# The Double Salts $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$
# ($Me^+$ = K, NH₄, Rb; $Me^{2+}$ = Co, Ni)

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The ability of the $Co^{2+}$ and $Ni^{2+}$ ions to form double salts of the carnallite formula type ($Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$) in aqueous-halide solutions is established. Two new double salts, $KBr \cdot NiBr_2 \cdot 6H_2O$ (PDF 45-196) and $RbBr \cdot CoBr_2 \cdot 6H_2O$ (PDF 45-198), are found in the $KBr$–$NiBr_2$–$H_2O$ and $RbBr$–$CoBr_2$–$H_2O$ systems, respectively. The structure of $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ (1) (PDF 45-193), to which the salts are isopointal, was determined by single crystal X-ray diffraction: monoclinic crystal system, space group $C2/c$, $a = 9.574(2)$ Å, $b = 9.756(2)$ Å, $c = 13.668(2)$ Å, $\beta = 90.10(2)°$, $V = 1276.6(5)$ Å³, $Z = 4$, $Dx = 2.208$, F.W. = 424.56, $R = 0.050$, $WR = 0.054$ for 743 reflections with $I > 2\sigma(I)$. The compounds have a distorted perovskite type structure by analogy with the monoclinic magnesium carnallites. The crystallization of the double salts $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ from aqueous-halide solutions is connected with the cations' ability to form the complexes $[Me^{2+}(H_2O)_6]$ and $[Me^+X_6]$. Geometric and metal–ligand interaction factors that affect the formation of these complexes are discussed. The "hard–soft" acid/base factor is used as a measure for metal-ligand interaction. The geometrical tolerance factor $t$ of all possible $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ ($Me^{2+}$ = Ni, Co) double salts is calculated. © 1997 Academic Press

## INTRODUCTION

Only reports of magnesium double salts of the carnallite formula type $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ (1:1:6), where $Me^{2+}$ = Mg; $Me^+$ = Li(H₂O), K, NH₄, Rb, Cs; $X^-$ = Cl, Br, I, can be found in the literature. The sole exceptions are $NH_4Br \cdot FeBr_2 \cdot 6H_2O$ (2) and the recently reported $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ (1) double salts. The magnesium carnallite type double salts have been investigated in detail. Fluorocarnallites and sodium carnallites do not exist. Almost all $Me^+X \cdot MgX_2 \cdot 6H_2O$ have similar perovskite type structures and crystallize in the monoclinic crystal system, space group $C2/c$ (3–5). It has been claimed that $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ (6), $RbCl \cdot MgCl_2 \cdot 6H_2O$ (7), and $CsCl \cdot MgCl_2 \cdot 6H_2O$ (8) belong to the triclinic crystal system, space group $P1$, but Marsh (9) showed that the

centrosymmetric monoclinic structures are correct. Potassium chlorocarnallite alone crystallizes in the orthorhombic crystal system, space group *Pnna* (10, 11).

The purpose of this paper is to report a study of the systems $KBr$–$NiBr_2$–$H_2O$ and $RbBr$–$CoBr_2$–$H_2O$ and rationalize the existence and the crystal structure type of the obtained $KBr \cdot NiBr_2 \cdot 6H_2O$ and $RbBr \cdot CoBr_2 \cdot 6H_2O$ double salts. Unit cell parameters of the double salts reported herein were measured on a single crystal X-ray diffractometer and used to index the powder patterns ($KBr \cdot NiBr_2 \cdot 6H_2O$ PDF 45–196, $RbBr \cdot CoBr_2 \cdot 6H_2O$ PDF 45–198, $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ PDF 45–193, (12)). The detailed structure of $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ was determined.

## EXPERIMENTAL

### Chemical Synthesis and Analyses

The $KBr$–$NiBr_2$–$H_2O$ and $RbBr$–$CoBr_2$–$H_2O$ systems were studied at 25°C by the method of isothermal decrease of supersaturation (13). Equilibrium was attained by continuous stirring for 24 h. Merck reagents (A.R.) were used. The compositions of the liquid and the corresponding wet solid phases were analyzed by titrimetic (complexometric for $Co^{2+}$ and $Ni^{2+}$ ions (14) and argentometric methods (Mohr's method) for the total amount of $Br^-$ ions (15)). The error in the volumetric analyses used was about 0.1–0.2%. The $Me^+Br$ content was calculated from the difference between the total amount of bromides and the bromides corresponding to the $Me^{2+}$ ions. The crystal water content in the double salts was established by gravimetric and TG analyses. The compositions of the thoroughly suction-dried solid phases were determined graphically by the Schreinemakers' method (16).

### X-ray Analysis

The unit cell parameters of the double salts $KBr \cdot NiBr_2 \cdot 6H_2O$ and $RbBr \cdot CoBr_2 \cdot 6H_2O$ were determined on an Enraf–Nonius CAD-4 single-crystal diffractometer.

Intensity data for $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ were collected on the same equipment. Crystal data and experimental details obtained using the Patterson method are summerized in Table 1.

## RESULTS

### The KBr–NiBr$_2$–H$_2$O System at 25°C

The results are presented in Fig. 1 and Table 2. A field of crystallization for the $KBr \cdot NiBr_2 \cdot 6H_2O$ double salt has been established.

### The RbBr–CoBr$_2$–H$_2$O System at 25°C

The results (see Fig. 2 and Table 3) are analogous to those of the previous system and $RbBr \cdot CoBr_2 \cdot 6H_2O$ double salt

### TABLE 1
### Crystal Data and Experimental Details for
### NH$_4$Br · NiBr$_2$ · 6H$_2$O

| | |
|---|---|
| Chemical formula | $Br_3NiO_6NH_{16}$ |
| Colour | Green |
| Formula weight | 424.56 |
| Crystal system | Monoclinic |
| Space group | $C2/c$ (15) |
| $a$, Å | 9.574(2) |
| $b$, Å | 9.756(2) |
| $c$, Å | 13.668(2) |
| $\beta$, ° | 90.10(2) |
| $V$, Å$^3$ | 1276.6(5) |
| $Z$ | 4 |
| Temperature, K | 292 |
| Crystal size, mm | $0.26 \times 0.16 \times 0.13$ |
| Density$_{calc}$, g·cm$^{-3}$ | 2.208 |
| $\mu$, cm$^{-1}$ | 10.82 |
| Absorption correction type | spherical |
| Absorption correction, $T_{min}/T_{max}$ | 0.213/0.235 |
| Radiation | $MoK\alpha$ (graphite monochromator) |
| $\lambda$ | 0.71073 |
| Scan mode | $\omega/2\theta$ |
| Total no. reflections | 3985 |
| No. equivalent reflections | 1864 |
| $R_{int}$ | 0.046 |
| $\theta$ limits, ° | 0–30 ($h = 0$–9; $k = -19$–19; $l = -9$–9) |
| Standards: no./interval, min/decay, % | 3/120/1.6 |
| No. observed reflections | 743 |
| Observed criterion | $I > 2 \cdot \sigma(I)$ |
| Structure solution | Patterson method |
| Refinement | on $F$ |
| Weighting scheme | $1/[\sigma^2(F) + (0.030.F)^2]$ |
| Hydrogen treatment | located and refined with fixed $U = 0.05$ Å$^2$ |
| Extinction expression | $F_c^{corr} = F_c/(1 + gF_c)$ |
| Extinction coefficient | $16.972 \cdot 10^{-7}$ |
| $R$ | 0.050 |
| $wR$ | 0.054 |
| Goodness of fit | 1.086 |
| $\Delta/\rho$ | 0.262 |
| $\Delta\rho_{max}$ | 0.825 |
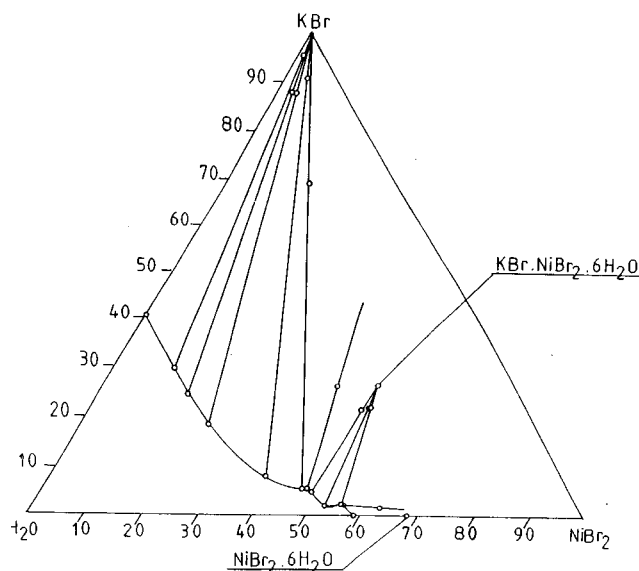


**FIG. 1.** Solubility diagram of the KBr–NiBr$_2$–H$_2$O system at 25°C (in mass %).

has been established. The compositions of both the previously unreported double salts were confirmed by chemical, X-ray and TG-analyses.

### Crystal Data of the Me$^+$X · Me$^{2+}$X$_2$ · 6H$_2$O Double Salts

The crystal data of the new double salts $KBr \cdot NiBr_2 \cdot 6H_2O$ and $RbBr \cdot CoBr_2 \cdot 6H_2O$ and the previously reported $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ double salt (1) are shown in Table 4. New measurements on single crystals of the

### TABLE 2
### Solubility in the KBr–NiBr$_2$–H$_2$O System at 25°C

| Liquid phase (mass %) | | Wet solid phase (mass %) | | Solid phase |
|---|---|---|---|---|
| KBr | NiBr$_2$ | KBr | NiBr$_2$ | |
| 40.6 | 0.00 | — | — | KBr |
| 30.0 | 10.4 | 95.7 | 0.73 | KBr |
| 24.8 | 15.4 | 88.1 | 2.67 | KBr |
| 19.0 | 22.2 | 87.9 | 3.33 | KBr |
| 8.20 | 38.7 | 91.0 | 3.82 | KBr |
| 5.94 | 46.8 | 69.1 | 15.1 | KBr |
| 6.02 | 47.3 | 26.3 | 42.2 | eutonic |
| 5.03 | 48.5 | 22.0 | 49.1 | $KBr \cdot NiBr_2 \cdot 6H_2O$ |
| 2.05 | 52.7 | 22.2 | 50.1 | $KBr \cdot NiBr_2 \cdot 6H_2O$ |
| 2.49 | 55.3 | 22.3 | 50.4 | $KBr \cdot NiBr_2 \cdot 6H_2O$ |
| 2.36 | 55.9 | 1.96 | 62.5 | eutonic |
| 0.00 | 58.8 | — | — | $NiBr_2 \cdot 6H_2O$ |
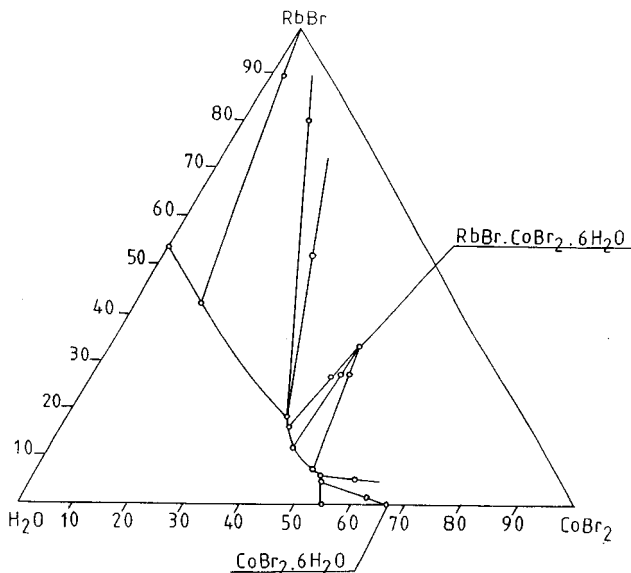
**FIG. 2.** Solubility diagram of the RbBr–CoBr$_2$–H$_2$O system at 25°C (in mass %).

NH$_4$Br · NiBr$_2$ · 6H$_2$O double salt were carried out[1] and the results (see Table 4) show that the three salts are isostructural and crystallize with a prismatic habit in a monoclinic crystal system, space group $C2/c$. Atomic coordinates of the ammonium salt are given in Table 5 and selected geometric data are summarized in Table 6. The atom numbering scheme is shown on Fig. 3. The structure of NH$_4$Br · NiBr$_2$ · 6H$_2$O is a pseudo-perovskite type and is built up of a 3D framework of corner-sharing [NH$_4$Br$_6$] octahedra and isolated [Ni(H$_2$O)$_6$]$^{2+}$ octahedra within the holes as shown on Fig. 3. The NH$_4^+$ cation is surrounded by

[1] Details of the X-ray analysis are deposited in the CIF format.

**TABLE 3**
**Solubility in the RbBr–CoBr$_2$–H$_2$O System at 25°C**

| Liquid phase (mass %) | | Wet solid phase (mass %) | | Solid phase |
|---|---|---|---|---|
| RbBr | CoBr$_2$ | RbBr | CoBr$_2$ | |
| 53.4 | 0.00 | — | — | RbBr |
| 42.2 | 11.6 | 89.2 | 2.19 | RbBr |
| 18.1 | 39.3 | 79.9 | 11.7 | eutonic |
| 18.2 | 39.2 | 52.0 | 26.7 | eutonic |
| 16.0 | 40.7 | 26.9 | 42.9 | RbBr · CoBr$_2$ · 6H$_2$O |
| 11.8 | 43.8 | 27.3 | 44.2 | RbBr · CoBr$_2$ · 6H$_2$O |
| 7.26 | 49.3 | 27.8 | 45.9 | RbBr · CoBr$_2$ · 6H$_2$O |
| 5.89 | 51.5 | 5.15 | 58.0 | eutonic |
| 4.74 | 52.7 | 1.47 | 62.2 | CoBr$_2$ · 6H$_2$O |
| 0.00 | 54.8 | — | — | CoBr$_2$ · 6H$_2$O |

**TABLE 4**
**Crystal Data of the $Me^+X \cdot Me^{2+}X_2 \cdot$ 6H$_2$O Double Salts**

| Parameter | KBr · NiBr$_2$ · 6H$_2$O | NH$_4$Br · NiBr$_2$ · 6H$_2$O | RbBr · CoBr$_2$ · 6H$_2$O |
|---|---|---|---|
| $a$, Å | 9.509(3) | 9.574(2) | 9.616(3) |
| $b$, Å | 9.693(2) | 9.756(2) | 9.832(5) |
| $c$, Å | 13.579(3) | 13.668(2) | 13.743(2) |
| $\beta$, ° | 90.06(2) | 90.10(2) | 90.09(2) |
| $Z$ | 4 | 4 | 4 |
| $V$, Å$^3$ | 1251.7(8) | 1276.6(5) | 1299.3(8) |
| $D_X$ | 2.365 | 2.208 | 2.516 |
| Space group | $C2/c$ | $C2/c$ | $C2/c$ |

six Br$^-$ anions at distances varying between 3.397(7) and 3.439(7) Å. Each Br$^-$ anion is surrounded by two NH$_4^+$ cations and four water molecules from the four [Ni(H$_2$O)$_6$]$^{2+}$ octahedra. The [Ni(H$_2$O)$_6$]$^{2+}$ octahedron is regular with Ni–O distances varying between 2.034(5) and 2.046(5) Å in close agreement with those in the $Me^+$Cl · MgCl$_2$ · 6H$_2$O double salts ($Me^+$ = K (11); Rb (9); Cs (8)). Each water molecule is H-bonded to two Br$^-$ ions. The Br ⋯ O H-bonding distances, varying between 3.308(5) and 3.357(5) Å, are a little shorter than the Br ⋯ N distances. The average Br ⋯ O ⋯ Br angle is 93.5(2)° and the Ni–O ⋯ Br angles are 123.1(2)° and 129.4(2)° respectively.

## Calculation of the $[Ni(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ Ionic Radii

Emons *et al.* (3) and Waisumi *et al.* (8) determined the ionic radius of $[Mg(H_2O)_6]^{2+}$ to be 2.90 Å by two different methods based (i) on the crystal parameters of the double

**TABLE 5**
**Positional and Equivalent Isotropic Displacement Parameters (Å) of the NH$_4$Br · NiBr$_2$ · 6H$_2$O Double Salt**

| Label | $x$ | $y$ | $z$ | $U_{iso/eq}$ |
|---|---|---|---|---|
| Br1 | 0.24657(9) | 0.25890(6) | 0.25257(7) | 0.0402(2) |
| Br2 | 0.00000 | 0.00000 | 0.00000 | 0.0421(3) |
| Ni | 0.50000 | 0.00000 | 050000 | 0.0217(3) |
| O1 | 0.4312(6) | 0.0102(5) | 0.3591(3) | 0.041(2) |
| O2 | 0.6731(5) | 0.1105(6) | 0.4616(4) | 0.040(1) |
| O3 | 0.3991(6) | 0.1785(5) | 0.5300(5) | 0.051(2) |
| N | 0.00000 | 0.003(1) | 0.25000 | 0.053(3) |
| H11 | 0.370(7) | 0.073(9) | 0.356(5) | 0.051 |
| H12 | 0.400(8) | − 0.043(8) | 0.354(6) | 0.051 |
| H21 | 0.332(8) | 0.103(9) | 0.081(6) | 0.051 |
| H22 | 0.226(8) | 0.075(9) | 0.018(6) | 0.051 |
| H31 | 0.141(8) | 0.310(9) | 0.448(7) | 0.051 |
| H32 | 0.064(8) | 0.263(9) | 0.496(7) | 0.051 |
| HN1 | 0.082(8) | − 0.010(8) | 0.239(6) | 0.051 |
| HN2 | − 0.010(9) | − 0.000(7) | 0.293(5) | 0.051 |

**TABLE 6**
**Selected Interatomic Distances (Å) and Hydrogen Bond Geometry (Å, °) of the $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ Double Salt**

| | | | | |
|---|---|---|---|---|
| Ni–O1 | 2.037(5) | | Br1–O3$^{iv}$ | 3.3414(9) |
| Ni–O1$^i$ | 2.037(5) | | Br1–N | 3.439(7) |
| Ni–O2 | 2.046(5) | | Br1–N$^v$ | 3.397(7) |
| Ni–O2$^i$ | 2.046(5) | | Br2–O2$^{iii}$ | 3.351(5) |
| Ni–O3 | 2.034(5) | | Br2–O2$^{vi}$ | 3.351(5) |
| Ni–O3$^i$ | 2.034(5) | | Br2–O3$^{vii}$ | 3.308(5) |
| Br1–O1 | 3.335(5) | | Br2–O3$^{viii}$ | 3.308(5) |
| Br1–O1$^{ii}$ | 3.350(5) | | Br2–N | 3.41709(8) |
| Br1–O2$^{iii}$ | 3.357(5) | | Br2–N$^{ix}$ | 3.41709(8) |

| D–H$\cdots$A | D–H | H$\cdots$A | D$\cdots$A | D–H$\cdots$A | A$\cdots$H$\cdots$A |
|---|---|---|---|---|---|
| O1–H11$\cdots$Br1 | 0.85(8) | 2.58(8) | 3.335(5) | 148(6) | |
| O1–H12$\cdots$Br1$^{vii}$ | 0.60(8) | 2.80(8) | 3.350(5) | 154(9) | |
| O2–H21$\cdots$Br1$^{iii}$ | 0.59(8) | 2.91(8) | 3.357(5) | 135(9) | |
| O2–H22$\cdots$Br2$^{iii}$ | 1.06(8) | 2.30(8) | 3.351(5) | 171(6) | |
| O3–H31$\cdots$Br1$^{iv}$ | 0.50(8) | 2.90(9) | 3.341(5) | 150(11) | |
| O3–H32$\cdots$Br2$^{ii}$ | 0.76(9) | 2.64(9) | 3.308(5) | 148(8) | |
| N–HN1$\cdots$Br1 | 0.81(7) | 3.06(8) | 3.439(7) | 111(6) | 113(2) |
| N–HN1$\cdots$Br1$^{vii}$ | | 2.79(8) | 3.397(7) | 133(7) | |
| N–HN2$\cdots$Br2$^x$ | 0.60(7) | 2.83(7) | 3.417(7) | 168(10) | |

*Note.* Symmetry codes: (i) $1 - x$, $-y$, $1 - z$; (ii) $1/2 - x$, $1/2 + y$, $1/2 - z$; (iii) $1 - x$, $y$, $1/2 - z$; (iv) $1/2 - x$, $1/2 - y$, $1 - z$; (v) $1/2 + x$, $1/2 + y$, $z$; (vi) $x - 1$, $-y$, $z - 1/2$; (vii) $1/2 - x$, $-1/2 + y$, $1/2 - z$; (viii) $-1/2 + x$, $1/2 - y$, $-1/2 + z$; (ix) $-x$, $-y$, $-z$; (x) $-x$, $y$, $1/2 - z$.

salt (3) and (ii) on the structural data of an ideal perovskite structure with $t = 1$ (Eq. 2). Waisumi *et al.* (8) selected the $RbCl \cdot MgCl_2 \cdot 6H_2O$ structure in which the distance Rb–Cl is very close to the sum of the ionic radii $r_{Rb^+}$ and $r_{Cl^-}$.

Radii of the hydrated metal ions $r_{[Ni(H_2O)_6]^{2+}} \approx 2.86$ Å and $r_{[Co(H_2O)_6]^{2+}} \approx 2.90$ Å) in the double salts were calculated by
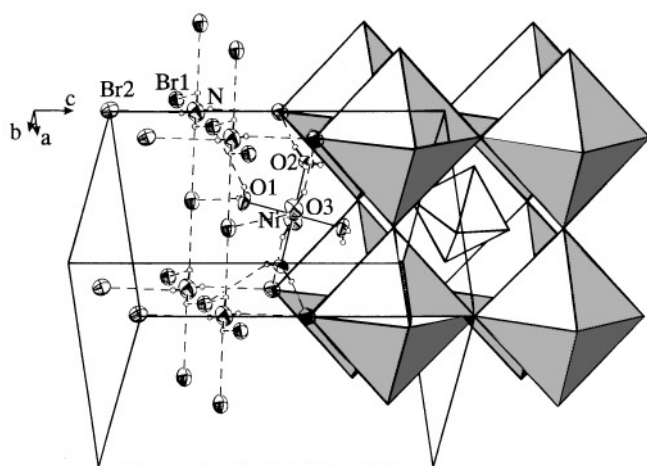


**FIG. 3.** A view of the pseudo-perovskite arrangement of the $[NH_4Br_6]$ (large octahedra) and $[Ni(H_2O)_6]$ (small octahedra) structural units. 30% probably thermal ellipsoids. H atoms are arbitrarily reduced..

the method of Emons *et al.* (3) by the formula

$$r_A = (\sqrt[3]{V_T}/\sqrt{2}) - r_X, \qquad [1]$$

where $r_A$ is the radius of the hexaaquacomplex $[Me(H_2O)_6]^{2+}$, $r_X$ is the radius of the halide ion, and $V_T$ is the volume of the perovskite subcell obtained from the unit cell parameters of the double salt.

### Tolerance Factor **t** for the $Me^+X \cdot NiX_2 \cdot 6H_2O$ and $Me^+X \cdot CoX_2 \cdot 6H_2O$ Double Salt Structures

The geometrical tolerance factors **t** for the crystal structures of the double salts $Me^+X \cdot NiX_2 \cdot 6H_2O$ and $Me^+X \cdot CoX_2 \cdot 6H_2O$ (Table 7) were calculated according to Goldschmidt's formula (17),

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

by assuming the $MeX \cdot MeX_2 \cdot 6H_2O$ salts to be distorted $ABX_3$ perovskites (3) where $r_A = r_{[Me(H_2O)_6]^{2+}}$; $r_B = r_{Me^+}$, and $r_X$ is the radius of the halide ion.

### DISCUSSION

We find that all the double salts $KBr \cdot NiBr_2 \cdot 6H_2O$, $RbBr \cdot CoBr_2 \cdot 6H_2O$, and $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ crystallize with monoclinic symmetry, space group $C2/c$, and have a distorted pseudo-perovskite type structure by analogy with the monoclinic magnesium carnallites $Me^+X \cdot MgX_2 \cdot 6H_2O$. Their crystal structures (Fig. 3) consist of networks formed by $[Me^+X_6]$ octahedra connected by common corners as well as of isolated $[Me^{2+}(H_2O)_6]$ octahedra situated in the network holes.

The formation of this structure of the $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ salts requires (i) a hexahalide coordination environment of the $Me^+$ ions, $[Me^+X_6]$, (ii) a hexaaqua coordination environment of the $Me^{2+}$ ions, $[Me^{2+}(H_2O)_6]$, and (iii) appropriate stacking of these coordination polyhedra. A geometric factor and the metal–ligand interactions affect the formation of these coordination polyhedra.

From the relationship $r_{Me^{2+}}/r_{O_w}$ or $r_{Me^+}/r_{X^-}$ (the Ahrens' ionic radii are denoted as $r$; oxygen from a water molecule as $O_w$) that determines the coordination number it follows that (i) for the $Co^{2+}$ and $Ni^{2+}$ ions formation of $[Me^{2+}(H_2O)_6]$ octahedra is allowed; and (ii) for the $Me^+$ ions the coordination environment of $X^-$ ions is $\geq 6$. A hexahalide coordination environment of the $Me^+$ ions $[Me^+X_6]$ is possible even in cases when coordination numbers larger than 6, e.g., 8, are allowed. It is known that all metal halides $Me^+X$ (except Na$X$) form $Me^+X \cdot MgX_2 \cdot 6H_2O$ double salts, the $Me^+$ ions being in a disturbed octahedral coordination of

**TABLE 7**
**Tolerance Factors t of the Possible $Me^+X \cdot Ni^{2+}X_2 \cdot 6H_2O$ and $Me^+X \cdot Co^{2+}X_2 \cdot 6H_2O$ Salts**

| $Me^+/X^-$ | $Me^+Br \cdot Ni^{2+}Br_2 \cdot 6H_2O$ | $Me^+I \cdot Ni^{2+}I_2 \cdot 6H_2O$ | $Me^+Br \cdot Co^{2+}Br_2 \cdot 6H_2O$ | $Me^+I \cdot Co^{2+}I_2 \cdot 6H_2O$ |
|---|---|---|---|---|
| $Li(H_2O)^+$ | 0.955 | 0.939 | 0.963 | 0.946 |
| $Na^+$ | 1.144 | 1.111 | 1.153 | 1.120 |
| $K^+$ | 1.020 | 0.999 | 1.029 | 1.007 |
| $NH_4^+$ | 1.005 | 0.986 | 1.014 | 0.993 |
| $Rb^+$ | 0.979 | 0.962 | 0.988 | 0.969 |
| $Cs^+$ | 0.939 | 0.924 | 0.947 | 0.932 |

*Note.* (Ionic radii used: $r_{Br^-} = 1.96$ Å; $r_{I^-} = 2.20$ Å; $r_{Na^+} = 1.02$ Å; $r_{K^+} = 1.38$ Å; $r_{Rb^+} = 1.52$ Å; $r_{Cs^+} = 1.67$ Å (25); $r_{Li(H_2O)^+} = 1.61$ Å; $r_{NH4^+} = 1.43$ Å (3, 26).

$X^-$. This indicates a loosening of the bonds in the octahedra $[Me^+X_6]$ and an increasing of the distance between the ions. As a result the structure may be considered as close packing of $[Me^{2+}(H_2O)_6]$ octahedra along with separate $Me^+$ and $X^-$ ions.

The $Me^{2+}$-ligand and $Me^+$-ligand chemical interactions in the ternary aqueous solutions compete with one another and exercise mutual effects. They can be interpreted on the basis of the Pearson's concept for "hard" and "soft" Lewis acids ($Me^+$ and $Me^{2+}$ ions) and bases ($X^-$ ions and $H_2O$ molecules) (18) by using the Klopman's scale of "hardness" and "softness" of cations and anions (19). The "hard–soft" factor determines the type of ligand in the coordination polyhedra (20–23). The $Me^+$ ions are relatively "soft" and formation of $[Me^+X_6]$ complexes in all halide solutions is possible. The $Co^{2+}$ and $Ni^{2+}$ ions are Lewis acids of intermediate "hardness" and in an aqueous-halide solution they coordinate preferentially to Lewis bases of intermediate "hardness". However, the Lewis bases under discussion exhibit different degrees of "hardness" and create differences in the coordination polyhedra in the halide solutions. $Me^+I \cdot Me^{2+}I_2 \cdot 6H_2O$ salts should be obtained in aqueous-iodide solutions because most likely only $[Me^{2+}(H_2O)_6]$ complexes are formed. The "soft" $I^-$ ions are not expected to coordinate with $Me^{2+}$ ions. $H_2O$ molecules and $Cl^-$ and $Br^-$ ions can coordinate the $Co^{2+}$ and $Ni^{2+}$ ions and, as a result, mixed aqua and halide complexes are observed in aqueous-chloride and bromide solutions. The differences in the geometric stabilities of the predominating mixed aqua–chloride and aqua–bromide complexes lead to crystallization of different double salts—$2Me^+Cl \cdot Me^{2+}Cl_2 \cdot 2H_2O$ and $Me^+Cl \cdot Me^{2+}Cl_2 \cdot 2H_2O$ in the chloride systems because of the stable mixed $[Me^{2+}(H_2O)_2Cl_4]$ complexes, and $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$ in the bromide systems because of the "softer" nature of $Br^-$ ions and the higher geometric stability of the aqua $[Me^{2+}(H_2O)_6]$ complexes as compared to that of the mixed $[Me^{2+}(H_2O)_2Br_4]$ complexes. Our studies on the systems KBr–NiBr$_2$–H$_2$O, RbBr–CoBr$_2$–H$_2$O, and NH$_4$Br–NiBr$_2$–H$_2$O (1) at 25°C

have proved our prediction about the existence of the salts $Me^+Br \cdot Me^{2+}Br_2 \cdot 6H_2O$. The $Cs^+$ ions exercise an additional effect and favor formation of anhydrous and low-hydrate double salts (23). Their peculiarities will be the subject of subsequent studies.

For perovskites to be formed the tolerance factor **t** must range from 0.8 to 1.1 according to Goldschmidt (17); to 1.0 according to Wells (24); and to 1.045–1.061 according to Emons *et al.* (3). When $t \leq 0.8$, an illmenite type structure is observed. Potassium magnesium carnallite, whose **t** value is 1.061, has a structure differing from that of the perovskite type. All cobalt and nickel salts $Me^+X \cdot Me^{2+}X_2 \cdot 6H_2O$ (Table 7) should have a perovskite type crystal structure. Perovskite type sodium salts $NaX \cdot Me^{2+}X_2 \cdot 6H_2O$ whose tolerance factor **t** is above the upper boundary of existence of the perovskite structures are not expected.

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