Isodimorphism of the Salts 2RbCl · M^{II}Cl$_2$ · 2H$_2$O (M^{II} = Mn, Fe, Co, Cu)

CHRISTO BALAREW AND STEFKA TEPAVITCHAROVA

Institute of General and Inorganic Chemistry, Department of Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

The three-component systems RbCl–MnCl$_2$–H$_2$O, 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · CuCl$_2$ · 2H$_2$O–H$_2$O, 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O have been studied at 25°C. In the 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · CuCl$_2$ · 2H$_2$O–H$_2$O system, a discontinuous series of mixed crystals is formed and in the 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O system, a continuous series is present.

The unit cell parameters of the 2RbCl · CoCl$_2$ · 2H$_2$O double salt were determined: $a = 5.586(2)$ Å, $b = 6.469(3)$ Å, $c = 6.988(2)$ Å, $\alpha = 65.31(3)°$, $\beta = 87.69(3)°$, $\gamma = 84.65(4)°$, volume 228.4 Å^3, $Z = 1$.

The results obtained and discussed in conjunction with the crystal structure data suggest that for $2M^I$Cl · M^{II}Cl$_2$ · 2H$_2$O type salts the triclinic structure is stable only when the large rubidium and cesium ions participate in combinations with non-Jahn–Teller metal(II) ions. In the cases of Jahn–Teller metal(II) ions or with potassium or ammonium ions a tetragonal structure is always stable.

Introduction

The variety of metal(I)–metal(II) chloride double salts is huge. Double salts are formed in most three-component systems M^ICl–M^{II}Cl$_2$–H$_2$O, where M^I = Li, K, NH$_4$, Rb, Cs, and M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ca. The systems with NaCl are exceptions with no double salts (excluding CdCl$_2$ and ZnCl$_2$). Table I shows the compositions of the double salts crystallized from these systems. Moreover, a great number of mainly anhydrous double salts have been obtained preparatively and their crystal structures studied. Amidst the variety, it is seen that certain compositions appear in most systems, for example, the salts $2M^I$Cl · M^{II}Cl$_2$ · 2H$_2$O (2:1:2). The study of their isodimorphism is the purpose of the present work.

The crystal structures of the $2M^I$Cl · M^{II}Cl$_2$ · 2H$_2$O salts fall into two types of crystal systems: tetragonal (2KCl · MnCl$_2$ · 2H$_2$O (*1*); 2NH$_4$Cl · MnCl$_2$ · 2H$_2$O (*2*); 2KCl · CuCl$_2$ · 2H$_2$O (*3, 4*); 2NH$_4$Cl · CuCl$_2$ · 2H$_2$O (*5–7*); 2RbCl · CuCl$_2$ · 2H$_2$O (*8, 9*); 2CsCl · CuCl$_2$ · 2H$_2$O (*9, 10*); 2NH$_4$Cl · FeCl$_2$ · 2H$_2$O (*11*)) and triclinic (2RbCl · MnCl$_2$ · 2H$_2$O (*12, 13*); 2CsCl · MnCl$_2$ · 2H$_2$O (*12–14*)). The only exceptions are the orthorhombic salt 2LiCl · ZnCl$_2$ · 2H$_2$O (*15*) whose structure differs essentially from the other structures due to the very small radius of the Li$^+$ ion and the 2LiCl · MnCl$_2$ · 2H$_2$O salt. These salts are left outside our discussion.

Experimental

The three-component systems 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · CuCl$_2$ · 2H$_2$O–H$_2$O

TABLE I

Composition[a] of the Known Double Salts Obtained in the M^ICl–M^{II}Cl$_2$–H$_2$O Systems

	Mg²⁺	Mn²⁺	Fe²⁺	Co²⁺	Ni²⁺	Cu²⁺	Zn²⁺	Cd²⁺
Li⁺	1:1:7 DS	1:1:2 2:1:4 1:1:5 4:1:0 2:1:2 4:1:10		1:1:2 4:1:2 2:1:4 4:1:10 3:2:6 7:2:18 MC	1:1:2 2:1:4 4:1:10	1:1:2[b]	2:1:2[b]	1:1:2,5 1:2:5 4:3:12
Na⁺	No	No	No	No	No	No	2:1:3[b]	1:1:2 3:4:13 1:1:3 3:4:14 1:2:5 8:1:16 2:1:3[b] 8:4:14 3:4:10
K⁺	1:1:6[b]	1:1:1 4:1:0[b] 1:1:2[b] 4:5:0 2:1:2[b] 5:3:0	No	1:1:2 2:1:0[b] MC	1:1:0[b] 4:7:14 5:5:9	1:1:0[b] 1:1:2 2:1:2[b]	1:1:1[b] MC 1:1:2[b] 2:1:0[b]	1:1:0[b] 1:3:4[b] 1:1:1 2:1:0 1:2:0 4:1:0[b]
NH₄⁺	1:1:6[b]	2:1:2[b] MC(α,β)	2:1:2[b] MC(α,β)	1:1:2 2:1:2 MC(α,β)	1:1:2 MC 1:4:0 3:2:0	1,5:1:2 2:1:2[b] 3:1:6	1:1:0 2:1:0[b] 3:1:0[b]	1:1:0[b] 4:1:0[b]
Rb⁺	1:1:6[b]	2:1:2[b]		1:1:2[b] 2:1:2		2:1:2[b]		1:1:0[b] 4:1:0[b]
Cs⁺	1:1:6	2:1:2[b] 1:1:2[b]		1:1:2[b] 2:1:0[b] 3:1:0[b]	1:1:0[b] 3:2:2[b] 2:1:0[b] 4:3:2 2:1:2[b]			1:1:0[b] 2:1:0[b] 3:2:0[b]

Note. DS = double salts with unknown composition. MC = mixed crystals.

[a] The ratio between the digits denotes the molar ratio of M^ICl : M^{II}Cl$_2$: H$_2$O in the double salts.

[b] Double salts with known structures.

and 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O were studied at 25°C by the solubility method using isothermal decrease of supersaturation (*16*). The double salts were prepared using compositions from the crystallization fields of the double salts found when studying the three-component aqueous-salt systems; namely, RbCl–CoCl$_2$–H$_2$O (*17*) and RbCl–CuCl$_2$–H$_2$O (*8*). To locate the crystallization field of the 2RbCl · MnCl$_2$ · 2H$_2$O double salt, for which no literature data are available, we undertook a study of the system RbCl–MnCl$_2$–H$_2$O at 25°C.

The salts used were "Merck analytical reagent" grade. The time to attain equilibrium in the systems studied was 6–7 days under continuous stirring. The composition of the solid phase considered as thoroughly suction dried was determined graphically by Schreinemakers' method (*18*) for the double salt 2RbCl · MnCl$_2$ · 2H$_2$O formation and by the method of algebraic indirect solid phase composition identification (*19*) for mixed crystal formation. The results obtained are confirmed by X-ray diffraction, differential thermal analysis, and thermogravimetric analysis.

The RbCl–MnCl$_2$–H$_2$O system at 25°C. The composition of the liquid and the corresponding wet solid phases were analyzed in the following way: Mn²⁺ was determined complexometrically by direct titration with 0.05 *M* EDTA in ammonia buffer with eryochrome black T as indicator in the presence of hydroxylamine hydrochloride or ascorbic acid as a reducing agent (*20*). The total amount of chloride was determined argentometrically (*21*). The RbCl concentration was calculated from the difference between the total chloride and MnCl$_2$-bonded chlorides. The results for this system are presented in Fig. 1 and Table II. The solubility isotherm consists of three branches, corresponding to pure RbCl, to the 2:1:2 double salt and to MnCl$_2$ · 4H$_2$O. The two
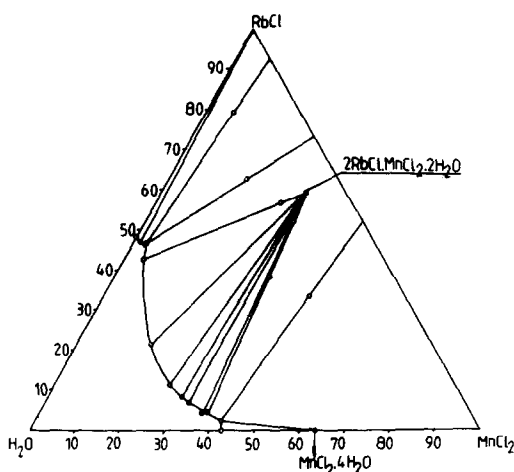
FIG. 1. Phase diagram of the three-component system RbCl–MnCl₂–H₂O at 25°C (in mass %).

TABLE II

SOLUBILITY IN THE RbCl–MnCl₂–H₂O SYSTEM AT 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		
MnCl₂	RbCl	MnCl₂	RbCl	Solid phase
0.00	48.60	0.00	99.90	RbCl
1.40	47.20	0.17	99.78	RbCl
2.92	47.08	6.04	79.64	Eutonics
2.79	46.81	17.24	62.84	Eutonics
4.13	43.00	27.76	56.86	2RbCl · MnCl₂ · 2H₂O
16.52	21.80	31.00	58.03	2RbCl · MnCl₂ · 2H₂O
25.68	11.32	31.42	57.97	2RbCl · MnCl₂ · 2H₂O
29.85	8.45	32.00	59.32	2RbCl · MnCl₂ · 2H₂O
31.90	7.25	32.27	53.55	2RbCl · MnCl₂ · 2H₂O
36.12	4.54	32.50	52.70	2RbCl · MnCl₂ · 2H₂O
37.29	4.59	34.16	38.56	2RbCl · MnCl₂ · 2H₂O
41.66	2.46	45.56	33.41	Eutonics
41.88	2.59	62.58	0.10	MnCl₂ · 4H₂O
42.50	0.00	61.47	0.00	MnCl₂ · 4H₂O

eutonics (or two-salt points) have the compositions 2.92% MnCl₂, 47.08% RbCl, and 41.66% MnCl₂, 2.46% RbCl, respectively. The existence of the double salt was confirmed by X-ray diffraction, differential thermal analysis, and thermogravimetric analysis (Fig. 2). The decrease in the sample weight of 9.17% at 100–140°C corresponds to the theoretical amount of water of crystallization (8.92%) for the double salt $2RbCl \cdot MnCl_2 \cdot 2H_2O$. The second endothermic peak in the DTA curve at 420°C corresponds to melting of the anhydrous double salt (*22*).

The *2RbCl · CoCl₂ · 2H₂O–2RbCl · CuCl₂ · 2H₂O–H₂O* system at 25°C. The composition of the liquid and the corresponding wet solid phases was analyzed by determining the sum of Cu^{2+} and Co^{2+} complexometrically in a back titration with a $ZnSO_4$ solution at pH 5.5–6.0 with xylenol orange as indicator. The Cu^{2+} concentration was found iodometrically. Figure 3 and Table III show the results from these experiments. The salts 2RbCl · CuCl₂ · 2H₂O and 2RbCl · CoCl₂ · 2H₂O were found to form discontinuous series of mixed crystals, i.e., the salts are isodimorphic. The
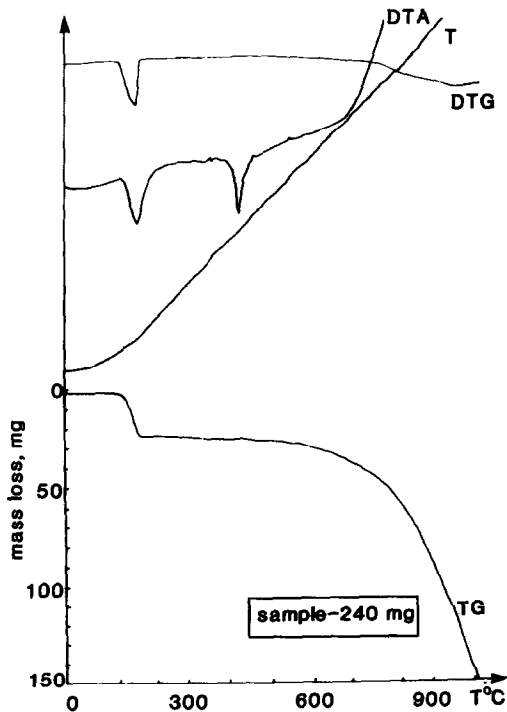

FIG. 2. Thermal data for the double salt 2RbCl · MnCl₂ · 2H₂O. Paulik–Paulik–Erdey apparatus; heating rate 10°C min⁻¹.

TABLE III

Solubility in the 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · CuCl$_2$ · 2H$_2$O–H$_2$O System at 25°C

Liquid phase (mass %)		Solid phase calculated as thoroughly suction dried (19) (mass %)		Liquid phase (molar parts)		Solid phase calculated as thoroughly suction dried (19) (molar parts)		
(1)[a]	(2)[b]	(1)[a]	(2)[b]	(1)[a]	(2)[b]	(1)[a]	(2)[b]	$D_{Co^{2+}/Cu^{2+}}$
0.00	37.80	0.00	100.00	0.00	1.00	0.00	1.00	—
3.75	34.22	1.92	98.08	0.10	0.90	0.02	0.98	0.18
6.60	33.74	4.37	95.63	0.16	0.84	0.04	0.96	0.23
8.16	31.97	5.50	94.50	0.20	0.80	0.06	0.94	0.23
10.07	30.29	4.00	96.00	0.25	0.75	0.04	0.96	0.12
11.16	28.76	3.69	96.31	0.28	0.72	0.04	0.96	0.10
13.45	26.17	3.65	96.34	0.34	0.66	0.04	0.96	0.07
30.16	9.38	3.76	96.24	0.76	0.24	0.04	0.96	0.01
31.44	10.03	4.38	95.62	0.76	0.24	0.04	0.96	0.02
47.58	1.14	4.62	95.38	0.98	0.02	0.05	0.95	0.001
53.11	0.50	7.06	92.93	0.99	0.01	0.07	0.93	Eutonics
53.68	0.42	72.93	27.07	0.99	0.01	0.73	0.27	0.03
54.07	0.45	87.44	12.56	0.99	0.01	0.88	0.12	0.06
54.73	0.00	100.00	0.00	1.00	0.00	1.00	0.00	—

[a] 2RbCl · CoCl$_2$ · 2H$_2$O.
[b] 2RbCl · CuCl$_2$ · 2H$_2$O.

copper ions replace the cobalt ions in 2RbCl · CoCl$_2$ · 2H$_2$O but the resulting mixed crystals possess a very narrow crystallization field. The cobalt ions only partially substitute for the copper ions in 2RbCl · CuCl$_2$ · 2H$_2$O, attaining saturation at a value of about 4–5% 2RbCl · CoCl$_2$ · 2H$_2$O and further inclusion of Co^{2+} is not observed. These results show that 2RbCl · CoCl$_2$ · 2H$_2$O does not belong to the tetragonal system of the 2 : 1 : 2 salts.

The 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O system at 25°C. Mn^{2+} was determined complexometrically by direct EDTA titration in ammonia buffer with eryochrome black T as indicator in the presence of hydrochloride as reducing agent. Sodium cyanide was used to mask the Co^{2+} ions as a stable cyanide complex. The sum of Mn^{2+} and Co^{2+} was determined complexometrically by back titration with a

calibrated ZnSO$_4$ solution in ammonia buffer with eryochrome black T as indicator. The results are shown in Fig. 4 and

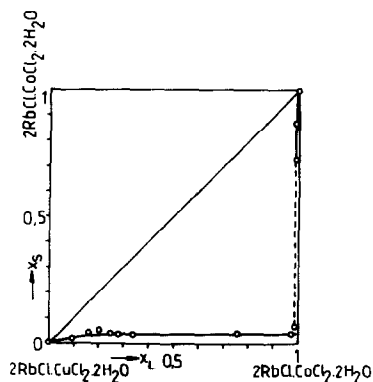Fig. 3. Distribution of the components in the 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · CuCl$_2$ · 2H$_2$O–H$_2$O system at 25°C (discontinuous series of mixed crystals).
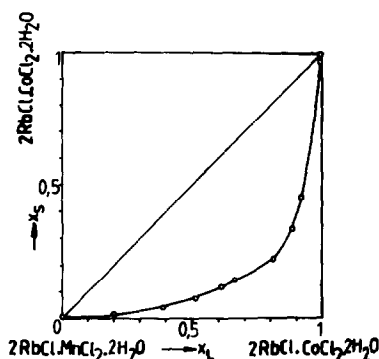
FIG. 4. Distribution of the components in the 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O system at 25°C (continuous series of mixed crystals).

Table IV. The salts 2RbCl · CoCl$_2$ · 2H$_2$O and 2RbCl · MnCl$_2$ · 2H$_2$O form a continuous series of mixed crystals, which is supported also by X-ray diffraction studies, i.e., the two salts are isomorphic. This means that the 2RbCl · CoCl$_2$ · 2H$_2$O structure is triclinic.

X-ray diffraction studies. A single-crystal CAD 4 diffractometer was used to determine the 2RbCl · CoCl$_2$ · 2H$_2$O and 2RbCl · MnCl$_2$ · 2H$_2$O double salt parameters by refining the angular positions of 18 reflexes in the 20–22° region:

2RbCl · CoCl$_2$ · 2H$_2$O	2RbCl · MnCl$_2$ · 2H$_2$O
a = 5.586(2) Å	a = 5.647(2) Å
b = 6.469(3) Å	b = 6.545(2) Å
c = 6.988(2) Å	c = 7.091(5) Å
α = 65.31(3)°	α = 65.05(4)°
β = 87.69(3)°	β = 87.24(4)°
γ = 84.65(4)°	γ = 84.34(2)°
Volume = 228.4 Å^3	Volume = 236.4 Å^3
Z = 1	Z = 1

Discussion

The results obtained and discussed in conjunction with the crystal structure data suggest that for $2M^{I}Cl · M^{II}Cl_2 · 2H_2O$ type salts the triclinic structure is stable

TABLE IV

SOLUBILITY IN THE 2RbCl · CoCl$_2$ · 2H$_2$O–2RbCl · MnCl$_2$ · 2H$_2$O–H$_2$O SYSTEM AT 25°C

| Liquid phase (mass %)		Solid phase calculated as thoroughly suction dried (19) (mass %)		Liquid phase (molar parts)		Solid phase calculated as thoroughly suction dried (19) (molar parts)		
(1)^a	(2)^b	(1)^a	(2)^l	(1)^a	(2)^b	(1)^a	(2)^b	D$_{Co^{2+}/Mn^{2+}}$
0.00	48.26	0.00	100.00	0.00	1.00	0.00	1.00	—
9.96	39.17	1.59	98.41	0.20	0.80	0.02	0.98	0.06
19.69	30.39	4.07	95.93	0.39	0.61	0.04	0.96	0.07
25.41	23.33	7.70	92.30	0.52	0.48	0.08	0.92	0.08
30.32	18.87	12.08	87.92	0.61	0.39	0.12	0.88	0.09
33.98	17.09	14.37	85.63	0.66	0.34	0.14	0.86	0.08
43.47	9.76	22.39	77.61	0.82	0.18	0.22	0.78	0.06
46.74	5.90	33.85	66.15	0.89	0.11	0.34	0.66	0.06
48.87	4.18	46.02	53.98	0.92	0.08	0.46	0.54	0.07
54.62	0.15	96.94	3.06	1.00	0.00	0.97	0.03	0.09
54.73	0.00	100.00	0.00	1.00	0.00	1.00	0.00	—

^{a} 2RbCl · CoCl$_2$ · 2H$_2$O.
^{b} 2RbCl · MnCl$_2$ · 2H$_2$O.
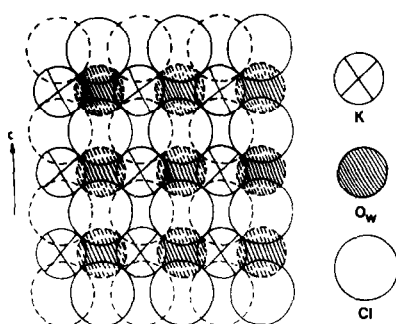
FIG. 5. Tetragonal structure of a salt of the type $2M^I\text{Cl} \cdot M^{II}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Projection in the [110] plane. (The atoms depicted in the same manner are located at approximately the same distance with respect to the viewer.)

only when the large rubidium and cesium ions participate in combinations with non-Jahn–Teller metal(II) ions. In the cases of Jahn–Teller metal(II) ions or with potassium or ammonium ions a tetragonal structure is always stable. The explanation can be the following: An octahedral environment is typical for the metal(II) ion in the crystal structures of the salts $2M^I\text{Cl} \cdot M^{II}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, where $M^{II} = $ Mn, Fe, Co, Cu. This environment is formed by four chloride ions and two water molecules $[M^{II}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$. In the Mn^{II} salts, for example, each manganese ion forms four equivalent Mn–Cl bonds. In the copper salts, due to the Jahn–Teller effect, the octahedra $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$ are strongly elongated along two of the Cu–Cl bonds giving two shorter and two longer Cu–Cl bonds in these compounds. The metal(I) ions are located with respect to the octahedra in such a way that, together with the six ligands forming the octahedra, they constitute $[M^I_2(\text{H}_2\text{O})_2\text{Cl}_4]$ parallelopipeds in whose center the metal(II) ions are located. The structures of these salts may be considered as a close-packed array resulting from the periodic arrangement of the parallelopipeds $[M^I_2(\text{H}_2\text{O})_2\text{Cl}_4]$. In the tetragonal salts, the parallelopipeds are stacked so that their

body diagonals connecting two chloride ions and two oxygen atoms from the metal (II) octahedron's equatorial positions are lying on a plane [110] (Fig. 5). The alternating chloride ions and water molecule's oxygen atoms form an atomic layer (A). Above and below this atomic layer, atomic layers B occur and these layers contain chloride ions and metal(I) ions. To be stable in this structure, the areas from layer A and layer B, occupied by the same number of atoms, have to be the same. This may be realized if the metal(I) ionic radius is close to the ionic radius of the oxygen as in the cases of potassium and ammonium salts. If the metal(I) ionic radius is larger than the radius of the oxygen as in rubidium and cesium salts, layers A have to expand correspondingly. However, this is possible within certain limits only for Jahn–Teller metal(II) ions, such as Cu^{2+}, since the expansion in layer B may be taken up by the elongated Cu–Cl bond lengths from layer A. These are, by the way, the two cases in which a tetragonal structure in the 2 : 1 : 2 salts is possible. In the case of an ionic radius of the metal(I) ion smaller than that of oxygen (such as the sodium ion) the structure would be unstable since atomic layers A cannot be subjected to contraction. And indeed 2 : 1 : 2 sodium salts are not known.

In the 2 : 1 : 2 chloride structures with rubidium or cesium and a non-Jahn–Teller metal(II) ion, because no distortion or atomic layer A expansion is possible, a regrouping of the parallelopipeds should occur. These polyhedra are shifted with respect to each other, as compared with the arrangement in the tetragonal structure, by an atomic layer. The two different atomic layers A and B are recombined in a general common atomic layer AB built up in the plane [111] of alternating chloride ion, metal(I) ion, chloride ion, water oxygen, etc. (see Fig. 6). The triclinic structure is obtained by consecutive stacking of these layers.
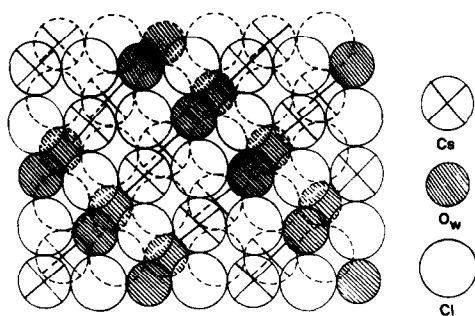
FIG. 6. Triclinic structure of a salt of the type $2M^ICl \cdot M^{II}Cl_2 \cdot 2H_2O$. Projection in the [111] plane. (The atoms depicted in the same manner are located at approximately the same distance with respect to the viewer.)

The explanation put forward here reveals possibilities to make certain predictions of the structures. Thus, for example, the mineral douglasite ($K_2FeCl_4 \cdot 2H_2O$), for which structural data are lacking, is expected to be tetragonal.

Acknowledgment

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