

Double Salts in the Systems $Me^+X-Me^{2+}X_2-H_2O$ ($Me^+ = K, NH_4, Rb, Cs$; $Me^{2+} = Mn, Co, Ni$; $X^- = Cl, Br$)

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The solubility diagrams of the systems $CsBr-Me^{2+}Br_2-H_2O$ ($Me^{2+} = Mn, Co, Ni$) and $NH_4Br-MnBr_2-H_2O$ have been determined at 25°C. Four previously unreported double salts, $2NH_4Br \cdot MnBr_2 \cdot 2H_2O$ (space group $P4_2/mnm$, $a = 7.886(1) \text{ \AA}$, $b = 7.886(1) \text{ \AA}$, $c = 8.529(2) \text{ \AA}$, $Z = 2$, $V = 530.4(2) \text{ \AA}^3$, $D_x = 2.797$), $2CsBr \cdot MnBr_2 \cdot 2H_2O$ (space group $P\bar{1}$, $a = 5.993(1) \text{ \AA}$, $b = 7.054(2) \text{ \AA}$, $c = 7.587(2) \text{ \AA}$, $\alpha = 66.02(2)^\circ$, $\beta = 87.87(2)^\circ$, $\gamma = 83.95(2)^\circ$, $Z = 1$, $V = 291.4(1) \text{ \AA}^3$, $D_x = 3.854$), $CsBr \cdot MnBr_2 \cdot 2H_2O$ (space group $Pcca$, $a = 9.523(2) \text{ \AA}$, $b = 7.514(1) \text{ \AA}$, $c = 11.951(3) \text{ \AA}$, $Z = 4$, $V = 855.2(3) \text{ \AA}^3$, $D_x = 3.600$), and $KCl \cdot NiCl_2 \cdot 2H_2O$, have been identified. The crystallization of double salts in the systems $Me^+X-Me^{2+}X_2-H_2O$ ($Me^+ = K, NH_4, Rb, Cs$; $Me^{2+} = Mn, Co, Ni$; $X^- = Cl, Br$) is explained using the Pauling rules of formation and arrangement of the coordination polyhedra in stable ionic crystal structures. The type of ligands that form polyhedra is determined using Pearson's "hard" and "soft" acids-bases concept. Composition and structural differences in the crystallized double salts are explained by the differences in stabilities of the Me^{2+} -polyhedra that predominate in the saturated solutions. © 1999 Academic Press

INTRODUCTION

The solubility diagrams of the systems $Me^+X-Me^{2+}X_2-H_2O$, where $Me^+ = K, NH_4, Rb, Cs$, $Me^{2+} = Mn, Co, Ni$, and $X^- = Cl, Br$, have been a subject of numerous investigations. Along with simple salts (anhydrous or hydrated), one or more double salts, typically of the formula type $mMe^+X \cdot Me^{2+}X_2 \cdot nH_2O$ ($m = 1, 2, 3$; $n = 0, 2, 6$) have been found to crystallize in every one of these systems. We could not find any data in the literature on six of these systems. In this paper investigations on four of them are reported, $CsBr-Me^{2+}Br_2-H_2O$ ($Me^{2+} = Mn, Co, Ni$) and $NH_4Br-MnBr_2-H_2O$ at 25°C. For the remaining two systems ($RbBr-MnBr_2-H_2O$ and $RbBr-NiBr_2-H_2O$) some predictions are made. The $KCl-NiCl_2-H_2O$ system has been partially investigated at 75°C as well. The data on double salt crystallization in the above systems are systematized.

The crystallization of the different double salts in the systems under consideration is discussed using Pauling rules concerning the formation and arrangement of coordination polyhedra in stable ionic crystal structures and Pearson's concept of "hard" and "soft" Lewis acids and bases for the ligands forming the polyhedra as well as the Klopman scale of hardness and softness.

EXPERIMENTAL

Chemical Synthesis and Analyses

The $CsBr-NiBr_2-H_2O$ system was investigated at 25°C by the isothermal evaporation method. The $CsBr-Me^{2+}Br_2-H_2O$ ($Me^{2+} = Mn, Co$) and $NH_4Br-MnBr_2-H_2O$ systems were studied at 25°C, and the $KCl-NiCl_2-H_2O$ system was partially investigated at 75°C by the method of isothermal decrease of the supersaturation (1). Equilibrium was attained under stirring for 24 h at 25°C and for 5–6 h at 75°C. The experiments were carried out with reagents p.a. (Merck).

The compositions of the liquid and the corresponding wet solid phases were analyzed by titrimetric methods, the error ranging from 0.1 to 0.2%. The Co^{2+} and Ni^{2+} ion concentrations were determined by complexometric back titration at pH 5.5–6 (acetate buffer) using Xylenolorange as indicator. The Mn^{2+} ion concentration was established by direct complexometric titration at pH 9.5–10 (ammonia buffer), using Eriochrome black T as indicator with hydroxylamine hydrochloride as reducing agent. The total concentration of X (Cl^- or Br^-) ions was determined argentometrically by the Mohr method. The Me^+X content was calculated from the difference between the total amount of X and the halide concentration corresponding to Me^{2+} ions. The water content in the crystal phases was determined gravimetrically, by the Karl-Fischer method and by TG analysis.

The composition of the solid phases (simple or double salts) considered as thoroughly suction dried was determined by the Schreinemakers method (2).

X-ray Powder Diffraction

The samples of the new established double salts $2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$, $2\text{CsBr} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CsBr} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$ were analyzed at room temperature on a DRON 3M diffractometer (Russia), equipped with a horizontal Bragg-Brentano goniometer of 192 mm radius and Cu-tube (BSV-24 normal focus, 2.0 kW) with a Ni-K β filter (in the diffracted beam), operating at 28 mA and 40 kV. A NaI (Tl) scintillation counter linked to a single channel pulse amplitude discriminator was used. A peak-height approach was adopted to evaluate the reflection position and intensity. The scan range was 8° to 60° 2θ and the scan speed was $1^\circ/\text{min}$. The experimental list of $(2\theta, I)$ was interpreted (Program PDI, Macicek, 1989) by means of the powder patterns calculated by the PWG Program (Macicek 1989, unpublished) from single crystal cell parameters.

RESULTS

The $\text{NH}_4\text{Br}-\text{MnBr}_2-\text{H}_2\text{O}$ System at 25°C

The results presented in Fig. 1 and Table 1 reveal a broad crystallization field for the previously unknown double salt $2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$ and crystallization fields of the salts NH_4Br and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$.

The $\text{CsBr}-\text{MnBr}_2-\text{H}_2\text{O}$ System at 25°C

The results in Fig. 2 and Table 2 show in addition to the simple salts CsBr and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, two new double salts: $\text{CsBr} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$ and $2\text{CsBr} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$.

The $\text{CsBr}-\text{CoBr}_2-\text{H}_2\text{O}$ System at 25°C

Figure 3 and Table 3 indicate crystallization of the simple salts CsBr and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ and the double salts $2\text{CsBr} \cdot \text{CoBr}_2$ and $3\text{CsBr} \cdot \text{CoBr}_2$.

The $\text{CsBr}-\text{NiBr}_2-\text{H}_2\text{O}$ System at 25°C

The results in Fig. 4 and Table 4 show crystallization fields of the simple salts CsBr and $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ and the double salt $\text{CsBr} \cdot \text{NiBr}_2$.

The compositions of all these double salts have been confirmed by Schreinemaker's method and by chemical and X-ray analyses.

The $\text{KCl}-\text{NiCl}_2-\text{H}_2\text{O}$ System at 75°C (3)

We studied several points of the crystallization field of the double salt $5\text{KCl} \cdot 5\text{NiCl}_2 \cdot 9\text{H}_2\text{O}$ established by Petrov *et al.* (3) and found its real composition to be $\text{KCl} \cdot \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (experimental data are: 30.84 mass% KCl ;

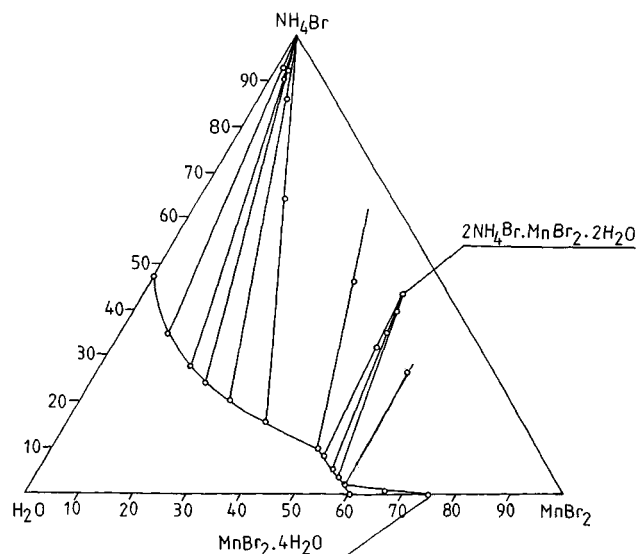


FIG. 1. Solubility diagram of the $\text{NH}_4\text{Br}-\text{MnBr}_2-\text{H}_2\text{O}$ system at 25°C (in mass %).

53.82 mass% NiCl_2 ; 15.18 mass % H_2O). The inaccuracy of the results of Petrov *et al.* is probably due to the very rapid dehydration of the nickel double salts $\text{Me}^+\text{Cl} \cdot \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (4) under air. For this reason all our efforts to measure the crystal structure parameters of the $\text{KCl} \cdot \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ salt have failed.

Crystal Data of the New Double Salts

The crystal structure parameters of the three new established double salts $2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$, $2\text{CsBr} \cdot$

TABLE 1
Solubility in the $\text{NH}_4\text{Br}-\text{MnBr}_2-\text{H}_2\text{O}$ System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
NH_4Br	MnBr_2	NH_4Br	MnBr_2	
47.1	0.0	—	—	NH_4Br
34.7	8.86	93.0	1.08	NH_4Br
27.6	16.4	90.3	2.51	NH_4Br
24.0	21.8	92.6	2.07	NH_4Br
20.0	28.0	86.0	5.10	NH_4Br
15.5	36.9	64.3	15.7	NH_4Br
9.88	49.7	46.5	37.5	Eutonic
8.02	51.5	32.1	49.0	$2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$
5.45	54.6	35.0	49.6	$2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$
3.98	56.4	39.9	48.7	$2\text{NH}_4\text{Br} \cdot \text{MnBr}_2 \cdot 2\text{H}_2\text{O}$
2.03	58.3	26.1	58.6	Eutonic
1.01	58.5	0.05	66.8	$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$
0.0	60.2	—	—	$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$

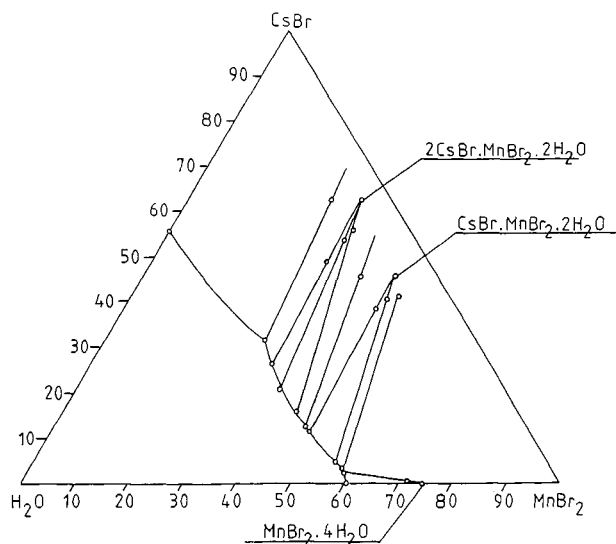


FIG. 2. Solubility diagram of the CsBr-MnBr₂-H₂O system at 25°C (in mass %).

MnBr₂·2H₂O, and CsBr·MnBr₂·2H₂O are shown in Table 5. All they crystallize in crystal system we have predicted earlier (5, 6).

Unfortunately we are not able to provide unit cell parameters for the salt KCl·NiCl₂·2H₂O because it is unstable under air. A series of experiments carried out in order to obtain powder X-ray diffraction data failed. In addition, all attempts to grow single crystals suitable for determination of the unit cell parameters of this double salt failed too. The problem concerning the preparation of single crystals and the determination of the unit cell parameters of KCl·NiCl₂·2H₂O still remains.

TABLE 2
Solubility in the CsBr-MnBr₂-H₂O System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
CsBr	MnBr ₂	CsBr	MnBr ₂	
55.2	0.0	—	—	CsBr
31.5	30.0	62.4	26.3	Eutonic
26.1	33.5	49.0	32.6	2CsBr·MnBr ₂ ·2H ₂ O
20.1	37.7	53.5	32.8	2CsBr·MnBr ₂ ·2H ₂ O
15.8	43.3	50.1	33.1	2CsBr·MnBr ₂ ·2H ₂ O
12.4	46.4	45.7	40.0	Eutonic
11.6	47.7	38.7	47.2	CsBr·MnBr ₂ ·2H ₂ O
4.58	56.1	40.1	47.7	CsBr·MnBr ₂ ·2H ₂ O
3.10	58.2	41.7	49.5	Eutonic
1.21	59.6	6.42	71.8	MnBr ₂ ·4H ₂ O
0.0	60.2	—	—	MnBr ₂ ·4H ₂ O

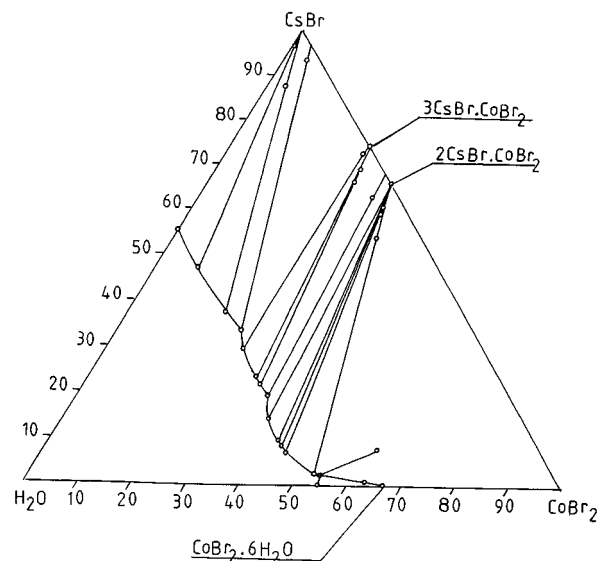


FIG. 3. Solubility diagram of the CsBr-CoBr₂-H₂O system at 25°C (in mass %).

CRYSTAL CHEMISTRY OF THE DOUBLE SALTS $mMe^+X \cdot Me^{2+}X_2 \cdot nH_2O$ ($m = 1, 2, 3; n = 0, 2, 6$)

Double salts of the type $mMe^+X \cdot Me^{2+}X_2 \cdot nH_2O$ ($m = 1, 2, 3; n = 0, 2, 6$) crystallize under standard conditions in the systems $Me^+X - Me^{2+}X_2 - H_2O$ ($Me^+ = K, NH_4, Rb, Cs; Me^{2+} = Mn, Co, Ni; X = Cl, Br$). Data on the composition of these salts at 25°C obtained by us as well as

TABLE 3
Solubility in the CsBr-CoBr₂-H₂O System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
CsBr	CoBr ₂	CsBr	CoBr ₂	
55.2	0.0	—	—	CsBr
47.8	8.11	97.5	0.49	CsBr
37.8	18.5	88.0	3.68	CsBr
34.4	23.0	93.4	4.42	Eutonic
30.0	25.5	72.8	25.2	3CsBr·CoBr ₂
24.0	31.2	69.0	26.3	3CsBr·CoBr ₂
21.9	32.8	61.3	27.0	3CsBr·CoBr ₂
18.2	35.8	63.3	32.4	Eutonic
14.8	38.7	66.0	33.9	2CsBr·CoBr ₂
10.0	42.6	66.0	33.9	2CsBr·CoBr ₂
8.60	44.1	61.0	35.2	2CsBr·CoBr ₂
7.60	41.3	59.1	35.5	2CsBr·CoBr ₂
3.30	53.0	54.6	37.1	2CsBr·CoBr ₂
2.80	54.3	7.40	62.0	Eutonic
2.80	54.3	1.03	63.6	CoBr ₂ ·6H ₂ O
0.0	54.0	—	—	CoBr ₂ ·6H ₂ O

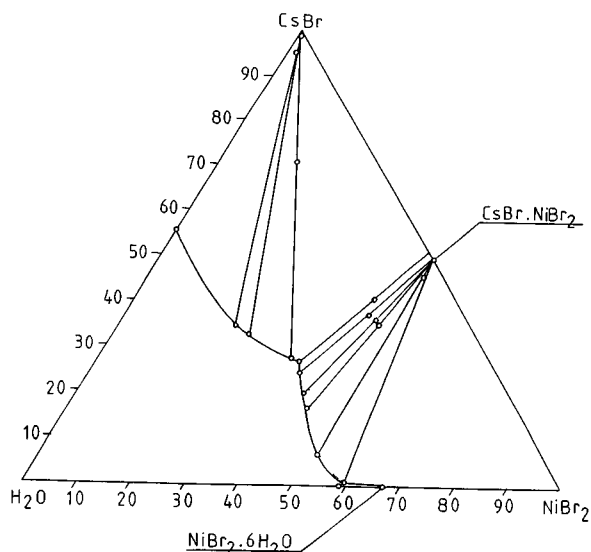


FIG. 4. Solubility diagram of the CsBr–NiBr₂–H₂O system at 25°C (in mass %).

taken from the literature are presented in Tables 6–8. Data for a broader temperature range are presented in these tables only in cases needed for discussions (exceptions from our conclusions). The analysis of the data shows that in the manganese systems crystallize double salts $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (2:1:2) and, in separate cases, $Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (1:1:2) (Table 6). The double salts crystallizing in the nickel systems (Table 8) are of the types $Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (1:1:2) and $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ (1:1:6). All three types of hydrated salts 2:1:2, 1:1:2, and 1:1:6 crystallize in the cobalt systems (Table 7). Anhydrous double salts $2Me^+X \cdot Me^{2+}X_2$ (2:1:0) and $3Me^+X \cdot$

TABLE 4
Solubility in the CsBr–NiBr₂–H₂O System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
CsBr	NiBr ₂	CsBr	NiBr ₂	
55.2	0.0	—	—	CsBr
34.9	21.9	95.3	1.52	CsBr
33.0	25.1	99.2	0.25	CsBr
28.0	35.8	70.6	14.6	CsBr
27.0	37.9	40.8	44.2	Eutonic
24.5	38.7	37.7	44.8	CsBr · NiBr ₂
20.0	41.8	36.3	47.0	CsBr · NiBr ₂
16.4	44.3	35.0	48.2	CsBr · NiBr ₂
6.20	51.4	45.7	50.9	CsBr · NiBr ₂
0.45	59.4	41.0	52.1	CsBr · NiBr ₂
0.45	59.4	0.21	64.0	NiBr ₂ · 6H ₂ O
0.0	58.8	—	—	NiBr ₂ · 6H ₂ O

TABLE 5
Unit Cells Parameters of the New Established Double Salts

Parameter	2NH ₄ Br · MnBr ₂ · 2H ₂ O	2CsBr · MnBr ₂ · 2H ₂ O	CsBr · MnBr ₂ · 2H ₂ O
<i>a</i> (Å)	7.886(1)	5.993(1)	9.523(2)
<i>b</i> (Å)	7.886(1)	7.054(2)	7.514(1)
<i>c</i> (Å)	8.529(2)	7.587(2)	11.951(3)
α (°)	90	66.02(2)	90
β (°)	90	87.87(2)	90
γ (°)	90	83.95(2)	90
<i>Z</i>	2	1	4
<i>V</i> (Å ³)	530.4(2)	291.4(1)	855.2(3)
<i>D_x</i>	2.797	3.854	3.600
Space group	<i>P4₂/mmm</i>	<i>P</i> $\bar{1}$	<i>Pcca</i>

$Me^{2+}X_2$ (3:1:0) are found in cesium cobalt systems. The anhydrous double salt $Me^+X \cdot Me^{2+}X_2$ (1:1:0) has been found only in the cesium nickel bromide system.

The crystal chemistry of the hydrated salts $Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (1:1:2), $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (2:1:2) and $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ (1:1:6) has been the subject of previous discussions (5–7). The principal structural units of the $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (2:1:2) and $Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ (1:1:2) salts are the mixed octahedra $[Me^{2+}(H_2O)_2X_4]$. With the salts (2:1:2) these octahedra are discrete (5), while with (1:1:2) they are condensed, sharing halogen ions (6). The aquaoctahedra $[Me^{2+}(H_2O)_6]$ participate in the structures of the salts $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$ (1:1:6) (7).

The double salts $Me^+X \cdot Me^{2+}X_2$ (1:1:0) usually crystallize in cubic or hexagonal crystal systems. Those in cubic

TABLE 6
Double Salts Obtained from MeX – MnX_2 – H_2O Systems^a

<i>MeX</i>	MnCl ₂	MnBr ₂	
<i>KX</i>	25–50°C (20) 1:1:2	25–75°C (21) 75°C (20) 2:1:2 1:1:2 4:1:0	25°C (5) No double salts
<i>NH₄X</i>	25°C (22) 2:1:2 MC: α , β^b	25°C (19) 2:1:2	
<i>RbX</i>	25°C (23) 2:1:2	(19) 2:1:2 ^c	
<i>CsX</i>	25°C (24) 2:1:2 1:1:2	25°C (19) 2:1:2 1:1:2	

^aThe ratio between the digits denotes the molar ratio $MeX:MnX_2:H_2O$ in the double salts.

^bMC, mixed crystals.

^cTheoretical predicted double salt.

TABLE 7
Double Salts Obtained from $MeX-CoX_2-H_2O$ Systems^a

MeX	$CoCl_2$		$CoBr_2$	
KX	0–40°C (25–27) No double salts	44–95°C (25–27) 1:1:2 MC – α, β^b	0–40°C (28) No double salts	45–115°C (28) MC ^b
NH_4X	25°C (29, 30) 2:1:2 MC: α, β^b		0–40°C (31) No double salts	42–100°C (31) 2:1:2
RbX	25°C (32) 1:1:2 2:1:2		25°C (7) 1:1:6	
CsX	25°C (32) 1:1:2 2:1:0 3:1:0		25°C (19) 2:1:0 3:1:0	

^aThe ratio between the digits denotes the molar ratio $MeX:CoX_2:H_2O$ in the double salts.

^bMC, mixed crystals.

TABLE 8
Double Salts Obtained from $MeX-NiX_2-H_2O$ Systems^a

MeX	$NiCl_2$		$NiBr_2$	
KX	–10–70°C (3, 33) No double salts	50°C (3) 4:7:14	75°C (19) 1:1:2	25°C (7) 1:1:6
NH_4X	25°C (34) 1:1:2 MC- α, β^b		25°C (5) 1:1:6	
RbX	25°C (4) 2:1:2	50–75°C (4) 2:1:2 1:1:2	(19) 1:1:6 ^c	
CsX	25°C (35) 1:1:2		25°C (19) 1:1:0	

^aThe ratio between the digits denotes the molar ratio $MeX:NiX_2:H_2O$ in the double salts.

^bMC, mixed crystals.

^cTheoretical predicted double salt.

systems have the ideal perovskite type structure (Fig. 5a), whereas those in a hexagonal system possess a distorted perovskite-type structure (Fig. 5b). Some 1:1:0 salts have structures intermediate (Fig. 5c, 5d, and 5e) between the cubic and the hexagonal types (8). The building units in all these structures are condensed octahedra $[Me^{2+}X_6]$ and isolated Me^+ ions. The octahedra are bonded by common corners, edges or faces depending on their stability deter-

mined according to the first Pauling rule (see Table 9). In cases when the $[Me^{2+}X_6]$ octahedra are stable, e.g., $[Mn^{2+}Cl_6]$, they are connected by common corners to nets that form a cubic perovskite-type structure (Fig. 5a (9)). In cases when the $[Me^{2+}X_6]$ octahedra are unstable, e.g., $[Ni^{2+}X_6]$, $[Co^{2+}X_6]$, and $[Mn^{2+}Br_6]$, stabilization is achieved at the expense of distortion. The octahedra are

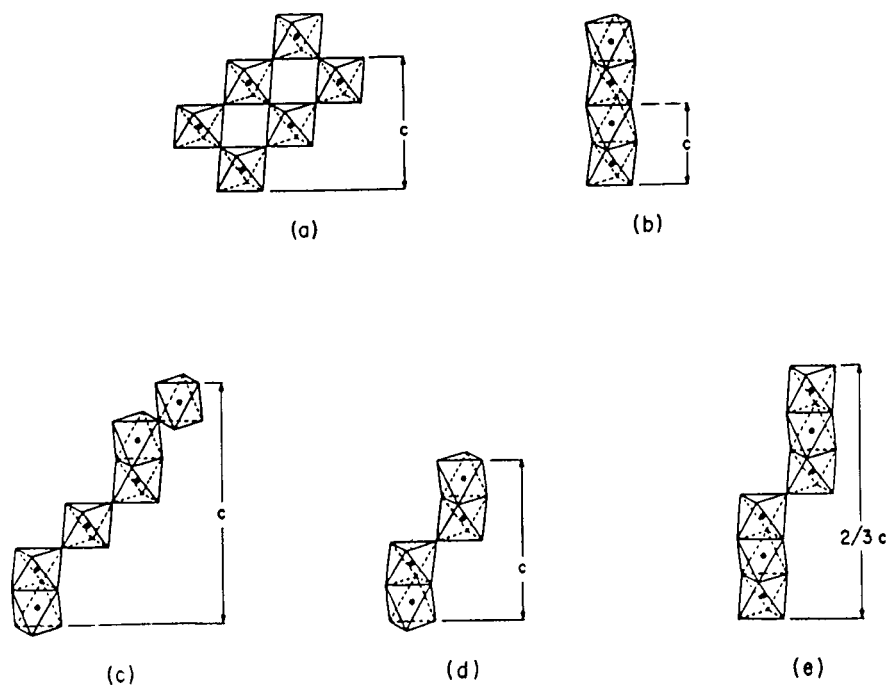


FIG. 5. Projection of octahedra network of (110) plane in a unit cell of $Me^+X \cdot Me^{2+}X_2$ salts (9). (a) Cubic (c) (e.g., $KCl \cdot MnCl_2$); (b) hexagonal (hex) (e.g., $CsBr \cdot NiBr_2$); (c) c:hex = 2:1 (e.g., $RbCl \cdot MgCl_2$); (d) c:hex = 1:1 (e.g., $CsBr \cdot CuBr_2$); (e) c:hex = 1:2 (e.g., $CsCl \cdot MnCl_2$).

TABLE 9
Stability of Me^{2+} -Polyhedra (Determined According to the First Pauling Rule ($r_{Me^{2+}}/r_L$))

Me^{2+} -polyhedra	Mn^{2+}		Co^{2+}		Ni^{2+}	
	Cl^-	Br^-	Cl^-	Br^-	Cl^-	Br^-
$[Me^{2+}(H_2O)_2X_4]$	Stable	Stable	Stable	^a	^a	Unstable
$[Me^{2+}(H_2O)_6]$	Stable	Stable	Stable	Stable	Stable	Stable
$[Me^{2+}X_6]$	Stable	^a	^a	Unstable	Unstable	Unstable
$[Me^{2+}X_4]$	Unstable	^a	^a	Stable	Stable	Stable

^aA polyhedra at the stability boundary of the corresponding geometric form.

bonded by common faces and form endless chains with the composition $[Me^{2+}X_3]_n^{2-}$, producing a hexagonal perovskite-type structure (Fig. 5b (9)). This hexagonal structure is additionally stabilized by the presence of the larger Me^+ ions (e.g., $CsBr \cdot NiBr_2$ (10)). Structures with chains of edge-bonded dimers $[Me_2^{2+}X_9]$ and trimers $[Me_3^{2+}X_{12}]$ are intermediate between the cubic and the hexagonal perovskite types (Figs. 5c–5e) (9).

The double salts $2Me^+X \cdot Me^{2+}X_2$ (2:1:0) crystallize in general in two main structural types; K_2NiF_4 (tetragonal) and β - K_2SO_4 (orthorhombic), and consist, respectively, of $[Me^{2+}X_6]$ octahedra and $[Me^{2+}X_4]$ tetrahedra. No double salts of nickel chlorides and bromides of this formula type have been reported previously. We characterized two cobalt salts: $2CsX \cdot CoX_2$ ($X^- = Cl, Br$) that belong to the structural type β - K_2SO_4 and consist of isolated $[Co^{2+}X_4]$ tetrahedra with Cs^+ ions situated between them (11). It is expected that all other 2:1:0 cobalt salts should belong to this structural type due to the pronounced trend of Co^{2+} ions toward tetrahedral coordination.

The cobalt salts $3CsX \cdot CoX_2$ ($X^- = Cl, Br$) crystallize in the tetragonal crystal system, space group $I4/mcm$. Similar to $2CsX \cdot CoX_2$ salts, their structures consist of isolated $[Co^{2+}X_4]$ tetrahedra and Cs^+ ions as well as free Cl^- ions (12).

Table 9 shows the expected Me^{2+} polyhedra participating in the structures of the double salts crystallizing in these systems. According to Pauling stable polyhedra are those satisfying the geometric conditions:

$$0.22 \leq r_{Me^{2+}}/r_L \leq 0.41 \text{ for coordination number 4} \quad [1],$$

and

$$0.41 \leq r_{Me^{2+}}/r_L \leq 0.73 \text{ for coordination number 6.} \quad [2]$$

DISCUSSION

Crystallization of double salts from multicomponent aqueous-salt systems depends on: (i) a sufficiently high thermodynamic activity in the solution of the complexes charac-

teristic of the double salt structure and (ii) the stability of the crystal structures formed by these complexes.

The stable ionic crystal structures follow the Pauling rules of formation and arrangement of the coordination polyhedra in structures. The types of ligands that form polyhedra around cations are determined by using Pearson's "hard" and "soft" Lewis acids and bases concept (13–16).

All the Me^{2+} complexes discussed above (Table 9) may exist statistically in the solutions under consideration. However, mixed complexes should predominate because from the viewpoint of the "hardness–softness" factor (14–17) and the corresponding Klopman scale (18), Mn^{2+} , Co^{2+} , and Ni^{2+} ions are Lewis acids intermediate in "hardness."

In cases when the predominating mixed $[Me^{2+}(H_2O)_2X_4]$ octahedra are stable, i.e., in the systems with the participation of $MnCl_2$, $MnBr_2$, and $CoCl_2$ (Table 9), crystallization of 2:1:2 double salts (Tables 6 and 7), where these octahedra are discrete, should be expected. The exceptions in potassium and cesium systems are mainly due to the effect of the size of K^+ and Cs^+ ions on the stability of the 2:1:2 salt structures (5, 16).

In systems in which $CoBr_2$ and $NiCl_2$ participate the mixed $[Co^{2+}(H_2O)_2Br_4]$ and $[Ni^{2+}(H_2O)_2Cl_4]$ octahedra are at the stability boundary (Table 9). Their stabilization in the crystal structure of the double salt may be achieved at the expense of distortion. Distorted and condensed octahedra sharing halogen ions build the crystal structures of the 1:1:2 double salts. Thus in the case of all nickel chloride systems under consideration, double salts 1:1:2 crystallize (Table 8). In the cobalt bromide systems no 1:1:2 double salt has been established, probably because the large Br^- ions create holes too large to be occupied by Me^+ ions and still do not yield a structure characteristic of 1:1:2 chloride salts (6). The only 1:1:2 bromide double salt established up to now contains large Cs^+ ions, i.e., $CsBr \cdot MnBr_2 \cdot 2H_2O$ (19). In the cobalt bromide systems double salts from other compositions are crystallizing formed by other stable polyhedra, i.e., the $[Co^{2+}(H_2O)_6]$ aqua octahedra (e.g., with $RbBr \cdot CoBr_2 \cdot 6H_2O$ salts (7)) or condensed $[Co^{2+}Br_4]$ bromide tetrahedra (e.g., with $mCsBr \cdot CoBr_2$ ($m = 2, 3$) salts) (Table 7).

TABLE 10
Tolerance Factors t of the Possible $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$ and $Me^+Br \cdot Me^{2+}Br_2$ ($Me^{2+} = Ni, Co$) Salts

$Me^+ \setminus X^-$	$Me^+Br \cdot Ni^{2+}Br_2 \cdot 6H_2O$	$Me^+Br \cdot Ni^{2+}Br_2$	$Me^+Br \cdot Co^{2+}Br_2 \cdot 6H_2O$	$Me^+Br \cdot Co^{2+}Br_2$
K^+	1.020	0.891	1.029	0.873
NH_4^+	1.005	0.904	1.014	0.886
Rb^+	0.979	0.929	0.988	0.910
Cs^+	0.939	0.969	0.947	0.949

Note. Ionic radii used: $r_{Br^-} = 0.196$ nm; $r_{K^+} = 0.138$ nm; $r_{Rb^+} = 0.152$ nm; $r_{Cs^+} = 0.167$ nm; $r_{Ni^{2+}} = 0.069$ nm; $r_{Co^{2+}}^{HS} = 0.0745$ nm (36); $r_{NH_4^+} = 0.143$ nm (37); $r_{[Ni(H_2O)_6]^{2+}} \cong 0.286$ nm; $r_{[Co(H_2O)_6]^{2+}} \cong 0.290$ nm (7).

In systems with $NiBr_2$ the mixed $[Ni^{2+}(H_2O)_2Br_4]$ octahedra are unstable (Table 9) and crystallization of 2:1:2 and 1:1:2 salts is improbable. $[Ni^{2+}(H_2O)_6]$ aqua octahedra and $[Ni^{2+}Br_4]$ tetrahedra are stable and could participate in the crystallization. However, only the $[Ni^{2+}(H_2O)_6]$ aqua octahedra is expected to determine the crystallization of 1:1:6 salts with a perovskite type crystal structure (7) (Table 8) because Ni^{2+} ions usually prefer octahedral coordination in their salts. Anhydrous $Me^+Br \cdot Ni^{2+}Br_2$ salts (8, 10) consisting of distorted $[Ni^{2+}Br_6]$ octahedra connected by common faces also possess distorted perovskite-type structures. We have calculated the geometrical tolerance factor t of the perovskite structure for the salts $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$ ($Me^{2+} = Ni, Co$) (7) and $Me^+Br \cdot Me^{2+}Br_2$ ($Me^{2+} = Ni, Co$) (Table 10) using Goldschmidt's formula (38),

$$r_A + r_X = t\sqrt{2}(r_B + r_X), \quad [3]$$

by assuming that they are distorted ABX_3 perovskites, where $r_A = r_{[Me(H_2O)_6]^{2+}}$, $r_B = r_{Me^+}$, and $r_X = r_{Br^-}$ for the salts 1:1:6 and $r_A = r_{Me^+}$, $r_B = r_{Me^{2+}}$, and $r_X = r_{Br^-}$ for the 1:1:0 salts.

For the ideal perovskite structure $t = 1.0$. The comparison between the analogous anhydrous and hydrated double salts in Table 10 shows that closer to the ideal perovskite structure are $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$ ($Me^+ = K, NH_4, Rb; Me^{2+} = Ni, Co$) and $CsBr \cdot NiBr_2$ salts. So their crystallization is expected. This is confirmed by the results shown in Tables 7 and 8. Crystallization of the salts $CsBr \cdot NiBr_2 \cdot 6H_2O$ and $Me^+Br \cdot CoBr_2 \cdot 6H_2O$ (K, NH_4, Cs) is also possible but at lower temperatures, while that of $Me^+Br \cdot Me^{2+}Br_2$ ($Me^+ = K, NH_4, Rb, Cs; Me^{2+} = Ni, Co$) is expected to occur at higher temperature.

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