

Invited Review

Double Salts Formation in the Systems $MX-MeX_2-H_2O$ ($M=K, NH_4, Rb, Cs$; $Me=Mg, Mn, Fe, Co, Ni, Cu$; $X=Cl, Br$)

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Summary. The data available on the solubility phase diagrams and on the crystallization of chloride and bromide double salts in the systems $MX-MeX_2-H_2O$ ($M=K, NH_4, Rb, Cs$; $Me=Mg, Mn, Fe, Co, Ni, Cu$; $X=Cl, Br$) over a wide temperature range are collected and systematized. Formation of mainly 6 formula types $mMX \cdot MeX_2 \cdot nH_2O$ ($m=1, 2, 3$; $n=0, 2, 6$) double salts are established. Using crystal structure elucidations the effect of M^+ , Me^{2+} , and X^- ions on the solubility diagrams and on the compositions of the double salts formed in these systems are discussed. The conclusion is drawn that the appearance of double salts in the solubility phase diagrams is a result of the equilibrium between the different ionic forms in the solution. The availability of a sufficient concentration (activity) of such complexes, which can be incorporated in the crystal structure during the crystal growth process through appropriate sticking, almost unchanged or with small changes, as *e.g.* condensation with elimination of halogenide ions and by linking together with other ions or complexes (*e.g.* M^+ , X^- ions) and H_2O – molecules, determines the solubility and hence the crystallization field of the respective double salt.

Keywords. Solubility; Phase diagrams; Structure elucidation; Chloride double salts; Bromide double salts.

Introduction

In a series of previous papers [1–18] we studied the systems of the type $MX-MeX_2-H_2O$ where $M^+ = K^+, NH_4^+, Rb^+, Cs^+$; $Me^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$, and $X^- = Cl^-, Br^-$. In almost all systems crystallization of double salts was established. There is a great variety in the compositions and

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Dedicated to Professor H. Gamsjäger on the occasion of his 70th Birthday

crystal structures of the double salts obtained. The aim of our works was to find some regularities concerning the formation of double salts in the above systems. Recently, *Emons* and *Voigt* [19] published an important survey about formation, decomposition, and properties of double salts from these types of systems.

The present work is an attempt to systematize the available experimental data for this type of systems with a view to elucidating the effect of the participating ions on the solubility diagrams and on the compositions and crystal structures of the crystallizing double salts.

Results

Composition of the Double Salts

Tables 1 and 2 show the compositions of the double salts crystallizing in the chloride and bromide systems. Some of these data are contestable by the reason of experimental difficulties encountered, as for example for the salt $5\text{KCl} \cdot 5\text{NiCl}_2 \cdot 9\text{H}_2\text{O}$ [44]. In fact, for this salt the composition $\text{KCl} \cdot \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ was established [18]. The formation of mixed crystals in some of these systems is also doubtful. This was proved for the system $\text{NH}_4\text{Cl}-\text{CoCl}_2-\text{H}_2\text{O}$ [64]. During fast crystallization, metastable phases may be formed, so that inner adsorption [65] of the incongruent soluble double salt $2\text{NH}_4\text{Cl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in the NH_4Cl dendrit crystals occurs. Equilibrium is reached very slowly in this case and it can last for weeks even under strong stirring.

Table 1. Double salts obtained from $M\text{Cl}-Me\text{Cl}_2-\text{H}_2\text{O}$ systems^a

	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
K^+	1:1:6 [20] 1:1:2 ^c 1.5:1:2 ^c	1:1:2 [23–25] 2:1:2 [23–25] 1:1:1 [26] 4:1:0 [23–25] 4:5:0 [25] 5:3:0 [25]	1:1:2 ^b [30] 2:1:2 ^c	1:1:2 [35–37] 1:1:1 ^c 2:1:0 [38] MC [38]	1:1:5 ^c 4:7:14 [44] 5:5:9 [44] → → 1:1:2 [18] 1:1:0 [44]	1:1:2 [47, 48] 2:1:2 [47, 48] 1:1:0 [47]
NH_4^+	1:1:6 [21]	2:1:2 [27] MC (α , β) [27]	2:1:2 [31] MC (α , β) [31–33]	1:1:2 [39, 40] 2:1:2 [39–41] MC (α , β) [39, 40]	1:1:6 ^c 1:1:2 [45] MC [39, 45, 46]	3:1:6 [49, 53] 1,5:1:2 [49] 2:1:2 [49–53] MC [50, 52]
Rb^+	1:1:6 [12, 22]	α -1:1:2 ^b [28] β -1:1:2 ^b [29] 2:1:2 [2]	1:1:2 ^b [30] 2:1:2 ^c	1:1:2 [42] 2:1:2 [42]	1:1:2 [6] 2:1:2 [6]	2:1:2 [54]
Cs^+	1:1:6 [22]	1:1:2 [3] 2:1:2 [3] 2:1:0 ^c	1:1:2 ^b [34] 2:1:2 ^c	1:1:2 [42, 43] 2:1:2 ^c 2:1:0 [42, 43] 3:1:0 [42, 43]	1:1:2 [7]	2:1:2 [55] 3:2:2 [55, 56] 4:3:2 [55] 1:1:0 [55] 2:1:0 [55]

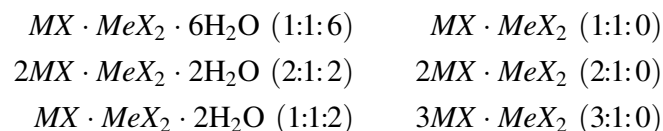
^a The numbers given denote the molar ratios of $M\text{Cl}:Me\text{Cl}_2:\text{H}_2\text{O}$ in the double salts; ^b Salt was obtained by a preparative method; ^c Data taken from Ref. [19]; MC = mixed crystals

Table 2. Double salts obtained from $MBr-MeBr_2-H_2O$ systems^a

	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
K^+	1:1:6 [11, 57]	No [13]		No [61] MC [61]	1:1:6 [15]	1:1:0 [62] No [14]
NH_4^+	1:1:6 [11, 58]	2:1:2 [18]	1:1:6 [60]	2:1:2 [41]	1:1:6 [13]	2:1:2 [14, 63] MC [14]
Rb^+	1:1:6 [11, 12, 59]	2:1:2 [17]		1:1:6 [15]	1:1:6 [16]	2:1:2 [14]
Cs^+	1:1:6 [11, 12]	1:1:2 [18] 2:1:2 [18]		2:1:0 [18] 3:1:0 [18]	1:1:0 [18]	2:1:0 [14] 1:1:0 [14]

^a The numbers given denote the molar ratio of $MBr:MeBr_2:H_2O$ in the double salts; MC = mixed crystals

The existence of the following formula type double salts in the systems $MX-MeX_2-H_2O$ is beyond doubt:



Subject of our discussions will be these types of double salts.

Crystal Structures of the Double Salts

Crystal structure data of the above 6 types of double salts are presented in Table 3.

$MX \cdot MeX_2 \cdot 6H_2O$ (1:1:6) The structures of these double salts consist of a three-dimensional network of corner-sharing $[MX_6]$ octahedra and isolated $[Me(H_2O)_6]$ octahedra in the octahedral holes of this network (Fig. 1).

$2MX \cdot MeX_2 \cdot 2H_2O$ (2:1:2) The principal structural units of these double salts are the mixed octahedra $[Me(H_2O)_2X_4]$ (Fig. 2). They crystallize in two structure types, in tetragonal (Fig. 2a) and in triclinic (Fig. 2b) crystal systems. Both structures consist of discrete $[Me(H_2O)_2X_4]$ octahedra and separate M^+ ions and the ratio r_{M^+}/r_{Ow} determines the appearance of the first or second structure type.

$MX \cdot MeX_2 \cdot 2H_2O$ (1:1:2) Three types of 1:1:2 salt structures occur, triclinic, orthorhombic, and monoclinic crystal systems. They consist of condensed mixed octahedra $[Me(H_2O)_2X_4]$, sharing halogenide ions (Fig. 3).

The structure of 1:1:2 salts crystallizing in the triclinic system is formed by discrete dimers of the mixed octahedra with common edges, sharing two halogenide ions (Fig. 3c). The orthorhombic (Fig. 3a) and monoclinic (Fig. 3b) salts possess chain type crystal structures. The mixed octahedra are connected to one another by common corners sharing halogenide ions. In the orthorhombic salts the coordinated water molecules are in *cis*-position whereas they are in *trans*-positions in the monoclinic salts.

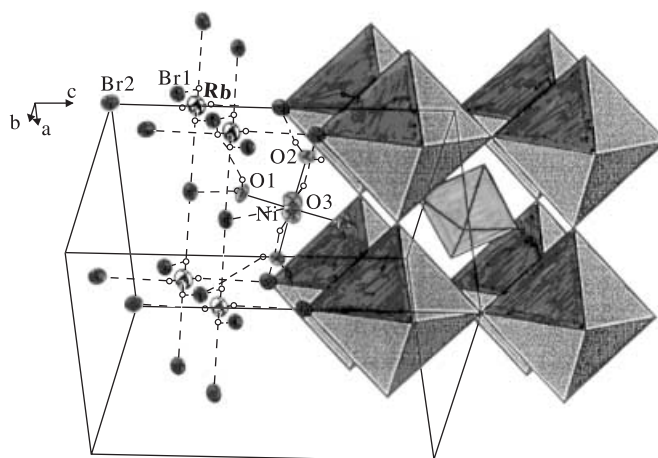
$MX \cdot MeX_2$ (1:1:0)^a The building units in the structures of these double salts are condensed octahedra $[MeX_6]$ bonded by common corners, edges or faces,

^a There is a large number of anhydrous double salts with highly varied compositions and structures obtained from melts. Most of them show several polymorphic forms. Our considerations are restricted only to those obtained from the aqueous systems under study

Table 3. Crystal structure data of double salts $mMX \cdot MeX_2 \cdot nH_2O$ ($m = 1, 2, 3; n = 0, 2, 6$)

Double salt type	Coordination polyhedra in the crystal structure	Crystal system	Space group
$MX \cdot MeX_2 \cdot 6H_2O$ (1:1:6)	$n[Me(H_2O)_6]^{2+} + [MX_{6/2}]_{3n/3}^{2n-}$	a) monoclinic b) orthorhombic	$C2/c$ $Pnna$
$2MX \cdot MeX_2 \cdot 2H_2O$ (2:1:2)	$[Me(H_2O)_2X_4]^{2-} + 2M^+$	a) tetragonal b) triclinic	$I4/mmm$ $P4_2/mnm$ $P\bar{1}$
$MX \cdot MeX_2 \cdot 2H_2O$ (1:1:2)	a) $[Me(H_2O)_2X_2X_{2/2}]_2^{2-} + 2M^+$ b) $[Me(H_2O)_2^{(cis)}X_2X_{2/2}]_n^{n-} + nM^+$ c) $[Me(H_2O)_2^{(trans)}X_2X_{2/2}]_n^{n-} + nM^+$	a) triclinic b) orthorhombic c) monoclinic	$P\bar{1}$ $Pcca$ $C2/c$
$MX \cdot MeX_2$ (1:1:0)	a) $[MeX_{6/2}]_{3n/3}^{n-} + nM^+$ b) $[MeX_{6/2}]_n^{n-} + nM^+$	a) cubic b) hexagonal c) cub:hex = 2:1 d) cub:hex = 1:1 e) cub:hex = 1:2	a
$2MX \cdot MeX_2$ (2:1:0)	a) $[MeX_2X_{4/2}]_{2n/2}^{2n-} + 2nM^+$ b) $[MeX_4]^{2-} + 2M^+$	a) tetragonal b) orthorhombic	$I4/mmm$ $Pnma$
$3MX \cdot MeX_2$ (3:1:0)	$[MeX_4]^{2-} + 3M^+ + X^-$	tetragonal	$I4/mcm$

^a There is large variety of structures including polymorphous modifications

**Fig. 1.** Crystal structure of $RbBr \cdot NiBr_2 \cdot 6H_2O$ double salt

and isolated M^+ ions. (Fig. 4). They crystallize in cubic or hexagonal crystal systems. These in cubic systems have the ideal perovskite type structure (Fig. 4a), whereas those in a hexagonal system possess a distorted perovskite type structure (Fig. 4b). Some 1:1:0 salts have intermediate structures (Fig. 4c, 4d, 4e) between the cubic (Fig. 4a) and hexagonal type (Fig. 4b).

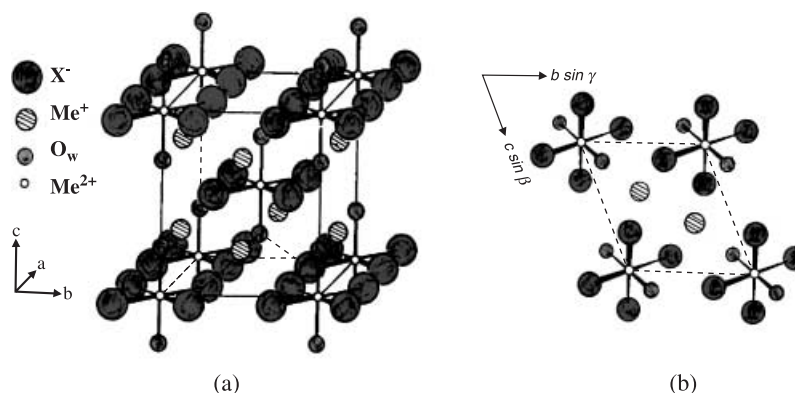


Fig. 2. Crystal structure of $2MX \cdot MeX_2 \cdot 2H_2O$ double salts; (a) tetragonal; (b) triclinic

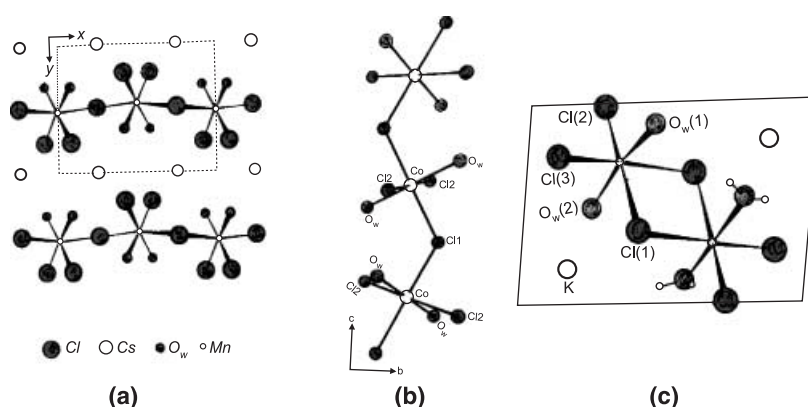


Fig. 3. Crystal structure of $MX \cdot MeX_2 \cdot 2H_2O$ double salts; (a) $CsCl \cdot MnCl_2 \cdot 2H_2O$ orthorhombic; (b) $RbCl \cdot CoCl_2 \cdot 2H_2O$ monoclinic; (c) $KCl \cdot MnCl_2 \cdot 2H_2O$ triclinic

$2MX \cdot MeX_2$ (2:1:0) These double salts crystallize, in general, in two main structures, K_2NiF_4 type (tetragonal) or $\beta-K_2SO_4$ type (orthorhombic) and consist, respectively, of $[MeX_6]$ octahedra or $[MeX_4]$ tetrahedra (Fig. 5).

$3MX \cdot MeX_2$ (3:1:0) The structures of these salts consist of discrete $[MeX_4]$ tetrahedra and isolated M^+ ions as well as free X^- ions.

Solution and Crystallization Mechanism

The inorganic simple or double salts should be considered as ionic coordination compounds. In their crystal structures the metal ions are coordinated by anions or water molecules and in this way coordination polyhedra are formed, which are linked together with other ions or water molecules through ionic (electrostatic) or hydrogen bonds. The coordination polyhedra may have common elements, thus forming dimers, chains, plains, or spatial networks.

The factors determining the arrangement of the structural units in a stable crystal structure are the sizes of ions and their charges (geometrical factors), the energy of metal-ligand bonds, and the energy determined by the positional symmetry of the ligands. The geometrical factor is discussed in terms of the *Pauling* rules for the

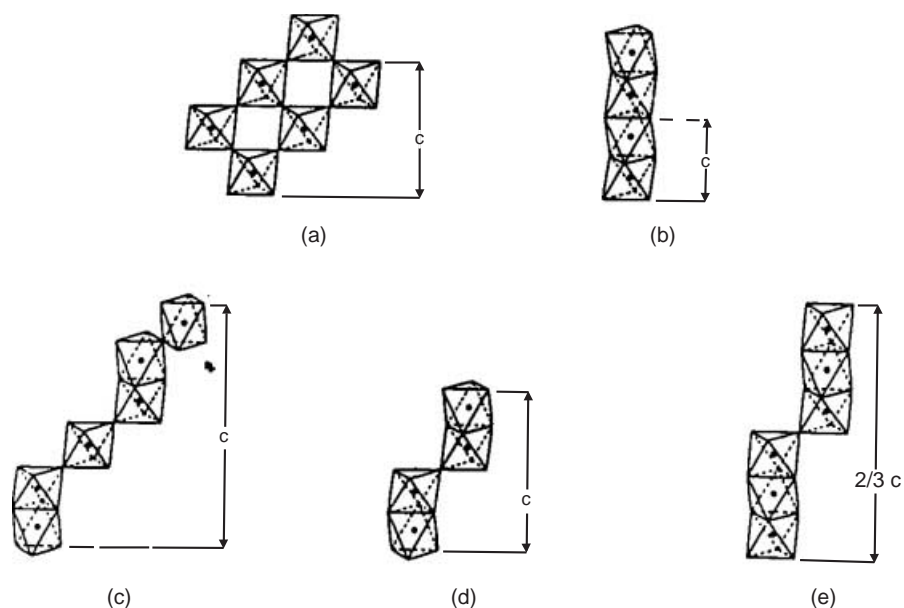


Fig. 4. Projection of octahedral network of (110) plane in a unit cell of $MX \cdot MeX_2$ salts [109]; (a) cubic (c); (b) hexagonal (hex); (c) $c:hex = 2:1$; (d) $c:hex = 1:1$; (e) $c:hex = 1:2$

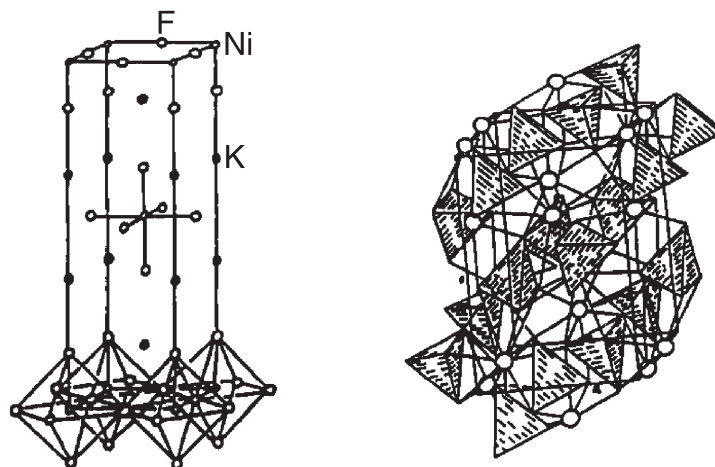


Fig. 5. Crystal structure of $2MX \cdot MeX_2$ double salts; (a) K_2NiF_4 structure type (tetragonal); (b) β - K_2SO_4 structure type (orthorhombic)

formation of coordination polyhedra and their linkage, which reflect the most probable space distribution of the ions as well as the tendency of the larger ions to arrange in a manner permitting the closest possible packing [1, 100, 101].

The higher the charge of the metal ions and the smaller its size, the stronger are the bonds between the metal ions and the ligands in the coordination polyhedra. The preference for coordination of the ligands towards the metal ions is discussed both in terms of *Pearson's* "hard-soft *Lewis* acids and bases" concept [102, 103] and in terms of the "bond-valence model", formulated by *Brown* [104, 105] about

Table 4. Dissolution and crystallization of the double salts $mMX \cdot MeX_2 \cdot nH_2O$ ($m = 1, 2, 3; n = 0, 2, 6$)

Double salt type	Crystal phase	Solution
1:1:6	$\{n[Me(H_2O)_6]^{2+} + [MX_{6/2}]_{3n/3}^{2n-}\} \rightleftharpoons$	$n[Me(H_2O)_6]^{2+} + n[MX_{6/2}]^{2-} \rightleftharpoons n[Me(H_2O)_6]^{2+} + nM^+ + 3nX^-$
2:1:2	$\{[Me(H_2O)_2X_4]^{2-} + 2M^+\} \rightleftharpoons$	$[Me(H_2O)_2X_4]^{2-} + 2M^+$
1:1:2	$\{[Me(H_2O)_2X_2X_{2/2}]_2^{2-} + 2M^+\} \rightleftharpoons$ $\{[Me(H_2O)_2X_2X_{2/2}]_n^{n-} + nM^+\} \rightleftharpoons$	$[Me(H_2O)_2X_2X_{2/2}]_2^{2-} + 2M^+ \rightleftharpoons 2[Me(H_2O)_2X_4]^{2-} - 2X^- + 2M^+$ $[Me(H_2O)_2X_2X_{2/2}]_n^{n-} + nM^+ \rightleftharpoons n[Me(H_2O)_2X_4]^{2-} - nX^- + nM^+$
1:1:0	$\{[MeX_{6/2}]_n^{n-} + nM^+\} \rightleftharpoons$	$[MeX_{6/2}]_n^{n-} + nM^+ \rightleftharpoons n[MeX_6]^{4-} - 3nX^- + nM^+$
2:1:0	$\{[MeX_2X_{4/2}]_{2n/2}^{2n-} + 2nM^+\} \rightleftharpoons$ $\{[MeX_4]^{2-} + 2M^+\} \rightleftharpoons$	$[MeX_2X_{4/2}]_{2n/2}^{2n-} + 4nM^+ \rightleftharpoons n[MeX_6]^{4-} - 2nX^- + 2nM^+$ $[MeX_4]^{2-} + 2M^+$

the valences available for metal-ligand bonds. The crystal field stabilization energy is considered as a factor which opposes some external influences and, therefore, limits the possibilities of deformation of the coordination polyhedra [1].

The solution mechanism of a salt can be divided provisionally in two stages: (i) the weakest bonds are broken first, which leads to liberation of the main structural units of the crystal: complexes, ions, or neutral molecules; (ii) the structural units getting free undergo additional changes: hydration, association, dissociation, or even transformation into other ionic forms until the stable equilibrium in the solution at the given composition and temperature is reached. The most probable stage (i) of the solution mechanism of the examined salts which can be obtained from aqueous solutions is presented in Table 4. Finally, after stage (ii), solutions are obtained in which all possible complexes exist in mutual equilibrium. In the saturated solutions under consideration, the following complexes are predominating: $[Me(H_2O)_6]^{2+}$, $[Me(H_2O)_4X_2]$, $[Me(H_2O)_2X_4]^{2-}$, $[MeX_6]^{4-}$, and $[MeX_4]^{2-}$. Depending on the conditions (composition of the solution and temperature), the equilibrium is shifted towards different ratios of these complexes.

The crystallization mechanism of congruently soluble salts is inverse to the solution process (see Table 4). The crystallization process starts when some of the complexes existing in the solution possess a sufficiently high activity to reach and surpass the solubility product of the crystallizing salt. These complexes or entities directly derivable from them (*e.g.* obtained by condensation with elimination of halogenide ions) together with other ions or molecules form the crystal structure. This means that important for the crystallization process is the activity of definite entities in the solution (complexes, molecules, or simple ions) that are able, directly or with minor changes, to be incorporated in the crystal structure.

Discussion

Table 5 shows systematized data on the space groups of the double salts 1:1:6, 2:1:2, 1:1:2, 1:1:0, 2:1:0, and 3:1:0 crystallizing in the $MX-MeX_2-H_2O$ systems.

Crystallization of different types of double salts and their structures are based on the requirements for arrangement of the ions, atoms, and molecules in the crystal structures. They should obey the *Pauling* rules for formation of coordination polyhedra and their linkage [100, 101], as well as the tendency of larger ions to

Table 5. Crystal space group data

	$MX-MgX_2-H_2O$	$MX-MnX_2-H_2O$	$MX-FeX_2-H_2O$
1:1:6	KCl · MgCl ₂ · 6H ₂ O NH ₄ Cl · MgCl ₂ · 6H ₂ O RbCl · MgCl ₂ · 6H ₂ O CsCl · MgCl ₂ · 6H ₂ O KBr · MgBr ₂ · 6H ₂ O NH ₄ Br · MgBr ₂ · 6H ₂ O RbBr · MgBr ₂ · 6H ₂ O CsBr · MgBr ₂ · 6H ₂ O	<i>Pnma</i> [66–68] <i>C2/c</i> [66, 69] <i>C2/c</i> [66, 70, 71] <i>C2/c</i> [70, 72] <i>C2/c</i> [66, 70] <i>C2/c</i> [70] <i>C2/c</i> [70] <i>C2/c</i> [70]	NH ₄ Br · FeBr ₂ · 6H ₂ O [60]
2:1:2		2KCl · MnCl ₂ · 2H ₂ O 2NH ₄ Cl · MnCl ₂ · 2H ₂ O 2RbCl · MnCl ₂ · 2H ₂ O 2CsCl · MnCl ₂ · 2H ₂ O 2NH ₄ Br · MnBr ₂ · 2H ₂ O 2RbBr · MnBr ₂ · 2H ₂ O 2CsBr · MnBr ₂ · 2H ₂ O KCl · MnCl ₂ · 2H ₂ O <i>β</i> -RbCl · MnCl ₂ · 2H ₂ O <i>α</i> -RbCl · MnCl ₂ · 2H ₂ O CsCl · MnCl ₂ · 2H ₂ O CsCl · MnBr ₂ · 2H ₂ O	2KCl · FeCl ₂ · 2H ₂ O 2NH ₄ Cl · FeCl ₂ · 2H ₂ O
1:1:2		<i>I4/mmm</i> [73] <i>P4₂/mmm</i> [74] <i>P1</i> [2, 75] <i>P1</i> [75] <i>P4₂/mmm</i> [18] <i>P1</i> [17] <i>P1</i> [18] <i>P1</i> [76] <i>P1</i> [29] <i>Pcca</i> [28] <i>Pcca</i> [77] <i>Pcca</i> [18]	<i>P4₂/mmm</i> [78] <i>P1</i> [30] RbCl · FeCl ₂ · 2H ₂ O [79] CsCl · FeCl ₂ · 2H ₂ O [34]

(continued)

Table 5 (continued)

	$MX-CoX_2-H_2O$	$MX-NiX_2-H_2O$	$MX-CuX_2-H_2O$
1:1:6	RbBr · CoBr ₂ · 6H ₂ O	KBr · NiBr ₂ · 6H ₂ O NH ₄ Br · NiBr ₂ · 6H ₂ O RbBr · NiBr ₂ · 6H ₂ O	C2/c [15] C2/c [13, 15] C2/c [16]
2:1:2	2NH ₄ Cl · CoCl ₂ · 2H ₂ O 2RbCl · CoCl ₂ · 2H ₂ O 2CsCl · CoCl ₂ · 2H ₂ O ^a 2NH ₄ Br · CoBr ₂ · 2H ₂ O	2RbCl · NiCl ₂ · 2H ₂ O	2KCl · CuCl ₂ · 2H ₂ O 2NH ₄ Cl · CuCl ₂ · 2H ₂ O 2RbCl · CuCl ₂ · 2H ₂ O 2CsCl · CuCl ₂ · 2H ₂ O 2NH ₄ Cl · CuBr ₂ · 2H ₂ O 2RbBr · CuBr ₂ · 2H ₂ O 2CsBr · CuBr ₂ · 2H ₂ O ^a KCl · CuCl ₂ · 2H ₂ O
1:1:2	KCl · CoCl ₂ · 2H ₂ O NH ₄ Cl · CoCl ₂ · 2H ₂ O RbCl · CoCl ₂ · 2H ₂ O CsCl · CoCl ₂ · 2H ₂ O	KCl · NiCl ₂ · 2H ₂ O [18] NH ₄ Cl · NiCl ₂ · 2H ₂ O RbCl · NiCl ₂ · 2H ₂ O CsCl · NiCl ₂ · 2H ₂ O ^a KCl · NiCl ₂ CsBr · NiBr ₂	P $\bar{1}$ [2, 80] P $\bar{1}$ [3] C2/c [81] Pcca [82] Pcca [10] P6 ₃ /mmc [89] P6 ₃ /mmc [18]
1:1:0			KCl · CuCl ₂ CsCl · CuCl ₂ CsBr · CuBr ₂
2:1:0	2KCl · CoCl ₂ 2CsCl · CoCl ₂ 2CsBr · CoBr ₂		P2 ₁ /c [83] Pnma [84–87] Pnma [86, 87]
3:1:0	3CsCl · CoCl ₂ 3CsBr · CoBr ₂		I4/mcm [88] I4/mcm [88]
			P2 ₁ /c [95] P6 ₁ 22 [96] C222 ₁ [97] Pnma [98] Pnma [97, 99]

^a Predicted crystal structure type

arrange in a manner permitting the closest possible packing. The sizes of the ions, their charges, the energy of metal-ligand bonds, and the electronic configurations of the metal ions determine the crystal structures of the salts under consideration and their polymorphism [1].

Double salts 1:1:6 are found in all systems with the participation of Mg^{2+} ions. They are the only stable double salt hydrates obtained from these systems under common conditions. The reason is the high stability of the hexaaquacomplexes $[Mg(H_2O)_6]^{2+}$ on account of the fact that Mg^{2+} ions are the hardest *Lewis* acid in comparison with all other ions participating in the systems under consideration [102, 103, 106, 107]. Double salts 1:1:6 are also formed in bromide systems with participation of Fe^{2+} , Co^{2+} , and Ni^{2+} ions, but with narrower crystallization fields in the solubility diagram as compared to those of the Mg^{2+} salts. This type of double salt does not appear in the chloride systems because the Br^- ions are softer *Lewis* bases than the Cl^- ions. The reason is that the $Me^{2+}-Br^-$ bond is weaker than the $Me^{2+}-Cl^-$ one. As a result, the equilibrium between the ionic forms in bromide solutions is shifted to a higher degree towards the complexes $[Me(H_2O)_6]^{2+}$ at the expense of $[Me(H_2O)_2Br_4]^{2-}$ complexes. This tendency must be even more widely realized in the iodide systems.

The double salts 1:1:6 crystallize in perovskite type structure, space group $C2/c$ (Fig. 1). Solely carnalite, $KCl \cdot MgCl_2 \cdot 6H_2O$, crystallizes in distorted perovskite type, space group $Pnna$, because the *Goldschmidt-Pauling* [100, 108] condition for realization of perovskite type structure is not fulfilled. The reason is the small size of K^+ ions.

Double salts 2:1:2 and 1:1:2 are formed in the $MX-MeX_2-H_2O$ systems with the participation of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . Within the temperature limits in which the MeX_2 salts crystallize with more than two water molecules the formation of these double salts from the single salt components must be endothermic. Therefore, in the solubility diagram the crystallization fields of 2:1:2 and 1:1:2 salts will appear and extend with rising temperature. The appearance of the 2:1:2 salts and then, only at higher temperatures, of the 1:1:2 salts gives evidence for a higher stability of the crystal structures with discrete $[Me(H_2O)_2X_4]^{2-}$ octahedra at lower temperatures. This means that at lower temperatures the equilibrium in solution is shifted to a higher degree towards free octahedral complexes.

The conclusion can be drawn that the appearance of crystallization fields of 2:1:2 and 1:1:2 salts and their width in the solubility diagram is a result of the equilibrium between the different ionic forms in solution. The availability of a sufficient concentration (activity) of such complexes which can be incorporated in the crystal structure during the crystal growth process through appropriate sticking, almost unchanged or with small changes, determines the solubility and hence the crystallization field of the respective double salt.

Double salts 2:1:2 are obtained from all systems under consideration with participation of Mn^{2+} and Cu^{2+} ions. Exceptions are the K^+ salts in bromide systems because of the smaller ionic radius of the K^+ ions, which results in an instability of the $2KBr \cdot MeBr_2 \cdot 2H_2O$ type structures. The salt $2CsBr \cdot CuBr_2 \cdot 2H_2O$, although unknown at this stage, is assumed to appear at lower temperatures.

Double salts 2:1:2 are also formed in the chloride systems of Fe^{2+} , Co^{2+} , and Ni^{2+} . As is mentioned above, 1:1:6 salts crystallize in the respective bromide

systems. Nevertheless, the salt $2\text{NH}_4\text{Br} \cdot \text{CoBr}_2 \cdot 2\text{H}_2\text{O}$ is known. However, it appears at temperatures above 42°C .

The 2:1:2 salts crystallize in tetragonal and in triclinic crystal systems (Fig. 2). The salts in which the smaller K^+ and NH_4^+ participate as well as all 2:1:2 Cu^{2+} salts crystallize in the tetragonal system, because of the *Jahn-Teller* effect. All remaining salts with participation of Rb^+ and Cs^+ ions crystallize in the triclinic system.

The double salts 1:1:2 are obtained mainly in chloride systems. The only bromide salt of this type known so far is $\text{CsBr} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$. Of the Cu^{2+} salts, only $\text{KCl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has been obtained.

The 1:1:2 salts crystallize in the triclinic, orthorhombic, and monoclinic systems (Fig. 3). Triclinic are the salts with participation of K^+ ions as well as the β -polymorphic form of $\text{RbCl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Their structures consist of the dimers $[\text{Me}(\text{H}_2\text{O})_2\text{X}_2\text{X}_{2/2}]_2^{2-}$ with a *trans*-position of H_2O molecules. The 1:1:2 salts with participation of Rb^+ and Cs^+ ions are orthorhombic. They are build of chains of octahedra $[\text{Me}(\text{H}_2\text{O})_2\text{X}_2\text{X}_{2/2}]_n^{n-}$ in which the water molecules are in *cis*-position. The structure of the monoclinic salts differs from the orthorhombic one only by the *trans*-position of the water molecules in the mixed octahedra. The sole known representative crystallizing in the monoclinic system is $\text{RbCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$.

The formation of 1:1:0 double salts depends on the stability of the $[\text{MeX}_6]^{4-}$ octahedra. In cases when they are stable, the octahedra are connected by common corners in a three-dimensional network and form a cubic perovskite type structure or distorted perovskite type structure (Fig. 4). When the $[\text{MeX}_6]^{4-}$ octahedra are unstable, stabilization is achieved at the expense of distortion. The octahedra are bonded by common faces and form an endless chain with the composition $[\text{MeX}_{6/2}]_n^{n-}$, producing a hexagonal packing. This structure is additionally stabilized by the presence of larger Me^+ ions. Structures with chains of edgebonded dimers $[\text{Me}_2\text{X}_{9/2}]_n^{n/2-}$ and trimers $[\text{Me}_3\text{X}_{12/2}]_n$ are intermediates between the cubic and the hexagonal types.

The double salts 2:1:0 crystallize in $\beta\text{-K}_2\text{SO}_4$ type (orthorhombic) or K_2NiF_4 type (tetragonal), depending on the Me^{2+} ions trend towards tetrahedral (as for Co^{2+} ions) or octahedral (as for Mg^{2+} ions) coordination, respectively (Fig. 5).

The cobalt salts $3\text{CsX} \cdot \text{CoX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) crystallize in the tetragonal crystal system, space group $I4/mcm$. Similarly to $2\text{CsX} \cdot \text{CoX}_2$ salts, their structures consist of isolated $[\text{CoX}_4]^{2-}$ tetrahedra and Cs^+ ions as well as free X^- ions.

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