCl_3,2H_2O$ is orthorhombic, space group *Pcca* with $a = 9.005$ Å, $b = 7.055$ Å, $c = 11.34$ Å. β-$RbMnCl_3,2H_2O$ is triclinic, space group $P\bar{1}$ with $a = 6.65$ Å, $b = 7.01$ Å, $c = 9.03$ Å, $\alpha = 92.3°$, $\beta = 109.4°$, $\gamma = 112.9°$. In both structures the manganese atom is octahedrally coordinated to four chlorine atoms and to two water molecules. The water molecules occupy *cis*-positions in the α-form and *trans*-positions in the β-form. The octahedra in the α-compound form infinite chains by corner sharing at a chlorine atom. The β-form contains discrete ions $[Mn_2Cl_6,4H_2O]^{2-}$.

Saunders [1] investigated aqueous solutions containing manganous chloride and a chloride of alkali metal or of ammonium with the intention of preparing double halides. The existence of $CsMnCl_3,2H_2O$ (orthorhombic), $Cs_2MnCl_4,2H_2O$ (triclinic), $Rb_2MnCl_4,2H_2O$ (triclinic), $KMnCl_3,2H_2O$ (triclinic), and $(NH_4)_2MnCl_4,2H_2O$ (monoclinic) was reported, whereas the attempt to prepare $RbMnCl_3,2H_2O$ was unsuccessful. This compound has now been obtained from a solution of $MnCl_2,4H_2O$ and RbCl (molar ratio 5:1) in hydrochloric acid. $RbMnCl_3,2H_2O$ exists in two crystal modifications; α-$RbMnCl_3,2H_2O$ (orthorhombic) is the stable form at 0°C, and β-$RbMnCl_3,2H_2O$ (triclinic) is the stable form at 25°C. Their structures have been determined to explain the difference between the two modifications. The present study forms part of a series of crystal structure investigations of hydrated halides containing manganese and alkali metals.[2–4]

EXPERIMENTAL

A mixture of α- and β-$RbMnCl_3,2H_2O$ is precipitated, when a saturated solution of $MnCl_2,4H_2O$ and RbCl (molar ratio 5:1) in 8 M HCl is cooled from 50°C to 20°C. A transformation from α-$RbMnCl_3,2H_2O$ to the β-form takes place if this mixture is allowed to stay in the mother-liquor for several months at 25°C, whereas β-$RbMnCl_3,2H_2O$ will be transformed to the α-form in the same time, if the temperature is 0°C. α-$RbMnCl_3,2H_2O$ forms pink needle shaped crystals. β-$RbMnCl_3,2H_2O$ is precipitated as a white

powder, but a grain growth during the above-mentioned period changes the powder to bigger pink crystals often forming cross-shaped twins.

Chemical analysis gave the following results: α-$RbMnCl_3,2H_2O$: Mn 19.63; Cl 37.65; H_2O 12.87; Rb 29.85. β-$RbMnCl_3,2H_2O$: Mn 19.49; Cl 37.49; H_2O 13.00; Rb 30.02. Calc.: Mn 19.43; Cl 37.61; H_2O 12.74; Rb 30.22. Mn was determined by complexometric titration with EDTA, Cl by potentiometric titration using $AgNO_3$ and the water gravimetrically by heating to 110°C. Rb was calculated as the balance. α- and β-$RbMnCl_3,2H_2O$ are losing the water at 69°C and 83°C, respectively. Both compounds have a density of 2.60 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 rubidium chloride as reference ($a_{RbCl} = 6.592$ Å). Fe$K\alpha$-radiation (Fe$K\alpha = 1.9360$ Å) was employed. Three dimensional intensity data were obtained from Weissenberg photographs by the multiple film technique using Mo$K\alpha$ radiation. The α-$RbMnCl_3,2H_2O$ data were collected with a crystal (dimension: 0.300 × 0.050 × 0.050 mm) oriented along the needle-axis (a-axis). Reflexions $0kl-5kl$ and $h0l$ were recorded and scaled together. The β-$RbMnCl_3,2H_2O$ data were obtained from two irregularly shaped single crystals (maximum dimension: 0.150 mm) oriented along [011] and [111], respectively. Eight levels around [011] and six levels around [111] were recorded. The intensities of the reflexions were measured on a Joyce-Loebl double-beam densitometer. 379 and 758 observed independent reflexions were obtained from the α- and from the β-compound, respectively. Corrections for Lorentz- and polarization-factors were computed, but no corrections for absorption were applied in spite of the rather high absorption coefficient ($\mu = 103$ cm^{-1}).

STRUCTURE DETERMINATION OF α-$RbMnCl_3,2H_2O$

The powder pattern of α-$RbMnCl_3,2H_2O$ shows that it is probably isostructural with $CsMnCl_3,2H_2O$.[2] Therefore structure-factors were calculated using the coordinates and temperature-factors of the atoms from this compound. The atomic scattering factors were taken from Vol. III of *International Tables of Crystallography* [5] and their parameters calculated according to the interpolation formula of Bassi.[6] A three dimensional Fourier synthesis was evaluated with signs obtained from this structure-factor calculation. A program written by Lauesen [7] was used. The electron density maps resulting from this synthesis led to better coordinates of all atoms.

The Bhuiya-Stanley [8] method was used for refinement. An ALGOL-program, D 45, written by Danielsen [9] was employed. With individual isotropic temperature factors the R-value was reduced to 8.8 % after a series of six cycles of refinements. At this stage a difference Fourier synthesis was evaluated. Peaks and troughs of electron density were observed around the Rb- and the Mn-atom. This effect must be due to anisotropy of the thermal motions or to absorption effects. The refinement was continued with anisotropic temperature factors using a block-diagonal least-squares ALGOL-program, G 3, written by Grønbæk.[10] After five cycles of refinement the R-value dropped to 5.7 %.

STRUCTURE DETERMINATION OF β-$RbMnCl_3,2H_2O$

The crystals showed no piezo-electric effect, so a centre of symmetry might be present. In a three dimensional Patterson function several prominent peaks with equal heights could be seen. These peaks must be due to overlapping

Table 1. Crystal data.

	α-$RbMnCl_3,2H_2O$	β-$RbMnCl_3 2H_2O$
Crystal system :	orthorhombic	triclinic
Space group :	$Pcca-D_{2h}^{8}$	$P\bar{1}-C_i^1$
Formula units per unit cell :	4	2
Unit cell :	$a = 9.005 \pm 0.005$ Å	$a = 6.65 \pm 0.01$ Å
	$b = 7.055 \pm 0.005$ Å	$b = 7.01 \pm 0.01$ Å
	$c = 11.340 \pm 0.005$ Å	$c = 9.03 \pm 0.01$ Å
		$\alpha = 92.3 \pm 0.1°$
		$\beta = 109.4 \pm 0.1°$
		$\gamma = 112.9 \pm 0.1°$
Density, calculated (20°C) :	2.62 g/cm³	2.62 g/cm³
Density, measured (20°C) :	2.60 g/cm³	2.60 g/cm³
Absorption coefficient(Mo$K\alpha$):	103 cm^{-1}	103 cm^{-1}
Residual factor, $R(hkl)$:	5.7 %	7.7 %

including all observed reflexions with $\sin\theta/\lambda < 0.7$.

Table 2. 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 factor coefficients and standard deviations (in brackets) have been multiplied by 10^4.

α-$RbMnCl_3,2H_2O$

Atom	x/a	y/b	z/c	B Å²
O	0.0738 (12)	0.6793 (12)	0.3716 (7)	2.0
Cl_I	0.2500 (0)	0.5000 (0)	0.1476 (4)	1.9
Cl_{II}	0.0866 (5)	0.2023 (4)	0.3893 (3)	1.5
Mn	0.0000 (0)	0.4600 (3)	0.2500 (0)	0.9
Rb	0.2500 (0)	0.0000 (0)	0.1475 (2)	3.0

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O	22 (22)	112 (17)	57 (8)	−70 (28)	25 (19)	−86 (18)
Cl_I	39 (11)	114 (7)	39 (2)	− 5 (12)	0 (0)	0 (0)
Cl_{II}	54 (9)	82 (4)	31 (2)	− 2 (9)	−3 (5)	16 (4)
Mn	45 (8)	46 (14)	27 (1)	0 (0)	−3 (5)	0 (0)
Rb	138 (6)	152 (3)	63 (1)	152 (7)	0 (0)	0 (0)

β-$RbMnCl_3,2H_2O$

Atom	x/a	y/b	z/c	B Å²
O_I	0.7485 (23)	0.7514 (26)	0.4915 (21)	3.7
O_{II}	0.7466 (26)	0.4410 (28)	0.1667 (21)	2.7
Cl_I	0.2442 (8)	0.7204 (8)	0.4960 (7)	2.0
Cl_{II}	0.7704 (8)	0.9588 (9)	0.1857 (7)	2.0
Cl_{III}	0.2461 (8)	0.4279 (8)	0.1646 (7)	1.9
Mn	0.9977 (5)	0.3331 (5)	0.3296 (4)	1.0
Rb	0.2589 (4)	0.9352 (4)	0.1774 (3)	2.3

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O_I	164 (47)	234 (59)	179 (39)	306 (94)	136 (72)	124 (78)
O_{II}	294 (53)	264 (55)	115 (32)	439 (95)	153 (69)	202 (71)
Cl_I	141 (14)	58 (14)	84 (10)	−16 (25)	112 (21)	−46 (20)
Cl_{II}	165 (14)	110 (15)	69 (9)	102 (25)	85 (18)	−15 (20)
Cl_{III}	151 (13)	107 (13)	85 (10)	129 (24)	115 (19)	32 (19)
Mn	80 (7)	85 (7)	62 (5)	102 (13)	56 (9)	44 (10)
Rb	187 (6)	194 (7)	95 (4)	217 (11)	94 (8)	68 (9)

vectors. Among several possible solutions a trial structure was chosen which gave the largest Rb—Rb-distances. $P\bar{1}$ was assumed. A three dimensional Fourier synthesis was calculated using signs based on the positions of the Rb- and of the Mn-atoms of the trial structure. In the Fourier maps all Cl- and O-atoms appeared clearly.

Table 3. Interatomic distances under 4.0 Å and, in brackets, standard deviations × 10^3 Å. Hydrogen bonds are indicated with h.

α-$RbMnCl_3,2H_2O$

Within octahedra

Mn	—	Cl_I	2.549	(2)	Cl_{II}	—	Cl_{II}	3.524	(4)
Mn	—	Cl_{II}	2.531	(3)	Cl_I	—	O	3.252	(9)
Mn	—	O	2.177	(9)	Cl_I	—	O	3.186	(11)
Cl_I	—	Cl_{II}	3.754	(4)	Cl_{II}	—	O	3.373	(9)
Cl_I	—	Cl_{II}	3.711	(4)	O	—	O	3.061	(12)

Between neighbouring octahedra

Cl_I	—	Cl_{II}	3.892	(4)	Cl_{II}	—	O	3.176	(12) h
Cl_I	—	O	3.730	(9)	Cl_{II}	—	O	3.183	(9) h
Cl_{II}	—	O	3.697	(9)					

From the rubidium-atom

Rb	—	Cl_I	3.528	(0)	Rb	—	Cl_{II}	3.573	(3)
Rb	—	Cl_{II}	3.424	(3)	Rb	—	O	3.755	(9)
Rb	—	Cl_{II}	3.377	(4)	Rb	—	O	3.697	(10)

β-$RbMnCl_3,2H_2O$

Within octahedra

Mn	—	Cl_I	2.624	(5)	Cl_{II}	—	Cl_{III}	3.635	(7)
Mn	—	Cl_I	2.543	(7)	Cl_I	—	O_I	3.374	(19)
Mn	—	Cl_{II}	2.488	(6)	Cl_I	—	O_I	3.332	(20)
Mn	—	Cl_{III}	2.501	(7)	Cl_I	—	O_{II}	3.403	(14)
Mn	—	O_I	2.202	(18)	Cl_I	—	O_{II}	3.281	(20)
Mn	—	O_{II}	2.228	(20)	Cl_{II}	—	O_I	3.336	(13)
Cl_I	—	Cl_I	3.530	(6)	Cl_{II}	—	O_{II}	3.453	(22)
Cl_I	—	Cl_{II}	3.628	(9)	Cl_{III}	—	O_I	3.391	(21)
Cl_I	—	Cl_{III}	3.566	(9)	Cl_{III}	—	O_{II}	3.365	(21)

Between neighbouring octahedra

Mn	—	Mn	3.774	(6)	Cl_{III}	—	O_I	3.469	(13)
Cl_{II}	—	Cl_{III}	3.930	(7)	Cl_{III}	—	O_{II}	3.287	(21) h
Cl_I	—	O_I	3.289	(19) h	Cl_{III}	—	O_{II}	3.175	(21) h
Cl_I	—	O_I	3.681	(20)	O_I	—	O_I	3.729	(21)
Cl_{II}	—	O_I	3.192	(21) h	O_I	—	O_I	3.832	(21)
Cl_{II}	—	O_{II}	3.566	(22)	O_I	—	O_{II}	3.575	(29)
Cl_{II}	—	O_{II}	3.784	(14)					

From the rubidium-atom

Rb	—	Cl_I	3.313	(6)	Rb	—	Cl_{III}	3.493	(7)
Rb	—	Cl_I	3.492	(4)	Rb	—	Cl_{III}	3.622	(4)
Rb	—	Cl_{II}	3.315	(7)	Rb	—	O_I	3.662	(20)
Rb	—	Cl_{II}	3.342	(7)	Rb	—	O_{II}	3.767	(18)
Rb	—	Cl_{II}	3.350	(7)	Rb	—	O_{II}	3.792	(16)
Rb	—	Cl_{III}	3.520	(7)	Rb	—	O_{II}	3.975	(21)

Table 4. Observed and calculated structure factors. F_{obs} and F_{calc} have been multiplied by 10.

α-$RbMnCl_3.2H_2O$

h	k	l	Fobs	Fcalc
0	0	4	1778	-1918
0	0	8	1345	1471
0	0	10	702	-671
0	1	2	744	711
0	1	4	1167	-1299
0	1	6	770	826
0	1	8	310	-270
0	1	10	275	243
0	1	12	286	-275
0	1	14	268	180
0	2	0	1200	1250
0	2	2	1372	-1266
0	2	4	409	321
0	2	6	562	539
0	2	8	315	310
0	2	10	1098	-1136
0	2	12	445	454
0	2	14	334	287
0	3	0	259	-239
0	3	2	291	227
0	3	4	633	-611
0	3	6	896	894
0	3	8	351	-335
0	3	10	210	-186
0	3	14	392	383
0	4	0	1649	1635
0	4	2	605	-576
0	4	4	660	-662
0	4	6	286	260
0	4	8	524	534
0	4	10	521	-519
0	5	0	585	599
0	5	2	200	168
0	5	4	703	-726
0	5	8	213	189
0	5	10	290	263
0	6	0	944	944
0	6	2	234	-196
0	6	4	692	-692
0	6	6	352	335
0	6	8	366	344
0	6	10	307	-291
0	7	2	214	-191
0	7	4	212	221
0	7	6	227	223
0	7	10	334	-300
0	8	0	585	402
0	8	2	389	393
0	8	4	279	252
0	8	6	870	981
0	8	8	310	320
0	8	10	891	-958
0	8	12	589	602
0	8	14	228	-190
0	9	0	196	297
0	9	2	632	-584
0	9	4	254	-277
0	9	6	338	354
0	9	8	222	-187
0	9	10	237	266
0	9	12	493	526
0	9	14	346	-344
0	10	0	205	-207
0	10	2	212	163
0	10	4	230	-205
0	10	6	261	203
0	10	8	202	-142
0	10	10	1927	-2046
0	10	12	918	-906
0	10	14	581	598
0	11	2	540	549
0	11	4	906	986
0	11	6	171	131
0	11	8	551	-574
0	11	10	176	125
0	12	0	1069	1013
0	12	2	196	173
0	12	4	865	947
0	12	6	236	-219
0	12	8	246	248
0	12	10	209	243
0	13	2	428	475
0	13	4	449	-528
0	13	6	568	-668
0	13	8	428	-522
0	13	10	307	-351
0	14	2	516	569
0	14	4	906	986
0	14	6	171	131
0	14	8	551	-574
0	14	10	176	125
1	2	10	261	-231
1	2	11	389	-375
1	2	12	305	289
1	3	1	282	-226
1	3	2	653	-674
1	3	3	729	774
1	3	4	168	145
1	3	5	465	-454
1	3	6	348	352
1	3	9	307	-287
1	3	11	371	377
1	4	1	1053	1059
1	4	2	914	-922
1	4	3	200	115
1	4	4	536	530
1	4	5	474	451
1	4	7	745	-779
1	4	8	589	-596
1	4	9	366	375
1	4	12	384	375
1	4	13	241	196
1	5	1	5225	-5311
1	5	2	170	-118
1	5	3	379	351
1	5	4	277	258
1	5	5	415	-391
1	5	7	425	429
1	5	8	301	-293
1	5	9	291	-260
1	5	12	246	192
1	5	13	222	-195
1	6	2	521	-513
1	6	3	702	-725
1	6	4	341	327
1	6	5	465	480
1	6	6	275	285
1	6	8	401	-386
1	6	9	258	243
1	6	11	401	-423
1	6	12	264	246
1	7	1	350	-346
1	7	2	340	-338
1	7	5	263	258
1	7	6	322	-320
1	7	7	247	206
1	7	9	339	347
1	7	9	206	-172
1	8	1	359	381
1	8	2	490	-510
1	8	5	213	183
1	8	6	322	315
1	8	7	305	-318
1	8	8	189	-176
1	8	9	185	168
1	9	3	202	233
1	9	5	191	-215
2	0	4	1163	1287
2	0	6	1428	-1535
2	0	8	371	401
2	0	10	373	380
2	0	14	550	-586
2	1	2	932	967
2	1	3	172	-185
2	1	4	270	-230
2	1	5	411	-455
2	1	6	221	189
2	1	8	508	-553
2	1	9	319	339
2	1	10	537	571
2	1	12	259	-274
2	1	13	224	-218
2	2	0	1461	-1429
2	2	1	650	596
2	2	2	320	-279
2	2	3	456	-435
2	2	4	1889	2002
2	2	5	443	-447
2	2	6	1056	-1102
2	2	7	189	177
2	2	8	174	-146
2	2	9	256	274
2	2	10	193	148
2	2	12	243	255
2	2	13	188	-156
2	2	14	334	-337
2	3	0	1111	-1084
2	3	1	268	-247
2	3	2	576	549
2	3	5	315	305
2	3	6	245	219
2	3	8	440	-438
2	3	9	245	-258
2	3	10	245	256
2	3	12	183	-164
2	3	14	202	189
2	4	0	647	-646
2	4	1	539	-491
2	4	3	319	309
2	4	4	934	946
2	4	5	511	495
2	4	6	799	-813
2	4	9	387	-381
2	4	10	331	324
2	4	13	246	236
2	4	14	279	-328
2	5	0	338	-334
2	5	1	132	154
2	5	2	277	285
2	5	3	132	-140
2	5	6	159	-171
2	5	10	286	310
2	6	0	504	-507
2	6	1	384	372
2	6	2	185	157
2	6	3	297	-291
2	6	4	403	398
2	6	5	331	-336
2	6	6	399	-397
2	6	7	156	130
2	6	9	240	243
2	6	10	290	304
2	7	0	239	-251
2	7	4	293	304
2	8	0	597	-648
2	8	2	196	206
2	8	4	304	309
2	8	8	265	-284
3	0	4	395	-423
3	0	6	1325	-1445
3	0	8	408	377
3	0	10	438	451
3	1	2	581	595
3	1	3	294	234
3	1	4	174	-174
3	1	5	148	-171
3	1	6	279	-282
3	1	8	165	134
3	2	1	282	253
3	2	2	391	365
3	2	3	350	-333
3	2	4	384	-357
3	2	5	342	343
3	2	7	261	-236
3	2	8	844	865
3	2	10	203	-178
3	2	12	580	-586
3	2	14	182	182
3	3	1	568	-549
3	3	2	195	180
3	3	3	356	320
3	3	4	382	-375
3	3	5	244	-230
3	3	7	288	293
3	3	8	417	421
3	3	9	278	-284
3	3	11	211	191
3	3	12	284	-280
3	4	1	363	368
3	4	2	1081	1035
3	4	3	489	-462
3	4	4	400	-377
3	4	5	479	446
3	4	6	578	-554
3	4	7	308	-314
3	4	8	400	406
3	4	9	242	223
3	4	11	220	-192
3	4	12	218	-216
3	5	1	568	-529
3	5	2	629	620
3	5	3	378	363
3	5	5	255	-265
3	5	6	392	-388
3	5	7	283	299
3	5	9	291	-311
3	5	11	236	234
3	6	1	276	289
3	6	2	777	778
3	6	3	368	-387
3	6	4	272	-269
3	6	5	410	421
3	6	6	466	-474
3	6	7	319	-310
3	6	8	303	308
3	6	9	200	178
3	7	1	363	-368
3	7	2	224	-158
3	7	3	276	285
3	7	4	152	-201
3	7	5	203	-207
3	7	7	226	207
3	7	8	220	259
3	7	9	248	-239
3	8	3	248	-263
3	8	4	216	-225
3	8	5	282	274
3	8	8	267	284
3	9	1	253	-244
4	0	6	296	333
4	0	8	430	435
4	0	10	980	-990
4	0	12	382	386
4	1	2	462	477
4	1	4	757	-811
4	1	5	296	-318
4	1	8	285	750
4	1	8	334	-328
4	1	9	333	291
4	2	0	2057	2094
4	2	1	373	371
4	2	2	808	-774
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5	1	1	183	-201
5	2	-10	188	-183
5	2	-5	228	218
5	2	-4	277	-304
5	2	-3	196	-205
5	3	-9	189	151
5	3	-8	178	-167
5	3	-3	202	173
5	4	-9	174	-168
5	4	-4	196	182
5	5	-8	108	112
6	-9	0	132	204
6	-8	-3	178	-279
6	-8	-2	181	-204
6	-8	-1	326	329
6	-8	0	147	171
6	-8	3	170	-219
6	-7	1	207	225
6	-7	2	126	-170
6	-7	3	167	-155
6	-7	4	139	97
6	-6	-5	205	188
6	-6	-3	231	-203
6	-6	-2	385	353
6	-6	-1	197	-195
6	-6	0	548	555
6	-6	1	194	175
6	-6	3	207	-193
6	-6	6	205	-194
6	-6	6	273	303
6	-5	-4	400	357
6	-5	-3	205	-227
6	-5	-2	237	-219
6	-5	0	71	112
6	-5	2	163	185
6	-5	3	234	-228
6	-5	4	178	-163
6	-4	-7	314	-317
6	-4	-6	220	-200
6	-4	-5	668	695
6	-4	-4	186	186
6	-4	-2	405	-370
6	-4	-1	344	-326
6	-4	1	668	674
6	-4	3	185	-156
6	-4	4	208	-213
6	-3	-7	151	-168
6	-3	-5	310	283
6	-3	-2	342	-317
6	-3	-1	256	-260
6	-3	0	205	208
6	-3	1	151	153
6	-3	4	217	-211
6	-2	-7	334	-321
6	-2	-6	305	-291
6	-2	-4	813	801
6	-2	-2	158	-167
6	-2	-1	417	-402
6	-2	0	187	-169
6	-2	2	564	589
6	-1	-8	238	224
6	-1	-7	204	-203
6	-1	-6	202	-222
6	-1	-5	171	168
6	-1	-4	177	98
6	-1	-1	299	-290
6	-1	0	224	-196
6	-1	1	267	288
6	0	-8	478	473
6	0	-6	374	-344
6	0	-5	193	-156
6	0	-3	677	707
6	0	-1	256	-230
6	0	0	274	-281
6	0	3	346	381
6	1	-6	174	-187
6	1	-5	166	-185
6	1	-4	255	254
6	1	0	109	-164
6	2	-11	136	-137
6	2	-8	434	427
6	2	-6	174	-156
6	2	-5	222	-241
6	2	-2	384	459
6	3	-9	127	132
6	3	-3	221	260
6	4	-7	245	288
7	-8	1	189	-222
7	-7	-2	185	172
7	-7	0	137	-107
7	-6	-4	275	-289
7	-6	-3	153	158
7	-6	-1	149	128
7	-6	0	151	130
7	-6	2	165	-237
7	-5	-5	75	-115
7	-5	-1	205	185
7	-4	-5	145	152
7	-4	-4	110	-177
7	-4	-3	274	-305
7	-4	-2	179	167
7	-4	0	122	103
7	-4	2	184	-153
7	-4	4	147	120
7	-3	-4	150	-155
7	-3	-3	156	160
7	-3	-2	138	-132
7	-3	0	165	174
7	-3	1	111	-143
7	-2	-8	189	-195
7	-2	-7	155	125
7	-2	-5	107	106
7	-2	-4	139	169
7	-2	-3	235	-207
7	-2	-2	234	-265
7	-2	-1	157	146
7	-1	-8	227	181
7	-1	-7	181	-145
7	-1	-5	165	182
7	-1	-3	148	-158
7	-1	-2	153	165
7	0	-8	200	-162
7	0	-7	164	-162
7	0	-3	183	168
7	0	-2	207	-202
7	1	-7	192	173
7	1	-6	138	-136
7	2	-7	139	-168
8	-8	-4	267	262
8	-8	0	210	-200
8	-7	-2	228	203
8	-7	-1	165	-136
8	-6	-5	276	-252
8	-6	-3	389	404
8	-6	-2	122	130
8	-6	-1	210	-152
8	-6	1	180	-181
8	-5	-7	271	237
8	-5	-6	150	-131
8	-5	-1	148	161
8	-5	0	173	-184
8	-4	-8	348	355
8	-4	-5	241	-218
8	-4	-4	245	-228
8	-4	-2	441	495
8	-4	1	197	-173
8	-3	-6	222	194
8	-3	-5	181	-184
8	-3	-4	121	-154
8	-3	1	193	-173
8	-2	-9	165	-156
8	-2	-7	443	440
8	-2	-4	252	-242
8	-2	-3	105	-127
8	-2	-1	408	446
8	-1	-4	170	-172
8	-1	-2	208	188
8	0	-6	174	484
8	0	-5	183	-174
8	0	0	242	303
9	-4	-6	153	-181
9	-4	-2	124	115
9	-3	-6	128	136
9	-2	-5	171	-157
9	-2	-4	124	95
9	-1	-5	126	136

The D 45 program was also used for β-$RbMnCl_3,2H_2O$. The *R*-value was 9.0 % after 6 cycles of refinement with isotropic temperature factors. Also in this compound effects of anisotropy around the Rb-atom in a subsequent difference Fourier could be seen. The refinement continued with program G 3 and was terminated at an *R*-value of 7.7 %.

CRYSTAL DATA

The crystal data are given in Table 1. The coordinates found, the temperature factors and standard deviations are given in Table 2, the interatomic distances in Table 3, and observed and calculated structure factors in Table 4.

DISCUSSION

In α- and in β-$RbMnCl_3,2H_2O$ the manganese atom is surrounded by four chlorine atoms and two water molecules forming distorted octahedra. In α-$RbMnCl_3,2H_2O$ (Fig. 1) the water molecules occupy *cis*-positions in the

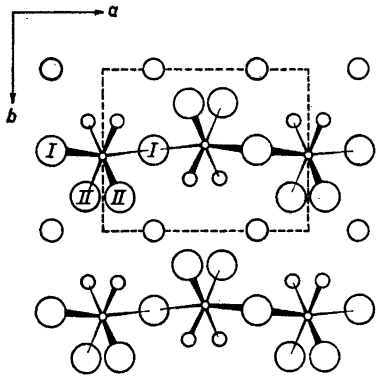

Fig. 1. α-$RbMnCl_3,2H_2O$. Projection of half the unit cell on (001).

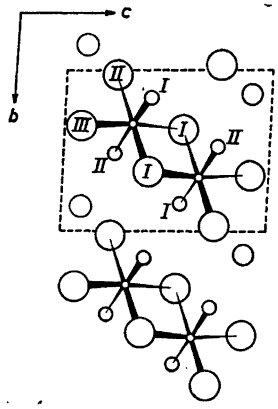

Fig. 2. β-$RbMnCl_3,2H_2O$. Projection on (100).

octahedra. The octahedra sharing corners are arranged in zig-zag chains. α-$RbMnCl_3,2H_2O$ is isostructural with $CsMnCl_3,2H_2O$.[2] In β-$RbMnCl_3,2H_2O$ (Fig. 2) the water molecules occupy *trans*-positions. The octahedra are joined in pairs by sharing edges and are thus forming groups $[Mn_2Cl_6,4H_2O]^{2-}$.

In both compounds the rubidium atoms have eight chlorine atoms as nearest neighbours. In α-$RbMnCl_3,2H_2O$ these eight atoms together with six oxygen atoms form a coordination similar to that in a body-centered cubic packing.[2] In β-$RbMnCl_3,2H_2O$ the eight chlorine atoms surround the rubidium atom in a CsCl arrangement.

The structures of α- and of β-$RbMnCl_3,2H_2O$ can be described as layer-structures (Fig. 3). The layers contain the Cl-, Rb-, and O-atoms. Between

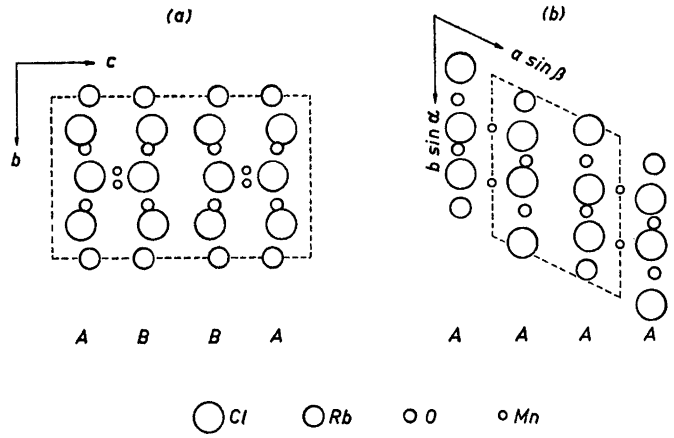

Fig. 3. (a) α-$RbMnCl_2,2H_2O$ seen in the direction of the *a*-axis. (b) β-$RbMnCl_3,2H_2O$ seen in the direction of the *c*-axis. The figure shows the layer-sequence in the two structures.

these layers the Mn-atoms are placed. Each layer consists of chains of Cl-atoms only, alternating with chains containing both the Rb- and the O-atoms (Figs. 4 and 5). In α-$RbMnCl_3,2H_2O$ the layers are parallel to (001); in

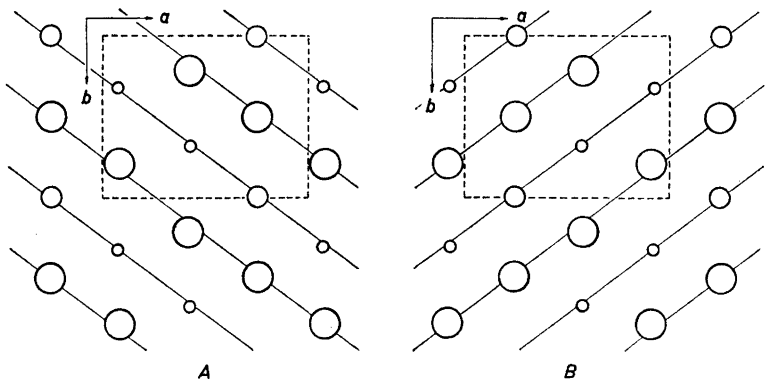

Fig. 4. α-$RbMnCl_3,2H_2O$. A- and B-layer. The alternating chains of Cl-atoms and of Rb- and O-atoms can be seen.

β-$RbMnCl_3,2H_2O$ the layers are parallel to (100). Two sorts of layers, A and B, exist in α-$RbMnCl_3,2H_2O$ (Fig. 4). In the A-layers the chains are parallel to [110], whereas the chains in the B-layers are parallel to [1$\bar{1}$0]. The layer-sequence in the α-form is:

—A—Mn—B—B—Mn—A—

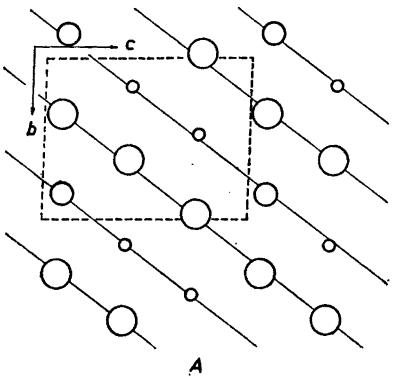

Fig. 5. β-$RbMnCl_3,2H_2O$. A-layer. The atoms are placed approximately in the same way as in the A-layers in α-$RbMnCl_3,2H_2O$.

In β-$RbMnCl_3,2H_2O$ (Fig. 5) the chains in all the layers are parallel to [011], so the sequence will be:

—A—Mn—A—A—Mn—A—

In both compounds the oxygen atoms have four chlorine atoms as nearest neighbours outside of the coordination polyhedron of the manganese atom. Two of the four chlorine atoms are placed at distances varying from 3.47 Å to 3.78 Å from the oxygen atom, and the two others are placed in distances from 3.18 Å to 3.29 Å from this atom. It is assumed, that the latter distances correspond to hydrogen bonds. The corresponding Cl—O—Cl angles are 108.1° in α-$RbMnCl_3,2H_2O$ and 101.6° and 102.8° in β-$RbMnCl_3,2H_2O$.

The occurrence of *cis-trans* isomerism in kinetically labile coordination compounds is rather uncommon. This work gives probably the first example with established *cis-trans* isomerism as explanation of the polymorphism. Another possible example is α- and β-$MnCl_2,4H_2O$. In the α-form, investigated by Zalkin, Forrester and Templeton,[11] the manganese atom is surrounded by four water molecules and two chlorine atoms in *cis*-octahedral coordination. If β-$MnCl_2,4H_2O$ is isostructural with $FeCl_2,4H_2O$ (Penfold and Grigor [12]) as suggested by Groth [13] the Cl-atoms here will occupy *trans*-positions in the octahedra. In $NaBr,2H_2O$ (Culot, Piret and Van Meersche [14]) the sodium atom is octahedrally coordinated to four water molecules and to two bromine atoms with the halide atoms adjacent. In $(C_6H_5)_4AsRuCl_4(H_2O)_2,H_2O$ (Hopkins, Zalkin, Templeton and Adamson [15]) two water molecules occupy *cis*-positions in the $RuCl_4(H_2O)_2^-$-octahedra. The existence of *trans*-isomers of the two latter compounds has not been published.

In α-$RbMnCl_3,2H_2O$ the Mn—O distance is 2.18 Å, and in the β-form the Mn—O distances are 2.20 Å and 2.23 Å. The differences are less than three times the largest of the estimated standard deviations of the bond lengths. In $MnCl_2,2H_2O$ (Morosin and Graeber [16]) with *trans*-octahedra in chains the Mn—O bond is 2.15 Å, and in $MnCl_2,4H_2O$ (Zalkin, Forrester and Templeton [11]) with isolated *cis*-octahedra the average Mn—O distance is 2.21 Å. The distances from manganese to chlorine vary in the *cis*-compounds from 2.48 Å

($MnCl_2,4H_2O$) to 2.55 Å (α-$RbMnCl_3,2H_2O$) and in the *trans*-compounds from 2.49 Å to 2.62 Å (β-$RbMnCl_3,2H_2O$).

In both compounds the $Mn-Cl_I$ bonds are longer than the other Mn—Cl bonds. The reason for this difference is probably that the Cl_I atoms are in contact with two Mn atoms (Figs. 1 and 2). The same difference can be seen in $CsMnCl_3,2H_2O$. In α-$RbMnCl_3,2H_2O$ the $Mn-Cl_{II}$ bond is opposite to a Mn—O bond. In $(C_6H_5)_4AsRuCl_4(H_2O)_2,H_2O$ and $Cs_2RuCl_5H_2O$ (Hopkins, Zalkin, Templeton and Adamson [17]) with chlorine and oxygen around ruthenium in discrete octahedra, the metal-chlorine bonds opposite the oxygens in the octahedra are shorter than those for which the opposite atoms are both chlorine atoms (2.33 Å and 2.31 Å compared with 2.36 Å and 2.35 Å).

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REFERENCES

1. Saunders, C. E. *Am. Chem. J.* **14** (1892) 127.
2. Jensen, S. J., Andersen, P. and Rasmussen, S. E. *Acta Chem. Scand.* **16** (1962) 1890.
3. Jensen, S. J. *Acta Chem. Scand.* **18** (1964) 2085.
4. Jensen, S. J. *7th Intern. Congr. Moscow* 1966, A 59.
5. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 202.
6. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
7. Lauesen, S. Fourier program, GIER machine code, printed at Regnecentralen.
8. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
9. Danielsen, J. Algol program, D 45, printed at the Department of Inorganic Chemistry, University of Aarhus.
10. Grønbæk Hazell, R. Algol program, G 3, printed at the Department of Inorganic Chemistry, University of Aarhus.
11. Zalkin, A., Forrester, J. D. and Templeton, D. H. *Inorg. Chem.* **3** (1964) 529.
12. Penfold, B. R. and Grigor, J. A. *Acta Cryst.* **12** (1959) 850.
13. Groth, P. *Chemische Krystallographie*, Leipzig Vol. I. (1906).
14. Culot, J. P., Piret, P. and Van Meerssche, M. *Bull. Soc. Franc. Mineral. Crist.* **85** (1962) 282.
15. Hopkins, T. E., Zalkin, A., Templeton, D. H. and Adamson, M. G. *Inorg. Chem.* **5** (1966) 1427.
16. Morosin, B. and Graeber, E. J. *J. Chem. Phys.* **42** (1965) 898.
17. Hopkins, T. E., Zalkin, A., Templeton, D. H. and Adamson, M. G. *Inorg. Chem.* **5** (1966) 1431.

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