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The Crystal Structures of $Cs_2MnCl_4,2H_2O$ and $Rb_2MnCl_4,2H_2O$

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$Cs_2MnCl_4,2H_2O$ and $Rb_2MnCl_4,2H_2O$ are isomorphous and crystallize in the triclinic system; space group $P\bar{1}$ with $a = 5.74$ Å, $b = 6.66$ Å, $c = 7.27$ Å, $\alpha = 67.0°$, $\beta = 87.8°$, $\gamma = 84.3°$ for $Cs_2MnCl_4,2H_2O$, and $a = 5.66$ Å, $b = 6.48$ Å, $c = 7.01$ Å, $\alpha = 66.7°$, $\beta = 87.7°$, $\gamma = 84.8°$ for $Rb_2MnCl_4,2H_2O$. There is one formula unit per unit cell. The structures were determined from two-dimensional Patterson projections. Each manganese atom is octahedrally coordinated to four chlorine atoms and two water molecules. The water molecules occupy *trans*-positions.

$CsMnCl_3,2H_2O$ is formed at 20°C from aqueous solutions containing 0.01 mole CsCl and 0.01 mole $MnCl_2$.[1] Another hydrate, $Cs_2MnCl_4,2H_2O$, is formed in a similar way from solutions containing 0.02 mole CsCl and 0.01 mole $MnCl_2$. From aqueous solutions containing RbCl and $MnCl_2$ only one compound, $Rb_2MnCl_4,2H_2O$, is formed at 20°C. The crystal structure of $CsMnCl_3,2H_2O$ has previously been reported.[1] A previous note [2] communicated preliminary results from an X-ray investigation of $Cs_2MnCl_4,2H_2O$ and $Rb_2MnCl_4,2H_2O$. The crystal structures of these compounds were determined to investigate the coordination around the manganous ion and the location of the water molecules. Saunders [2a] reported the existence of the three double halides.

EXPERIMENTAL

$Cs_2MnCl_4,2H_2O$ was prepared from an aqueous solution containing 0.02 mole CsCl and 0.01 mole $MnCl_2,4H_2O$ (Merck p.a.) and slow evaporation at 20°C. The crystals formed pale pink prisms elongated along the [011] direction. Chemical analysis gave the following results: Mn 10.90; Cl 28.25; H_2O 7.55; Cs 53.30. Calc. for $Cs_2MnCl_4,2H_2O$: Mn 11.01; Cl 28.45; H_2O 7.23; Cs 53.31. Mn was determined by complexometric titration with EDTA, Cl by potentiometric titration using $AgNO_3$, and the water gravimetrically by heating to 105°C. Cs was calculated as the balance. The crystals decompose at 84°C. The density was 3.23 g/cm³ (20°C) as measured by flotation in a mixture of acetylene tetrabromide and methylene iodide.

$Rb_2MnCl_4,2H_2O$ was prepared in a similar way using RbCl and $MnCl_2,4H_2O$ and showed the same shape and colour as the cesium compound. Chemical analysis gave:

Mn 13.49; Cl 34.78; H_2O 9.08; Rb 42.65. Calc. for $Rb_2MnCl_4,2H_2O$: Mn 13.60; Cl 35.13; H_2O 8.92; Rb 42.35. The crystals decompose at 93°C. The density was 2.81 g/cm³ (20°C) as measured in a mixture of carbon tetrachloride and acetylene tetrabromide.

Unit cell dimensions were determined from Guinier powder diagrams using CsCl or RbCl as reference. Fe$K\alpha$ radiation was employed. The choice of unit cell in the triclinic system followed the rules according to the Dirichlet reduced cell (Balashov and Ursell [3]): $|a| < |b| < |c|$, where a, b, and c are the three shortest noncoplanar translations. α, β, and γ are homogeneous, *i.e.* either all acute or all obtuse. The powder diagrams showed that $Cs_2MnCl_4,2H_2O$ and $Rb_2MnCl_4,2H_2O$ are probably isostructural.

Microscopic and X-ray examinations of crystals of $Cs_2MnCl_4,2H_2O$ and $Rb_2MnCl_4,2H_2O$ revealed that they were generally twinned with twin-axis normal to (011). For intensity measurements crystal fragments, which appeared to be untwinned, were used. The dimensions of the $Cs_2MnCl_4,2H_2O$-crystals were 0.060 × 0.150 × 0.400 mm³ and 0.050 × 0.150 × 0.200 mm³ and the dimensions of the $Rb_2MnCl_4,2H_2O$-crystals were 0.050 × 0.300 × 0.200 mm³ and 0.050 × 0.100 × 0.200 mm³. Because of the rather high absorption coefficients of the crystals ($\mu Cs_2MnCl_4,2H_2O$ = 100 cm^{-1} and $\mu Rb_2MnCl_4,2H_2O$ = 139 cm^{-1} for Mo$K\alpha$) and because of their shape, intensity measurements are affected by absorption errors. It was not possible due to clevage to grind the crystals to a more ideal shape. However, no correction for absorption was applied.

The $h0l$ and $0kl$ reflexions were recorded with the smaller $Cs_2MnCl_4,2H_2O$- and $Rb_2MnCl_4,2H_2O$-crystals and the $hk0$ reflexions with the bigger crystals. Integrated Weissenberg photographs were prepared using Mo$K\alpha$ radiation. The multiple film technique with Ni-foil interleaves was employed. The intensities of the reflexions were measured on a Joyce-Loebl double-beam densitometer and corrected for Lorentz- and polarization-factors using a digital computer. The crystals showed no piezo-electric effect. Thus a centre of symmetry might be present.

STRUCTURE DETERMINATION OF $Cs_2MnCl_4,2H_2O$

The unit cell contains one unit of $Cs_2MnCl_4,2H_2O$. Thus the Mn-atom must occupy a special position if a centre of symmetry is present. The parameters of the cesium and of the manganese atoms were obtained from (100) and (010) Patterson projections. When the Cs-atom is placed in x, y, z and $-x$, $-y$, $-z$, the Mn-atom must be at 0, ½, ½ and the space group $P\bar{1}$ is possible. The signs of the structure factors $F(h0l)$ and $F(0kl)$ were calculated from the contributions of the Cs- and Mn-atoms. The positions of the Cl- and O-atoms were obtained from Fourier projections along the a- and b-axes using these signs.

For refinement a method suggested by Bhuiya and Stanley [4] was used. The geometric parameters and individual isotropic temperature factors of each atom are varied in turn and the values yielding the lowest residual factor, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, are chosen. For the computations an Algol-programme written for the computer GIER by Danielsen [5] was used.

The atomic scattering factors were calculated by means of the following expression according to Bassi:[6]

$$f(x) = N - \frac{x}{a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4}$$

where $x = \sin\Theta/\lambda$ and N = the atomic number of the atom. The parameters used are given in Table 1.

The $h0l$, $0kl$, and $hk0$ reflexions were first refined individually. A series of 6 cycles of refinements was computed for each projection. The R-values

Table 1. Parameters for the atomic scattering factor.

	N	a_0	a_1	a_2	a_3	a_4
Cs	55	2.4224×10^{-3}	-3.2128×10^{-3}	6.5857×10^{-2}	-8.3668×10^{-2}	4.9582
Rb	36	4.5857×10^{-3}	-7.1539×10^{-3}	7.7647×10^{-2}	-6.2351×10^{-2}	2.7202×10^{-2}
½Mn	12½	4.5925×10^{-3}	2.8568×10^{-2}	1.0014×10^{-1}	-1.2940×10^{-1}	1.1959×10^{-1}
Cl	17	5.3006×10^{-3}	3.1046×10^{-3}	2.0229×10^{-2}	1.9064×10^{-1}	-1.5990×10^{-1}
O	8	1.1906×10^{-2}	5.1983×10^{-3}	8.1682×10^{-2}	9.5267×10^{-2}	-4.2875×10^{-2}

were reduced from $R(h0l) = 43$ %, $R(0kl) = 20.9$ % and $R(hk0) = 14.7$ % to $R(h0l) = 9.7$ %, $R(0kl) = 8.7$ % and $R(hk0) = 10.7$ % excluding all non-observed reflexions. Difference Fourier projections were evaluated at this stage. In the *h0l*- and *hk*0-difference synthesis small peaks and troughs of electron density could be seen around the Cs-atom. This is probably due to absorption effects. Because of the rather small *R*-values no attempt was made to eliminate these anomalies. Finally the three projections were refined together leaving an *R*-value at 9.9 %.

STRUCTURE DETERMINATION OF $Rb_2MnCl_4,2H_2O$

The powder pattern of $Rb_2MnCl_4,2H_2O$ shows that the structure of this compound is probably the same as that of $Cs_2MnCl_4,2H_2O$. Therefore the Rb- and Mn-atoms were given the same coordinates as the Cs- and Mn-atoms in the analogous cesium compound. Structure-factors were calculated from the contributions of these atoms. Fourier projections along the *a*- and *b*-axis using signs from the structure factor calculation gave the positions of the Cl- and O-atoms.

The Bhuiya-Stanley method of refinement was also used for Rb_2MnCl_4, $2H_2O$. The parameters for the atomic scattering factor for rubidium are recorded in Table 1. A series of 6 cycles of refinements was calculated for each projection. The *R*-values were reduced from $R(0kl) = 18.2$ %, $R(hk0) = 17.3$ % and $R(h0l) = 15.6$ % to $R(0kl) = 8.8$ %, $R(hk0) = 13.4$ % and $R(h0l) = 12.9$ %. Data from the three projections refined together gave $R(hkl) = 11.9$ %. The neglect of absorption errors is a probable explanation of the fact that the $R(hk0)$ and $R(h0l)$ values are greater than the $R(0kl)$-value. When the crystal is oriented along the *c*-axis the maximum and minimum dimensions at right angles to the axis of rotation are 0.300 mm and 0.050 mm. Difference Fourier projections evaluated at this stage confirmed this assumption. Anomalies of the patterns indicative of improper anisotropic absorption allowance were observed around the Rb-atom and to a small extent around the other atoms in the *hk*0- and *h0l*-projection. These anomalies appeared especially in the *hk*0-projection (Fig. 1). To improve the accuracy of the positions of the lighter atoms a method suggested by Kartha and Ahmed [7] was used. In the next cycle of refinement the rubidium atom was represented in the structure factor calculations by two isotropic, fractional atoms placed symmetrically around

the atom centre with the coordinates (0.214, 0.165, 0.117) and (0.264, 0.165, 0.117). By this method $R(hk0)$ was reduced to 10.6 % and $R(h0l)$ to 11.8 %. In difference projections evaluated after these calculations were carried out the anomalies practically disappeared. Finally all observed data were refined together leaving an R-value at 10.4 %. This method of refinement caused only minor changes in the positions of the lighter atoms.

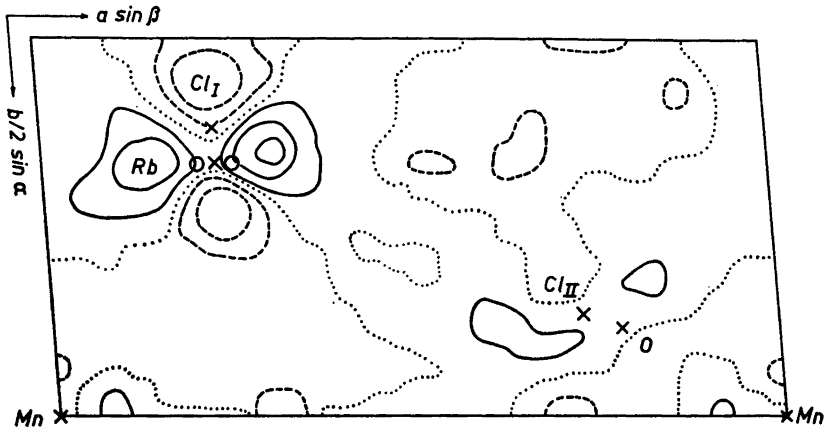

Fig. 1. $Rb_2MnCl_4,2H_2O$. Difference synthesis. Projection on (001) showing clover-leaf pattern obtained using $hk0$ data uncorrected for absorption. Contours are at intervals of 1 eÅ^{-2}; negative contours are broken and zero contours dotted. The small crosses show the final atom locations. The small circles show the Rb-atoms of half weight each.

CRYSTAL DATA

The pertinent crystal data are given below:

	$Cs_2MnCl_4,2H_2O$	$Rb_2MnCl_4,2H_2O$
Crystal system	: triclinic	triclinic
Space group	: $P\bar{1}-C_i^1$	$P\bar{1}-C_i^1$
Formula units per unit cell	: 1	1
Unit cell	: $a = 5.74 \pm 0.01$ Å	$a = 5.66 \pm 0.01$ Å
	: $b = 6.66 \pm 0.01$ Å	$b = 6.48 \pm 0.01$ Å
	: $c = 7.27 \pm 0.01$ Å	$c = 7.01 \pm 0.01$ Å
	: $\alpha = 67.0 \pm 0.1°$	$\alpha = 66.7 \pm 0.1°$
	: $\beta = 87.8 \pm 0.1°$	$\beta = 87.7 \pm 0.1°$
	: $\gamma = 84.3 \pm 0.1°$	$\gamma = 84.8 \pm 0.1°$
Density, calculated	: 3.25 g/cm^3	2.85 g/cm^3
Density, measured	: 3.23 g/cm^3	2.81 g/cm^3
Absorption coefficient(MoKα)	: 100 cm^{-1}	139 cm^{-1}
$F(000)$	: 219	181
Residual factor, $R(hkl)$	: 9.9 %	10.4 %

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

Table 2. Atomic coordinates, standard deviations and temperature factors.

Atom	x/a	y/b	z/c	σ_x Å	σ_y Å	σ_z Å	B Å²	σ_B Å²
				$Cs_2MnCl_4,2H_2O$				
Cs	0.244	0.168	0.115	0.003	0.003	0.004	3.7	0.05
Mn	0.000	0.500	0.500				0.6	0.15
Cl_I	0.774	0.877	0.375	0.013	0.012	0.014	1.5	0.2
Cl_{II}	0.259	0.630	0.192	0.012	0.011	0.012	1.1	0.2
O	0.771	0.378	0.353	0.030	0.028	0.030	0.7	0.5
				$Rb_2MnCl_4,2H_2O$				
Rb	0.239	0.165	0.117	0.005	0.005	0.005	1.8	0.1
Mn	0.000	0.500	0.500				0.9	0.1
Cl_I	0.757	0.879	0.373	0.010	0.009	0.010	1.7	0.2
Cl_{II}	0.259	0.638	0.170	0.010	0.009	0.010	1.5	0.2
O	0.781	0.377	0.345	0.031	0.030	0.031	2.3	0.5

Table 3. Interatomic distances in Å and, in brackets, standard deviations × 10^2 Å.

$Cs_2MnCl_4,2H_2O$.

Within octahedra			Between neighbouring octahedra		
$Mn-Cl_I$	2.54	(1)	Cl_I-Cl_I	4.09	(2)
$Mn-Cl_{II}$	2.54	(1)	Cl_I-Cl_I	4.03	(2)
$Mn-O$	2.13	(3)	Cl_I-Cl_{II}	4.03	(2)
Cl_I-Cl_{II}	3.57	(2)	Cl_I-Cl_{II}	4.14	(2)
Cl_I-Cl_{II}	3.62	(2)	$Cl_{II}-Cl_{II}$	4.55	(2)
Cl_I-O	3.24	(3)	Cl_I-O	3.28	(3)
Cl_I-O	3.39	(3)	Cl_I-O	3.81	(3)
$Cl_{II}-O$	3.29	(3)	$Cl_{II}-O$	3.99	(3)
$Cl_{II}-O$	3.34	(3)	$Cl_{II}-O$	3.25	(3)
			From the cesium-atom:		
$Cs-Cl_I$	3.61	(1)	$Cs-Cs$	4.49	(1)
$Cs-Cl_I$	3.70	(1)	$Cs-Cs$	4.72	(1)
$Cs-Cl_I$	3.52	(1)	$Cs-Cs$	4.21	(1)
$Cs-Cl_I$	3.60	(1)	$Cs-O$	3.56	(3)
$Cs-Cl_{II}$	3.40	(1)	$Cs-O$	3.62	(3)
$Cs-Cl_{II}$	3.35	(1)	$Cs-O$	4.15	(3)
$Cs-Cl_{II}$	3.54	(1)	$Cs-O$	4.15	(3)
$Cs-Cl_{II}$	3.58	(1)			

$Rb_2MnCl_4,2H_2O$.

Within octahedra:			Between neighbouring octahedra:		
$Mn-Cl_I$	2.54	(1)	Cl_I-Cl_I	4.07	(2)
$Mn-Cl_{II}$	2.58	(1)	Cl_I-Cl_I	3.88	(2)
$Mn-O$	2.08	(4)	Cl_I-Cl_{II}	3.85	(2)
Cl_I-Cl_{II}	3.61	(1)	Cl_I-Cl_{II}	3.91	(2)
Cl_I-Cl_{II}	3.63	(1)	$Cl_{II}-Cl_{II}$	4.28	(2)
Cl_I-O	3.25	(3)	Cl_I-O	3.17	(3)
Cl_I-O	3.33	(3)	Cl_I-O	3.71	(3)
$Cl_{II}-O$	3.26	(3)	$Cl_{II}-O$	3.67	(3)
$Cl_{II}-O$	3.37	(3)	$Cl_{II}-O$	3.29	(3)
			From the rubidium-atom:		
$Rb-Cl_I$	3.47	(1)	$Rb-Rb$	4.33	(1)
$Rb-Cl_I$	3.56	(1)	$Rb-Rb$	4.63	(1)
$Rb-Cl_I$	3.46	(1)	$Rb-Rb$	4.15	(1)
$Rb-Cl_I$	3.47	(1)	$Rb-O$	3.42	(3)
$Rb-Cl_{II}$	3.28	(1)	$Rb-O$	3.45	(3)
$Rb-Cl_{II}$	3.24	(1)	$Rb-O$	4.02	(3)
$Rb-Cl_{II}$	3.38	(1)	$Rb-O$	4.09	(3)
$Rb-Cl_{II}$	3.45	(1)			

Table 4. Observed and calculated structure factors. Not observed reflexions are indicated with 0.

$Cs_2MnCl_4,2H_2O$.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	1	0	23	18	3	$\bar{5}$	0	24	22
0	2	0	37	− 29	3	$\bar{6}$	0	23	23
0	3	0	100	− 94	3	$\bar{7}$	0	33	− 32
0	4	0	63	− 59	3	$\bar{8}$	0	11	− 9
0	5	0	25	22	4	1	0	22	29
0	6	0	57	56	4	2	0	6	− 5
0	7	0	0	2	4	3	0	50	− 59
0	8	0	10	11	4	4	0	42	− 44
0	9	0	23	− 22	4	5	0	6	6
1	1	0	105	− 93	4	6	0	35	37
1	2	0	142	−122	4	7	0	0	0
1	3	0	16	− 15	4	8	0	8	11
1	4	0	75	75	4	$\bar{1}$	0	0	− 1
1	5	0	33	32	4	$\bar{2}$	0	27	− 34
1	6	0	35	34	4	$\bar{3}$	0	56	− 62
1	7	0	39	− 37	4	$\bar{4}$	0	27	− 29
1	8	0	17	− 13	4	$\bar{5}$	0	20	21
1	9	0	0	− 1	4	$\bar{6}$	0	35	37
1	$\bar{1}$	0	65	58	4	$\bar{7}$	0	0	− 2
1	$\bar{2}$	0	164	154	5	1	0	32	− 41
1	$\bar{3}$	0	31	− 29	5	2	0	52	− 61
1	$\bar{4}$	0	48	− 52	5	3	0	16	− 19
1	$\bar{5}$	0	55	− 53	5	4	0	32	35
1	$\bar{6}$	0	13	− 12	5	5	0	14	13
1	$\bar{7}$	0	26	22	5	6	0	23	25
1	$\bar{8}$	0	27	25	5	7	0	19	− 20
2	1	0	64	− 67	5	$\bar{1}$	0	31	39
2	2	0	55	51	5	$\bar{2}$	0	57	68
2	3	0	47	52	5	$\bar{3}$	0	22	− 27
2	4	0	85	84	5	$\bar{4}$	0	27	− 30
2	5	0	37	− 37	5	$\bar{5}$	0	26	− 25
2	6	0	33	− 32	5	$\bar{6}$	0	0	− 3
2	7	0	22	− 17	6	1	0	32	− 37
2	8	0	0	1	6	2	0	14	14
2	9	0	14	9	6	3	0	13	15
2	$\bar{1}$	0	41	− 45	6	4	0	37	42
2	$\bar{2}$	0	72	72	6	5	0	11	− 13
2	$\bar{3}$	0	52	56	6	6	0	13	− 10
2	$\bar{4}$	0	79	71	6	7	0	9	− 8
2	$\bar{5}$	0	46	− 46	6	$\bar{1}$	0	8	− 9
2	$\bar{6}$	0	32	− 33	6	$\bar{2}$	0	32	38
2	$\bar{7}$	0	17	− 15	6	$\bar{3}$	0	20	21
2	$\bar{8}$	0	0	2	6	$\bar{4}$	0	24	28
3	1	0	27	37	6	$\bar{5}$	0	22	− 26
3	2	0	116	126	7	1	0	5	2
3	3	0	9	− 8	7	2	0	41	46
3	4	0	31	− 33	7	3	0	0	0
3	5	0	43	− 46	7	4	0	7	− 5
3	6	0	16	− 15	7	5	0	14	− 15
3	7	0	16	15	7	6	0	8	− 5
3	8	0	25	22	7	$\bar{1}$	0	30	− 33
3	$\bar{1}$	0	74	− 88	7	$\bar{2}$	0	20	− 22
3	$\bar{2}$	0	74	− 82	7	$\bar{3}$	0	8	7
3	$\bar{3}$	0	7	5	7	$\bar{4}$	0	22	26
3	$\bar{4}$	0	64	67	8	1	0	10	8

h	k	l	F_o	F_c
8	2	0	0	6
8	3	0	13	− 14
8	4	0	13	− 12
8	$\bar{1}$	0	8	− 10
8	$\bar{2}$	0	10	− 10
0	0	1	43	35
0	0	2	19	9
0	0	3	67	− 62
0	0	4	83	− 81
0	0	5	47	− 47
0	0	6	0	2
0	0	7	17	− 12
0	0	8	33	34
0	0	9	10	9
0	0	10	19	17
0	1	1	13	14
0	1	2	84	− 79
0	1	3	48	− 52
0	1	4	102	− 98
0	1	5	0	2
0	1	6	27	30
0	1	7	55	56
0	1	8	34	32
0	1	9	0	6
0	1	10	19	− 21
0	1	$\bar{1}$	88	73
0	1	$\bar{2}$	81	77
0	1	$\bar{3}$	76	67
0	1	$\bar{4}$	28	− 26
0	1	$\bar{5}$	31	− 35
0	1	$\bar{6}$	73	− 74
0	1	$\bar{7}$	16	− 14
0	1	$\bar{8}$	0	3
0	1	$\bar{9}$	18	18
0	2	1	106	−109
0	2	2	115	−118
0	2	3	28	− 24
0	2	4	62	61
0	2	5	28	32
0	2	6	73	74
0	2	7	0	3
0	2	8	0	7
0	2	9	0	− 8
0	2	10	19	− 15
0	2	$\bar{1}$	19	− 7
0	2	$\bar{2}$	126	123
0	2	$\bar{3}$	40	39
0	2	$\bar{4}$	44	39
0	2	$\bar{5}$	0	2
0	2	$\bar{6}$	19	− 18
0	2	$\bar{7}$	25	− 23
0	2	$\bar{8}$	13	− 10
0	3	1	13	− 17
0	3	2	44	− 39
0	3	3	50	50
0	3	4	49	54
0	3	5	67	73
0	3	6	34	30
0	3	7	0	− 9
0	3	8	50	− 52
0	3	9	23	− 19
0	3	10	23	− 20
0	3	$\bar{1}$	49	− 50
0	3	$\bar{2}$	43	− 36
0	3	$\bar{3}$	32	32
0	3	$\bar{4}$	56	54
0	3	$\bar{5}$	57	53
0	3	$\bar{6}$	0	1
0	3	$\bar{7}$	0	− 3
0	3	$\bar{8}$	26	− 28
0	4	1	19	16
0	4	2	87	93
0	4	3	50	56
0	4	4	70	78
0	4	5	37	− 36
0	4	6	32	− 32
0	4	7	37	− 35
0	4	8	26	− 22
0	4	9	0	− 10
0	4	10	0	10
0	4	$\bar{1}$	73	− 70
0	4	$\bar{2}$	32	− 32
0	4	$\bar{3}$	35	− 35
0	4	$\bar{4}$	32	31
0	4	$\bar{5}$	0	3
0	4	$\bar{6}$	26	22
0	5	1	71	66
0	5	2	37	36
0	5	3	28	28
0	5	4	15	− 11
0	5	5	29	− 30
0	5	6	60	− 64
0	5	7	20	− 19
0	5	8	19	− 17
0	5	9	33	34
0	5	10	24	20
0	5	$\bar{1}$	29	22
0	5	$\bar{2}$	56	− 49
0	5	$\bar{3}$	41	− 37
0	5	$\bar{4}$	37	− 33
0	5	$\bar{5}$	0	3
0	5	$\bar{6}$	17	15
0	6	1	29	26
0	6	2	41	37
0	6	3	59	− 60
0	6	4	50	− 51
0	6	5	40	− 39
0	6	6	0	− 6
0	6	7	20	19
0	6	8	34	31
0	6	9	0	0
0	6	10	22	19
0	6	$\bar{1}$	27	24
0	6	$\bar{2}$	13	− 6
0	6	$\bar{3}$	17	− 13
0	6	$\bar{4}$	0	− 4

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	6	$\bar{5}$	25	− 24	3	0	7	25	− 23
0	7	1	22	− 15	3	0	8	11	− 11
0	7	2	35	− 33	3	0	9	11	− 15
0	7	3	27	− 21	4	0	0	101	115
0	7	4	37	− 32	4	0	1	19	26
0	7	5	0	8	4	0	2	26	27
0	7	6	0	− 1	4	0	3	38	− 41
0	7	7	44	39	4	0	4	46	− 46
0	7	8	27	22	4	0	5	30	− 26
0	7	$\bar{1}$	40	35	4	0	6	8	− 9
0	7	$\bar{2}$	25	21	4	0	7	10	− 12
0	7	$\bar{3}$	27	23	4	0	8	20	22
0	7	$\bar{4}$	15	− 16	4	0	9	0	3
0	8	1	44	− 38	5	0	0	34	29
0	8	2	33	− 25	5	0	1	39	− 49
0	8	3	22	− 17	5	0	2	48	− 55
0	8	4	0	9	5	0	3	27	− 29
0	8	5	40	32	5	0	4	0	− 5
0	8	6	41	36	5	0	5	0	− 2
0	8	7	0	− 6	5	0	6	32	29
0	8	8	0	5	5	0	7	0	1
0	8	9	24	− 19	5	0	8	23	21
0	8	$\bar{1}$	0	− 4	6	0	0	45	− 49
0	8	$\bar{2}$	19	13	6	0	1	27	− 30
0	9	1	0	− 2	6	0	2	0	− 3
0	9	2	0	− 2	6	0	3	0	10
0	9	3	31	23	6	0	4	35	37
0	9	4	0	3	6	0	5	0	− 1
0	9	5	27	20	6	0	6	23	20
0	9	6	0	4	7	0	0	0	− 5
0	9	7	0	2	7	0	1	10	15
1	0	0	36	32	7	0	2	39	39
1	0	1	97	− 86	7	0	3	0	0
1	0	2	141	−125	8	0	0	30	33
1	0	3	66	− 59	1	0	$\bar{1}$	43	37
1	0	4	17	11	1	0	$\bar{2}$	178	169
1	0	5	0	3	1	0	$\bar{3}$	27	29
1	0	6	60	61	1	0	$\bar{4}$	9	7
1	0	7	11	12	1	0	$\bar{5}$	33	− 31
1	0	8	25	23	1	0	$\bar{6}$	41	− 42
1	0	9	0	3	1	0	$\bar{7}$	30	− 31
2	0	0	121	−134	1	0	$\bar{8}$	0	− 3
2	0	1	70	− 68	1	0	$\bar{9}$	11	− 15
2	0	2	20	12	2	0	$\bar{1}$	70	− 79
2	0	3	22	24	2	0	$\bar{2}$	41	39
2	0	4	101	97	2	0	$\bar{3}$	27	27
2	0	5	12	16	2	0	$\bar{4}$	98	101
2	0	6	27	26	2	0	$\bar{5}$	13	20
2	0	7	0	− 4	2	0	$\bar{6}$	11	9
2	0	8	20	− 16	2	0	$\bar{7}$	8	− 7
2	0	9	22	− 20	2	0	$\bar{8}$	13	− 15
3	0	0	0	− 1	2	0	$\bar{9}$	15	− 21
3	0	1	30	39	3	0	$\bar{1}$	60	− 67
3	0	2	118	122	3	0	$\bar{2}$	86	− 96
3	0	3	21	20	3	0	$\bar{3}$	52	− 57
3	0	4	29	25	3	0	$\bar{4}$	30	28
3	0	5	23	− 22	3	0	$\bar{5}$	6	7
3	0	6	34	− 29	3	0	$\bar{6}$	49	51

h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	0	$\bar{7}$	8	10	5	0	$\bar{3}$	12	20
3	0	$\bar{8}$	12	10	5	0	$\bar{4}$	6	− 9
4	0	$\bar{1}$	25	35	5	0	$\bar{5}$	23	− 22
4	0	$\bar{2}$	0	7	5	0	$\bar{6}$	16	− 18
4	0	$\bar{3}$	42	− 47	6	0	$\bar{1}$	34	− 40
4	0	$\bar{4}$	47	− 52	6	0	$\bar{2}$	19	27
4	0	$\bar{5}$	29	− 33	6	0	$\bar{3}$	11	14
4	0	$\bar{6}$	12	15	6	0	$\bar{4}$	36	44
4	0	$\bar{7}$	7	− 7	7	0	$\bar{1}$	25	− 26
4	0	$\bar{8}$	19	21	7	0	$\bar{2}$	32	− 31
5	0	$\bar{1}$	22	25	7	0	$\bar{3}$	19	− 24
5	0	$\bar{2}$	68	81	7	0	$\bar{4}$	14	21

$Rb_2MnCl_4,2H_2O$

0	1	0	0	3	3	2	0	85	88
0	2	0	16	− 11	3	3	0	0	− 4
0	3	0	56	− 55	3	4	0	14	− 10
0	4	0	42	− 42	3	5	0	26	− 26
0	5	0	0	1	3	6	0	17	− 14
0	6	0	35	35	3	7	0	0	− 1
0	7	0	0	− 1	3	8	0	17	17
0	8	0	15	12	3	$\bar{1}$	0	42	− 48
0	9	0	11	− 12	3	$\bar{2}$	0	45	− 49
1	1	0	58	− 64	3	$\bar{3}$	0	0	− 6
1	2	0	103	− 90	3	$\bar{4}$	0	39	38
1	3	0	24	− 20	3	$\bar{5}$	0	9	3
1	4	0	50	46	3	$\bar{6}$	0	24	21
1	5	0	12	10	3	$\bar{7}$	0	15	− 15
1	6	0	36	32	3	$\bar{8}$	0	9	− 5
1	7	0	18	− 17	4	1	0	9	8
1	8	0	9	− 9	4	2	0	5	7
1	$\bar{1}$	0	28	24	4	3	0	27	− 29
1	$\bar{2}$	0	130	122	4	4	0	30	− 28
1	$\bar{3}$	0	23	− 19	4	5	0	7	− 9
1	$\bar{4}$	0	23	− 23	4	6	0	24	22
1	$\bar{5}$	0	32	− 29	4	7	0	0	− 1
1	$\bar{6}$	0	15	− 12	4	8	0	11	12
1	$\bar{7}$	0	7	5	4	$\bar{1}$	0	7	− 8
1	$\bar{8}$	0	18	19	4	$\bar{2}$	0	12	− 10
2	1	0	44	− 48	4	$\bar{3}$	0	32	− 29
2	2	0	40	34	4	$\bar{4}$	0	22	− 18
2	3	0	18	17	4	$\bar{5}$	0	0	3
2	4	0	69	65	4	$\bar{6}$	0	21	21
2	5	0	19	− 16	4	$\bar{7}$	0	0	− 5
2	6	0	16	− 15	5	1	0	17	− 19
2	7	0	12	− 13	5	2	0	31	− 31
2	8	0	0	− 2	5	3	0	16	− 19
2	$\bar{1}$	0	28	− 33	5	4	0	19	18
2	$\bar{2}$	0	49	49	5	5	0	0	1
2	$\bar{3}$	0	23	17	5	6	0	20	22
2	$\bar{4}$	0	60	54	5	7	0	10	− 6
2	$\bar{5}$	0	24	− 23	5	$\bar{1}$	0	13	9
2	$\bar{6}$	0	16	− 15	5	$\bar{2}$	0	40	43
2	$\bar{7}$	0	13	− 10	5	$\bar{3}$	0	14	− 14
2	$\bar{8}$	0	0	0	5	$\bar{4}$	0	11	− 9
3	1	0	7	8	5	$\bar{5}$	0	15	− 12

h	k	l	F_o	F_c
5	$\bar{6}$	0	7	− 4
6	1	0	20	− 21
6	2	0	9	9
6	3	0	0	− 1
6	4	0	28	28
6	5	0	0	− 2
6	6	0	0	− 2
6	7	0	7	− 7
6	$\bar{1}$	0	5	− 7
6	$\bar{2}$	0	19	18
6	$\bar{3}$	0	6	2
6	$\bar{4}$	0	20	21
6	$\bar{5}$	0	12	− 11
7	1	0	0	− 6
7	2	0	27	26
7	3	0	0	1
7	4	0	0	2
7	$\bar{5}$	0	8	− 7
7	$\bar{1}$	0	17	− 14
7	$\bar{2}$	0	14	− 11
7	$\bar{3}$	0	0	− 2
7	$\bar{4}$	0	13	11
8	1	0	0	1
8	2	0	0	5
8	3	0	8	− 5
8	$\bar{1}$	0	8	− 7
8	$\bar{2}$	0	4	1
0	0	1	20	12
0	0	2	12	7
0	0	3	45	− 44
0	0	4	52	− 54
0	0	5	28	− 25
0	0	6	20	16
0	0	7	0	− 4
0	0	8	19	23
0	0	9	0	− 2
0	1	1	10	17
0	1	2	45	− 52
0	1	3	11	− 8
0	1	4	63	− 64
0	1	5	0	2
0	1	6	0	8
0	1	7	24	27
0	1	8	17	22
0	1	9	12	11
0	1	10	12	− 16
0	1	$\bar{1}$	48	39
0	1	$\bar{2}$	38	35
0	1	$\bar{3}$	45	43
0	1	$\bar{4}$	16	− 17
0	1	$\bar{5}$	0	− 3
0	1	$\bar{6}$	40	− 46
0	1	$\bar{7}$	0	− 10
0	1	$\bar{8}$	0	− 1
0	2	0	16	− 11
0	2	1	71	− 75
0	2	2	76	− 87
0	2	3	17	− 17
0	2	4	46	50
0	2	5	13	14
0	2	6	45	50
0	2	7	10	− 10
0	2	8	0	− 3
0	2	9	0	− 9
0	2	10	0	− 5
0	2	$\bar{1}$	20	− 13
0	2	$\bar{2}$	100	96
0	2	$\bar{3}$	17	15
0	2	$\bar{4}$	18	17
0	2	$\bar{5}$	10	− 9
0	2	$\bar{6}$	14	− 16
0	2	$\bar{7}$	14	− 12
0	2	$\bar{8}$	0	3
0	3	1	13	8
0	3	2	35	− 35
0	3	3	31	31
0	3	4	15	17
0	3	5	32	34
0	3	6	21	19
0	3	7	0	5
0	3	8	25	− 30
0	3	9	12	− 8
0	3	10	17	− 19
0	3	$\bar{1}$	17	− 17
0	3	$\bar{2}$	27	− 23
0	3	$\bar{3}$	0	11
0	3	$\bar{4}$	23	24
0	3	$\bar{5}$	31	34
0	3	$\bar{6}$	0	0
0	3	$\bar{7}$	0	4
0	4	1	10	6
0	4	2	55	61
0	4	3	25	24
0	4	4	55	58
0	4	5	31	− 30
0	4	6	20	− 20
0	4	7	22	− 23
0	4	8	11	− 9
0	4	9	0	0
0	4	10	13	12
0	4	$\bar{1}$	46	− 45
0	4	$\bar{2}$	11	− 10
0	4	$\bar{3}$	21	− 19
0	4	$\bar{4}$	31	32
0	4	$\bar{5}$	0	2
0	4	$\bar{6}$	0	10
0	4	$\bar{7}$	0	2
0	5	1	34	36
0	5	2	12	11
0	5	3	16	14
0	5	4	0	− 2
0	5	5	0	− 6
0	5	6	32	− 35
0	5	7	0	− 4
0	5	8	19	− 20
0	5	9	17	16

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	5	10	12	13	1	0	8	0	6
0	5	$\bar{1}$	26	21	1	0	9	0	− 2
0	5	$\bar{2}$	29	− 28	1	0	$\bar{1}$	15	15
0	5	$\bar{3}$	14	− 16	1	0	$\bar{2}$	142	132
0	5	$\bar{4}$	18	− 20	1	0	$\bar{3}$	0	7
0	5	$\bar{5}$	0	− 2	1	0	$\bar{4}$	0	− 1
0	6	1	15	13	1	0	$\bar{5}$	27	− 27
0	6	2	34	33	1	0	$\bar{6}$	23	− 26
0	6	3	39	− 39	1	0	$\bar{7}$	14	− 13
0	6	4	27	− 27	1	0	$\bar{8}$	14	10
0	6	5	26	− 26	1	0	$\bar{9}$	11	− 6
0	6	6	0	− 4	2	0	0	74	− 95
0	6	7	12	13	2	0	1	41	− 45
0	6	8	22	24	2	0	2	21	17
0	6	9	0	− 1	2	0	3	8	4
0	6	10	0	10	2	0	4	69	69
0	6	$\bar{1}$	14	11	2	0	5	0	− 2
0	6	$\bar{2}$	14	− 10	2	0	6	12	7
0	6	$\bar{3}$	15	− 15	2	0	7	12	− 7
0	6	$\bar{4}$	0	− 2	2	0	8	11	− 8
0	6	$\bar{5}$	13	− 13	2	0	9	0	− 7
0	7	1	11	− 7	2	0	$\bar{1}$	43	− 50
0	7	2	16	− 15	2	0	$\bar{2}$	37	37
0	7	3	11	− 6	2	0	$\bar{3}$	10	11
0	7	4	22	− 20	2	0	$\bar{4}$	71	71
0	7	5	12	9	2	0	$\bar{5}$	0	1
0	7	6	13	− 10	2	0	$\bar{6}$	0	− 2
0	7	7	23	20	2	0	$\bar{7}$	13	− 13
0	7	8	12	12	2	0	$\bar{8}$	15	− 10
0	7	9	13	9	2	0	$\bar{9}$	0	− 7
0	7	$\bar{1}$	22	21	3	0	0	0	4
0	7	$\bar{2}$	0	7	3	0	1	9	8
0	7	$\bar{3}$	19	18	3	0	2	79	85
0	8	1	27	− 27	3	0	3	0	− 1
0	8	2	12	− 15	3	0	4	12	11
0	8	3	17	− 14	3	0	5	18	− 15
0	8	4	0	4	3	0	6	17	− 17
0	8	5	22	19	3	0	7	14	− 8
0	8	6	25	26	3	0	8	0	4
0	8	7	0	− 3	3	0	9	13	− 9
0	8	8	0	4	3	0	$\bar{1}$	35	− 41
0	8	$\bar{1}$	0	0	3	0	$\bar{2}$	54	− 57
0	8	$\bar{2}$	13	13	3	0	$\bar{3}$	30	− 30
0	9	1	0	0	3	0	$\bar{4}$	27	28
0	9	2	0	− 4	3	0	$\bar{5}$	0	5
0	9	3	16	16	3	0	$\bar{6}$	32	36
0	9	4	0	− 3	3	0	$\bar{7}$	0	− 3
0	9	5	17	13	3	0	$\bar{8}$	0	0
0	9	6	0	2	3	0	$\bar{9}$	0	− 6
0	9	7	0	2	4	0	0	64	73
1	0	0	33	30	4	0	1	0	2
1	0	1	61	− 59	4	0	2	14	16
1	0	2	103	− 93	4	0	3	21	− 22
1	0	3	43	− 38	4	0	4	28	− 25
1	0	4	25	21	4	0	5	15	− 10
1	0	5	0	0	4	0	6	0	6
1	0	6	42	44	4	0	7	0	− 8
1	0	7	0	− 2	4	0	8	12	14

h	k	l	F_o	F_c	h	k	l	F_o	F_c
4	0	$\bar{1}$	8	5	6	0	4	22	24
4	0	$\bar{2}$	0	− 4	6	0	5	0	− 9
4	0	$\bar{3}$	26	− 29	6	0	6	0	6
4	0	$\bar{4}$	30	− 29	6	0	$\bar{1}$	18	− 17
4	0	$\bar{5}$	13	− 14	6	0	$\bar{2}$	17	18
4	0	$\bar{6}$	17	18	6	0	$\bar{3}$	0	2
4	0	$\bar{7}$	0	0	6	0	$\bar{4}$	22	27
4	0	$\bar{8}$	13	16	6	0	$\bar{5}$	0	− 4
5	0	0	22	19	6	0	$\bar{6}$	0	− 4
5	0	1	21	− 23	7	0	0	0	2
5	0	2	27	− 27	7	0	1	0	0
5	0	3	16	− 11	7	0	2	24	23
5	0	4	13	7	7	0	3	0	− 9
5	0	5	0	− 5	7	0	4	0	5
5	0	6	21	20	7	0	5	0	− 5
5	0	7	0	− 7	7	0	$\bar{1}$	14	− 10
5	0	$\bar{1}$	8	3	7	0	$\bar{2}$	18	− 13
5	0	$\bar{2}$	45	49	7	0	$\bar{3}$	11	− 9
5	0	$\bar{3}$	0	0	7	0	$\bar{4}$	13	14
5	0	$\bar{4}$	0	− 6	7	0	$\bar{5}$	0	0
5	0	$\bar{5}$	16	− 17	8	0	0	22	18
5	0	$\bar{6}$	9	− 11	8	0	1	0	− 7
5	0	$\bar{7}$	0	− 5	8	0	2	0	5
6	0	0	26	− 22	8	0	3	12	− 8
6	0	1	15	− 12	8	0	$\bar{1}$	0	− 1
6	0	2	0	5	8	0	$\bar{2}$	0	0
6	0	3	0	− 1					

The coordinates found, their standard deviations and the temperature factors are given in Table 2. The interatomic distances found are given in Table 3 and observed and calculated structure factors in Table 4.
All crystallographic calculations (Lp-corrections, refinements, distances, and fouriers) were carried out on the computer GIER using Algol-programs written by Danielsen.[5]

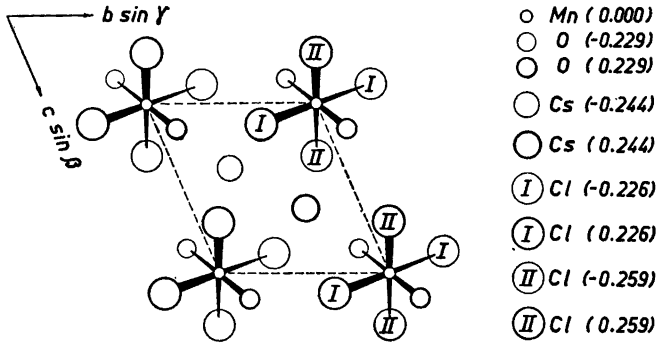

Fig. 2. $Cs_2MnCl_4,2H_2O$. Projection along the a-axis. Figures in brackets indicate the x-values of the atomic parameters.

DISCUSSION

Each manganese atom is surrounded by four chlorine atoms and two water molecules forming discrete groups $[MnCl_4,2H_2O]^{2-}$. The four chlorine atoms are situated almost exactly at the corners of a square. The water molecules, placed on opposite sides of the square, complete a *trans*-octahedral coordination (Fig. 2). The water molecule has two chlorine atoms as nearest negative neighbours at relatively short distances (3.17—3.29 Å). The angle Cl—O—Cl is 107° ($Cs_2MnCl_4,2H_2O$) and 105° ($Rb_2MnCl_4,2H_2O$). These facts suggest that hydrogen-bonds bind the octahedra together. The Cs(Rb)-atom is surrounded by eight chlorine atoms and four oxygen-atoms. The packing around the Cs(Rb)-atom may either be described as a distorted CsCl arrangement with eight Cl-atoms as neighbours, or as a close packing with twelve Cl and O-atoms as neighbours. The structure may be described as being of a distorted Cs_2PuCl_6-type (Zachariasen [8]). The atomic radii of Pu^{4+} and Mn^{2+} are nearly equal, the Pu—Cl distance is 2.62 Å and the Mn—Cl distance found in $Cs_2MnCl_4,2H_2O$ is 2.54 Å, and in $Rb_2MnCl_4,2H_2O$ 2.54 Å and 2.58 Å. The interatomic distances between Mn and Cl and between Mn and O are nearly the same as the corresponding distances in $CsMnCl_3,2H_2O$. In $CsMnCl_3,2H_2O$ Mn—Cl is 2.50 Å and 2.57 Å and Mn—O is 2.08 Å. The main difference between the structures of $CsMnCl_3,2H_2O$ and $Cs_2MnCl_4,2H_2O$ is the *cis*-coordination of the water molecules in the former compound and the *trans* configuration of the latter. Established *cis-trans* isomerism is rather uncommon for kinetically labile coordination compounds.

The Cs—Cl distances 3.35 and 3.40 are shorter than the distance to be expected from the sum of Pauling's ionic radii (3.50 Å),[9] but several other compounds containing Cs and Cl also have small Cs—Cl distances. In Cs_2CoCl_4 (Porai-Kochitz [10]) the shortest Cs—Cl distance is 3.39 Å, in $CsCuCl_3$ (Wells [11]) the shortest distance is 3.40 Å, and in $Cs_3Re_2Cl_{12}$ Bertrand, Cotton and Dollase [12] have found Cs-atoms in distances of 3.29 Å and 3.32 Å from Cl-atoms.

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