

# On the Existence of the Double Salts $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$

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Received April 21, 1992; in revised form February 26, 1993; accepted April 19, 1993

The existence of double salts  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  (where  $Me^+ = Na, K, NH_4, Rb, Cs$ ;  $Me^{2+} = Mn, Fe, Co, Ni$ ;  $X^- =$  halide ion) is explained by the stability of  $[Me^{2+}(H_2O)_2X_4]^{2-}$  complexes and by the most probable spatial distribution of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  and the  $Me^+$  ions. The stability of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  complexes is discussed on the basis of the "hard-soft" factor. The most probable distribution of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  and the  $Me^+$  ions is determined by the radius-ratio conditions:

i.  $Me^+$  in a surrounding of 8  $X^-$  ions

$$r_{Me^+}/r_{X^-} = 0.73-1.00,$$

ii.  $Me^{2+}$  with an octahedral coordination environment of  $4X^-$  and  $2O_w$

$$6r_{Me^{2+}}/(4r_{X^-} + 2r_{O_w}) = 0.41-0.73.$$

The crystal structure type (tetragonal or triclinic) depends on an additional condition:

$$r_{Me^+} = tr_{O_w}.$$

When the tolerance factor  $t = 0.90-1.03$ , a tetragonal structure will be formed, while when  $t > 1.03$ , a triclinic structure should appear. The available literature data for this type of double salts as well as our studies on the systems  $KBr-MnBr_2-H_2O$  and  $NH_4Br-NiBr_2-H_2O$  at  $25^\circ C$  described in this paper confirm the above conclusion. In the system  $NH_4Br-NiBr_2-H_2O$  at  $25^\circ C$  a new double salt was found, namely  $NH_4Br \cdot NiBr_2 \cdot 6H_2O$  ( $a = 6.835(1) \text{ \AA}$ ,  $b = 13.668(3) \text{ \AA}$ ,  $c = 6.834(1) \text{ \AA}$ ,  $\beta = 91.08(1)^\circ$ ,  $V = 638.3(2) \text{ \AA}^3$ , space group  $P2_1/n$ ). © 1994 Academic Press, Inc.

## INTRODUCTION

The crystal chemistry of salts of the  $2Me^+Cl \cdot Me^{2+}Cl_2 \cdot 2H_2O$  type ( $Me^+ = K, NH_4, Rb, Cs$ ;  $Me^{2+} = Mn, Fe, Co, Ni, Cu$ ) was discussed in a previous paper (1). It was shown that these salts crystallize in two structural types: tetragonal and triclinic. It was established that this isodimorphism is determined mainly by the size of the  $Me^+$

ion and by the electronic configuration of the  $Me^{2+}$  ion, where the presence of a Jahn-Teller ion is of decisive importance.

Chlorides are the most studied salts of the type  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  ( $X^- =$  halide ion). Data on bromides and fluorides are scarce, while for iodides no data at all could be found.

The purpose of the present work is to make some generalizations regarding the existence of the double salts  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  ( $Me^+ = Na, K, NH_4, Rb, Cs$ ;  $Me^{2+} = Mg, Mn, Fe, Co, Ni, Cu$ ;  $X^- = F, Cl, Br, I$ ) as well as to establish in which of the two structural types they would be expected to crystallize.

The investigation of the systems in which  $KBr$  or  $NiBr_2$  participates was of special interest to us, because according to the theoretical concept developed in the present work, one should not expect the double bromide salts  $2Me^+Br \cdot Me^{2+}Br_2 \cdot 2H_2O$ , where  $Me^+ = K^+$  or  $Me^{2+} = Ni^{2+}$ , to exist.

## EXPERIMENTAL

The  $KBr-MnBr_2-H_2O$  and  $NH_4Br-NiBr_2-H_2O$  systems were studied at  $25^\circ C$  by the method of isothermal decrease in the supersaturation (2). Merck reagents (A.R.) were used. The equilibrium was attained after stirring for 24 hr. The composition of the solid phases was determined by the graphical Schreinemakers' method (3).

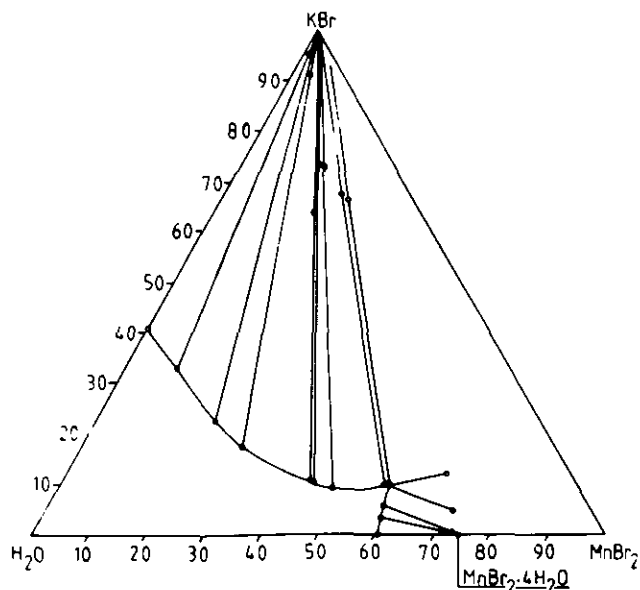
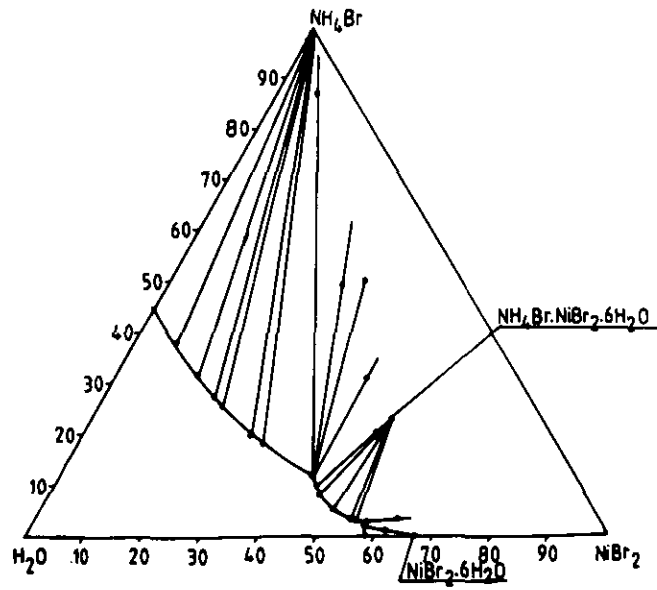
The compositions of the liquid and the corresponding wet solid phases were analyzed by the following methods.

The concentration of  $Mn^{2+}$  was determined complexometrically by direct titration with 0.05 M EDTA at pH 9.5–10 (ammonia buffer) using Eriochrome black T as an indicator in the presence of hydroxylamine hydrochloride as a reducing agent.

The concentration of  $Ni^{2+}$  was established by complexometric back titration with 0.05 M  $ZnSO_4$  in acetate buffer (pH 5.5–6) using Xylenolorange as an indicator.

The total amount of  $Br^-$  was found argentometrically by the Mohr method utilizing titration with an  $AgNO_3$  solution at pH 7–10 in the presence of  $K_2CrO_4$ .

The error of these volumetrical analyses is about 0.1–0.2%.

FIG. 1. Solubility diagram of the KBr-MnBr<sub>2</sub>-H<sub>2</sub>O system at 25°C.FIG. 2. Solubility diagram of the NH<sub>4</sub>Br-NiBr<sub>2</sub>-H<sub>2</sub>O system at 25°C.

The  $Me^+Br$  content was calculated from the difference between the total amount of bromides and the bromides corresponding to the  $Me^{2+}$  ions. In particular cases gravimetric  $K^+$ -determinations using the tetraphenylborate method (4) or  $NH_4^+$  determination using the Parnas-Wagner method were carried out, and the results are in a very good agreement with those calculated from the argentometrical  $Br^-$  determinations.

The unit cell parameters of the  $NH_4Br \cdot NiBr_2 \cdot 6H_2O$  single crystals obtained were determined on a Enraf-Nonius CAD-4 diffractometer (MoK $\alpha$  radiation, graphite

monochromator) from 14 well-centered reflections within the range  $20^\circ \leq \theta \leq 22^\circ$ .

## EXPERIMENTAL RESULTS

### The KBr-MnBr<sub>2</sub>-H<sub>2</sub>O System at 25°C

The results are presented in Fig. 1 and Table 1. The system is a simple eutonic (two salt) type.

### The NH<sub>4</sub>Br-NiBr<sub>2</sub>-H<sub>2</sub>O System at 25°C

The results are given in Fig. 2 and Table 2. Along with the crystallization fields of the pure  $NH_4Br$  and  $NiBr_2 \cdot 6H_2O$  salts, a double salt with the composition  $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ , which has not been reported previously, was found. The crystals are green with a prismatic habit. This double salt crystallizes in a monoclinic crystal system with unit cell parameters  $a = 6.835(1) \text{ \AA}$ ,  $b = 13.668(3) \text{ \AA}$ ,  $c = 6.834(1) \text{ \AA}$ ,  $\beta = 91.08(1)^\circ$ ,  $V = 638.3(2) \text{ \AA}^3$ , space group  $P2_1/n$ .

TABLE 1  
Solubility in the KBr-MnBr<sub>2</sub>-H<sub>2</sub>O System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
KBr	MnBr <sub>2</sub>	KBr	MnBr <sub>2</sub>	
40.6	0.00	—	—	KBr
33.1	9.37	95.2	0.91	KBr
22.5	21.0	95.7	1.35	KBr
17.6	28.1	91.1	3.05	KBr
10.7	43.4	64.1	17.7	KBr
10.2	44.1	73.6	13.3	KBr
9.4	47.9	73.0	14.6	KBr
10.1	56.5	67.8	20.2	KBr
10.1	57.4	66.6	22.0	Eutonic
9.84	57.3	12.1	66.2	Eutonic
9.79	57.3	5.07	71.3	Eutonic
6.00	58.5	0.80	73.3	MnBr <sub>2</sub> · 4H <sub>2</sub> O
3.64	59.3	1.04	71.3	MnBr <sub>2</sub> · 4H <sub>2</sub> O
—	60.2	—	—	MnBr <sub>2</sub> · 4H <sub>2</sub> O

## DISCUSSION ON THE EXISTENCE AND THE STRUCTURES OF THE $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$ SALTS

The crystal structures of the double salts of type  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  ( $Me^+ = Na, K, NH_4, Rb, Cs$ ;  $Me^{2+} = Mn, Fe, Co, Ni, Cu$ ;  $X^- = F, Cl, Br$ ) consist of periodic arrangements of the discrete octahedral complex ions  $[Me^{2+}(H_2O)_2X_4]^{2-}$  and of separate  $Me^+$  ions, situated in holes between the  $X^-$  ions or  $X^-$  ions and the  $H_2O$  molecules. The existence of salts with such a crystal structure type is determined by:

TABLE 2  
Solubility in the  $NH_4Br-NiBr_2-H_2O$  System at 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		Solid phase
$NH_4Br$	$NiBr_2$	$NH_4Br$	$NiBr_2$	
44.1	0.00	—	—	$NH_4Br$
37.8	7.34	97.3	0.20	$NH_4Br$
31.5	14.1	99.1	0.10	$NH_4Br$
27.2	18.8	98.4	0.52	$NH_4Br$
25.4	21.2	98.2	0.55	$NH_4Br$
19.7	29.1	98.8	0.32	$NH_4Br$
18.1	31.7	97.0	1.20	$NH_4Br$
12.1	43.2	87.6	6.67	Eutonic
11.8	43.1	49.4	29.9	Eutonic
11.7	43.3	50.4	33.1	Eutonic
11.9	43.7	31.0	43.2	Eutonic
9.53	45.1	20.2	50.2	$NH_4Br \cdot NiBr_2 \cdot 6H_2O$
8.27	46.5	22.3	51.6	$NH_4Br \cdot NiBr_2 \cdot 6H_2O$
5.20	50.2	19.2	51.2	$NH_4Br \cdot NiBr_2 \cdot 6H_2O$
3.36	54.3	22.1	51.3	$NH_4Br \cdot NiBr_2 \cdot 6H_2O$
2.95	55.3	19.1	52.0	$NH_4Br \cdot NiBr_2 \cdot 6H_2O$
2.92	57.7	3.31	62.4	Eutonic
1.99	57.2	1.25	61.2	$NiBr_2 \cdot 6H_2O$
0.00	58.8	—	—	$NiBr_2 \cdot 6H_2O$

- the stability of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  complexes, and
- the most probable spatial distribution of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  and the  $Me^+$  ions.

The formation of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  complexes is connected with appropriate  $Me^{2+}$ -ligand bond energies for  $X^-$  and for  $H_2O$  ligands. We discuss this ability using the "hard-soft" factor (5-7). The hard Lewis acids, such as  $Mg^{2+}$  ions, prefer to coordinate with the harder Lewis bases (e.g.,  $H_2O$ ) and this leads to a coordination environment,  $[Mg(H_2O)_6]^{2+}$ , containing only  $H_2O$  molecules. For this reason the double salt  $2MeX \cdot MgX_2 \cdot 2H_2O$  formation should not be expected. Carnallite type double salts

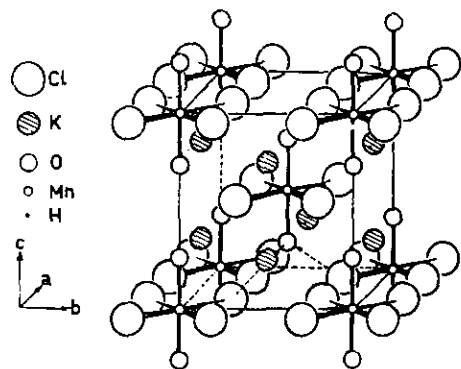


FIG. 3. Arrangement of the atoms in  $2KCl \cdot MnCl_2 \cdot 2H_2O$  (tetragonal structure) (10).

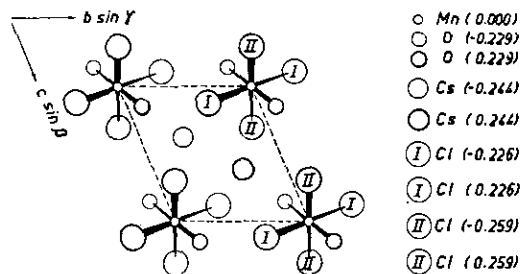


FIG. 4. Projection of the crystal structure of  $2CsCl \cdot MnCl_2 \cdot 2H_2O$  (triclinic structure). Figures in parentheses indicate the  $x$  values of the atomic parameters (12).

$MeX \cdot MgX_2 \cdot 6H_2O$  are formed instead. The  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  ions are intermediate in hardness among the Lewis acids (8, 9). This determines the formation of mixed aquahalido complexes, including  $[Me^{2+}(H_2O)_2X_4]^{2-}$ . The latter are especially characteristic in combinations with  $Cl^-$  and  $Br^-$  ions, which are intermediate in softness among the Lewis bases. The  $F^-$  ions are harder Lewis bases than the  $H_2O$  molecules and they form with Lewis acids of intermediate hardness mixed (mostly  $[Me^{2+}(H_2O)_2F_4]^{2-}$ ) or solely aqueous surroundings (5). The  $I^-$  ions, which are softer Lewis bases than the  $Cl^-$  and  $Br^-$  ions, do not participate in the coordination polyhedra around the  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ , or  $Ni^{2+}$  ions and therefore predominantly  $[Me(H_2O)_6]^{2+}$  complexes exist (5). For this reason formation of the double salts  $2Me^+I \cdot Me^{2+}I_2 \cdot 2H_2O$  should not be expected.

The most probable spatial distribution of the  $[Me^{2+}(H_2O)_2X_4]^{2-}$  and the  $Me^+$  ions, because of the predominantly ionic interaction between them, is determined by the geometrical factors following the electrostatic laws.

Let us consider first the tetragonal type crystal structure using the data on the double salt  $2KCl \cdot MnCl_2 \cdot 2H_2O$  (10) (Fig. 3) as an example. This structure consists of a periodic arrangement of the discrete octahedral complex

TABLE 3  
Possible Double Salts of the Type  $2Me^+Cl \cdot Me^{2+}Cl_2 \cdot 2H_2O$

$Me^+$	$Mn^{2+}$	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$
$K^+$	$I4/mmm^a$	$P4_2/mnm^b$	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm^a$
$NH_4^+$	$P4_2/mnm^a$	$P4_2/mnm^a$	$P4_2/mnm^b$	$P4_2/mnm$	$P4_2/mnm^a$
$Rb^+$	$P\bar{1}^a$	$P\bar{1}$	$P\bar{1}^a$	$P\bar{1}^a$	$P4_2/mnm^a$
$Cs^+$	$P\bar{1}^a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P4_2/mnm^a$

<sup>a</sup> Double salt with a known crystal structure,

<sup>b</sup> A known double salt.

TABLE 4  
Possible Double Salts of the Type  $2Me^+Br \cdot Me^{2+}Br_2 \cdot 2H_2O$

$Me^+$	$Mn^{2+}$	$Fe^{2+}$	$Co^{2+}$	$Cu^{2+}$
$NH_4^+$	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm^b$	$P4_2/mnm^a$
$Rb^+$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P4_2/mnm^b$
$Cs^+$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P4_2/mnm$

<sup>a</sup> Double salt with a known crystal structure.

<sup>b</sup> A known double salt.

ions  $[Mn^{2+}(H_2O)_2Cl_4]^{2-}$  and separate  $K^+$  ions. The latter are surrounded by 8  $Cl^-$  ions in a CsCl arrangement. From radius-ratio considerations the existence and stability of the tetragonal double salts of the type  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  (analogous in structure to that considered in Fig. 3) will depend on the following conditions:

i.  $Me^+$  ions in a surrounding of  $8X^-$  ions

$$r_{Me^+}/r_{X^-} = 0.73-1.00, \quad (1)$$

ii.  $Me^{2+}$  ions in an octahedral coordination environment with the  $4X^-$  and  $2O_w$  being averaged

$$6r_{Me^{2+}}/(4r_{X^-} + 2r_{O_w}) = 0.41-0.73. \quad (2)$$

The Ahrens ionic radii are denoted by  $r$ ;  $O_w$  means oxygen from a water molecule.

The triclinic structure type of the  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  salts consists, analogous to the tetragonal type, of octahedral  $[Me^{2+}(H_2O)_2Cl_4]^{2-}$  complexes and separate  $Me^+$  ions (12) (Fig. 4). However, the  $Me^+$  ions are surrounded in this case by a 8  $Cl^-$  ions and 4  $O_w$  atoms, the  $Me^+$ -chloride sublattice having a distorted CsCl arrangement (e.g.,  $2CsCl \cdot MnCl_2 \cdot 2H_2O$  (12) and  $2RbCl \cdot MnCl_2 \cdot 2H_2O$  (12)). Hence, the existence and stability of this type of structure would depend on the same conditions (1) and (2) as in the case of the tetragonal structure.

The formation of the tetragonal or the triclinic structure would be determined by the additional condition

$$r_{Me^+} = tr_{O_w}. \quad (3)$$

The tetragonal structure will appear at tolerance factor values  $t = 0.90-1.03$ , while the triclinic structure is expected at  $t$  values larger than 1.03. Condition (3) takes into account the relation between the ionic radii of the  $Me^+$  ions and  $O_w$  and its decisive role in the isodimorphism of the  $2Me^+Cl \cdot MeCl_2 \cdot 2H_2O$  double salt type as discussed in a previous paper (1).

The cases with participation of Jahn-Teller  $Me^{2+}$  ions (e.g.,  $Cu^{2+}$ ), for which a tetragonal structure of the  $2Me^+X \cdot CuX_2 \cdot 2H_2O$  salts is always realized, were also discussed previously (1).

The expected structure types of the double salts  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  (chlorides and bromides) that fulfill the above conditions are given in Table 3 and 4.

Sodium double salts of the type  $2Me^+X \cdot Me^{2+}X_2 \cdot 2H_2O$  should not exist at all because they do not satisfy condition (1). In the case of bromide systems, potassium and nickel double salts of the above type should also not be expected. In the case of potassium salts, condition (1) is not satisfied and for nickel salts, condition (2) is not satisfied. The results obtained in the present paper for the systems  $KBr-MnBr_2-H_2O$  and  $NH_4Br-NiBr_2-H_2O$  confirm this statement.

#### ACKNOWLEDGMENTS

This work was supported by the Bulgarian Ministry of Culture, Science and Education, Project X-81, and the Alexander von Humboldt Foundation, Germany. The authors are grateful to Dr. J. Macicek for the unit cell parameter determination of  $NH_4Br \cdot NiBr_2 \cdot 6H_2O$ .

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