Double Salts Obtained from Me^+X–CuX_2–H_2O Systems (Me^+ = K$^+$, NH$_4^+$, Rb$^+$, Cs$^+$; X^- = Cl$^-$, Br$^-$)

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The solubility diagrams of the Me^+Br–CuBr$_2$–H$_2$O (Me^+ = K$^+$, NH$_4^+$, Rb$^+$, Cs$^+$) systems are studied. The results obtained are compared with literature data on the corresponding chloride systems in order to estimate the effect of the halide ion (Br$^-$ or Cl$^-$) on the solubility diagrams and on the compositions of the double salts formed in these systems. The differences in composition and structure of the double salts are explained by the metal–ligand interactions on the basis of Pearson's concept of hard and soft Lewis acids and bases, as well as by crystal chemistry considerations for the most probable spacial situation of the building elements in the crystal structure. © 1995 Academic Press, Inc.

INTRODUCTION

The solubility diagrams of Me^+Cl–CuCl$_2$–H$_2$O (Me^+ = Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Rb$^+$, and Cs$^+$) systems are described in the literature over wide temperature ranges (1–16). In all these systems except that with NaCl, double salts are formed. The following compositions of the double salts appear most frequently: $2Me^+$Cl · CuCl$_2$ · 2H$_2$O, Me^+Cl · CuCl$_2$ · 2H$_2$O, Me^+Cl · CuCl$_2$, and $2Me^+$Cl · CuCl$_2$. Of the respective bromide systems, there are data only on NH$_4$Br–CuBr$_2$–H$_2$O at 20°C (17) where the double salt 2NH$_4$Br · CuBr$_2$ · 2H$_2$O is established.

In the present paper, studies on the solubility diagrams of the Me^+Br–CuBr$_2$–H$_2$O systems (where Me^+ = K$^+$, NH$_4^+$, Rb$^+$, and Cs$^+$) are described. The solubility diagrams and the compositions of the double salts formed in bromide systems are compared with these of the respective chloride systems. The aim of the study is to clarify how the change of the halide ion (substitution of Br$^-$ for Cl$^-$) influences the solubility diagrams and the compositions of the double salts formed in these systems.

EXPERIMENTAL

The Me^+Br–CuBr$_2$–H$_2$O (Me^+ = NH$_4^+$, Rb$^+$, and Cs$^+$) systems were studied at 25°C by the method of isothermal decrease of the supersaturation (18). The KBr–CuBr$_2$–H$_2$O system was studied at 10, 25, and 75°C. The equilibria at 10 and 25°C were attained with stirring for 24 h, while at 75°C, 5–6 hr were sufficient to reach equilibrium. The experiments were carried out with Merck reagents (A.R.).

The compositions of the liquid and the corresponding wet solid phase were analyzed by the following methods:

The concentration of Cu^{2+} was determined by direct complexometric titration at pH 5.5–6 (acetate buffer) with xylenolorange as indicator. The total amount of Br$^-$ was found by the Volhard method. The error of these volumetrical analyses was about 0.1–0.2%. The Me^+Br content was calculated from the difference between the total amount of Br$^-$ and the bromides corresponding to Cu^{2+} ions.

The solid-phase compositions of the simple or double salts obtained from these systems were determined graphically by Schreinemakers' method (19), while in the case of mixed crystal formation the algebraic variant of Schreinemakers' method for indirect identification of the solid-phase composition (20) was used.

The phase compositions of the solid samples were controlled by a DRON-3 X-ray powder diffractometer using Co$K\alpha$ radiation, with a β filter and a scintillation detector at a scanning rate of 2°/min.

The double salts obtained were studied thermogravimetrically with a Paulik–Paulik–Erdey 1500 apparatus (Type 3427) at a heating rate of 10°C.min^{-1} under atmospheric air, a sample weight of 200 mg, and a sensitivity of 1/200 mg.

RESULTS

The KBr–CuBr$_2$–H$_2$O System at 10, 25, and 75°C

The results from the study of the KBr–CuBr$_2$–H$_2$O system are presented in Fig. 1 and Tables 1 (10°C), 2 (25°C) and 3 (75°C). It is established that at all three temperatures the system is of a simple eutonic type.

The NH$_4$Br–CuBr$_2$–H$_2$O System at 25°C

The results from the investigation of the NH$_4$Br–CuBr$_2$–H$_2$O system at 25°C are shown in Fig. 2 and Table 4. Three crystallization fields are established: (i) of pure
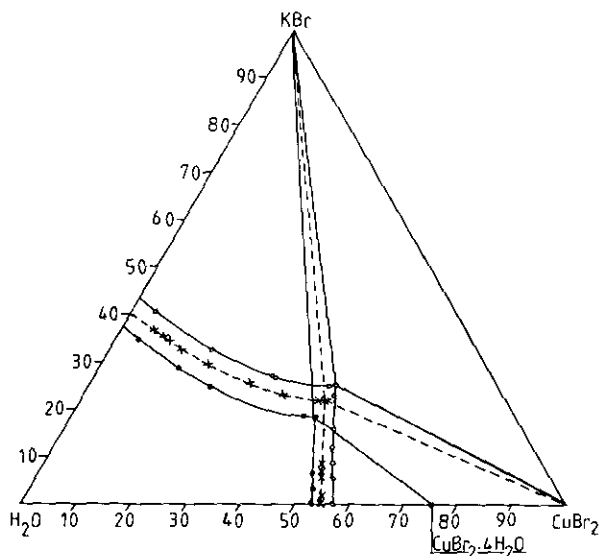
FIG. 1.   Solubility diagram of the KBr–CuBr₂–H₂O system at 10°C,
●; 25°C, ×; 75°C, ○ (in mass%).

TABLE 2
Solubility in the KBr–CuBr₂–H₂O System at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		
KBr	CuBr₂	KBr	CuBr₂	Solid phase
40.6	0.0	—	—	KBr
36.9	6.02	98.8	0.10	KBr
35.1	8.83	93.7	0.95	KBr
34.6	10.1	84.7	2.56	KBr
33.4	13.3	94.9	1.33	KBr
29.2	19.7	90.5	2.88	KBr
25.8	29.4	86.0	5.85	KBr
23.0	36.2	83.9	7.80	KBr
22.2	45.1	60.0	36.3	Eutonic
22.2	44.1	36.5	55.0	Eutonic
10.5	50.0	7.80	78.8	CuBr₂
8.90	51.0	2.02	92.3	CuBr₂
8.08	51.9	2.35	88.0	CuBr₂
6.70	52.2	2.10	86.1	CuBr₂
2.07	55.2	1.00	83.3	CuBr₂
0.0	55.6	—	—	CuBr₂

CuBr₂, (ii) of the double salt 2NH₄Br · CuBr₂ · 2H₂O, and (iii) of mixed crystals on the basis of NH₄Br. Figure 3 shows the powder X-ray diffraction patterns of pure NH₄Br and the double salt 2NH₄Br · CuBr₂ · 2H₂O, which are similar to the literature data (21), and of two solid phases from the mixed crystals crystallization field. Figure 4 shows DT analysis data on the double salt 2NH₄Br · CuBr₂ · 2H₂O.

The RbBr–CuBr₂–H₂O System at 25°C

In the RbBr–CuBr₂–H₂O system at 25°C (Fig. 5 and Table 5), three crystallization fields are established: those of pure RbBr and CuBr₂ and that of a double salt with the composition 2RbBr · CuBr₂ · 2H₂O. This double salt is

not described in the literature. The composition is confirmed by chemical, X-ray, and TG analyses. The TG analysis (Fig. 6) shows an analogy with the double salt 2NH₄Br · CuBr₂ · 2H₂O. Thermal dehydration of the rubidium double salt proceeds in the temperature interval between 100 and 200°C. After heating to 400°C, the anhydrous CuBr₂ loses half of its bromide content as Br₂. Above 400°C, the mixture of RbBr and CuBr undergoes the following changes: RbBr melts at about 680°C, while CuBr disproportionates to metal Cu and Br₂:

TABLE 1
Solubility in the KBr–CuBr₂–H₂O System at 10°C

Liquid phase (mass%)		Wet solid phase (mass%)		
KBr	CuBr₂	KBr	CuBr₂	Solid phase
37.9	0.0	—	—	KBr
34.8	4.69	96.6	0.40	KBr
28.2	14.8	90.9	4.73	KBr
24.8	22.6	99.0	0.68	KBr
17.2	44.0	76.9	12.4	KBr
17.5	45.5	33.0	51.8	Eutonic
6.39	51.0	2.03	70.0	CuBr₂ · 4H₂O
3.50	52.1	0.91	73.0	CuBr₂ · 4H₂O
0.0	53.7	— .	—	CuBr₂ · 4H₂O

TABLE 3
Solubility in the KBr–CuBr₂–H₂O System at 75°C

Liquid phase (mass%)		Wet solid phase (mass%)		
KBr	CuBr₂	KBr	CuBr₂	Solid phase
40.8	4.81	88.1	1.00	KBr
32.6	18.8	87.9	3.50	KBr
27.0	32.6	75.3	11.4	KBr
26.8	33.4	78.1	10.1	KBr
24.8	45.6	55.9	26.2	KBr
25.0	45.2	34.5	62.4	Eutonic
23.0	46.1	2.85	94.0	CuBr₂
14.9	49.4	2.20	92.1	CuBr₂
12.2	51.2	2.25	90.4	CuBr₂
8.89	53.0	3.50	90.5	CuBr₂
5.50	54.3	1.30	90.2	CuBr₂
0.0	56.7	—	—	CuBr₂
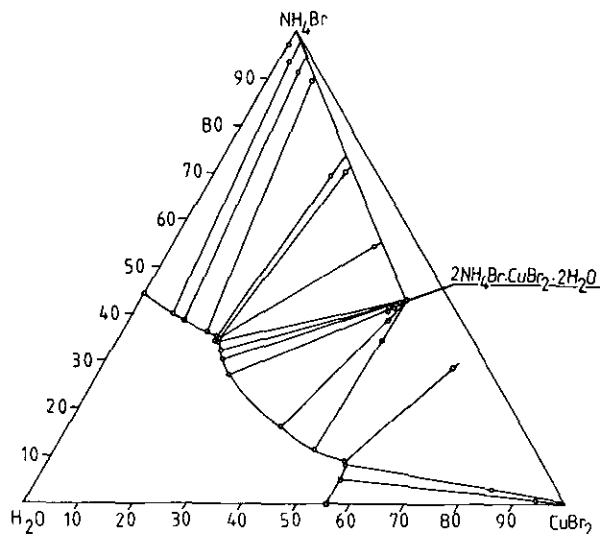
FIG. 2. Solubility diagram of the NH_4Br-$CuBr_2$-H_2O system at 25°C (in mass%).

$$2RbBr \cdot CuBr_2 \cdot 2H_2O \xrightarrow[100-200°C]{-2H_2O} 2RbBr \cdot CuBr_2 \xrightarrow[200-400°C]{-1/2Br_2}$$

$$RbBr + CuBr \xrightarrow[400-800°C]{-1/2Br_2} RbBr + Cu.$$
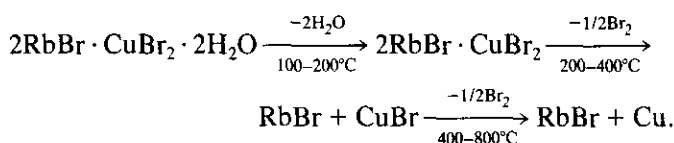
The CsBr-CuBr₂-H₂O System at 25°C

·The results from the study of this system are given in Fig. 7 and Table 6. Four crystallization fields are estab-

lished: those of the pure CsBr and CuBr₂ salts and those of the double salts 2CsBr · CuBr₂ and CsBr · CuBr₂. The compositions of the double salts obtained are confirmed by chemical, X-ray, and TG analyses.

DISCUSSION

Comparison of the results on chloride and bromide systems, Me^+X-CuX_2-H_2O (Me^+ = K⁺, NH_4^+, Rb⁺, and Cs⁺) (Table 7), reveals a significant similarity: in all systems, except for the KBr-CuBr₂-H₂O system, crystallization fields of double salts appear. At low temperatures the double salts are hydrated, while at high temperatures they dehydrate to anhydrous salts. The greatest similarity is found with ammonium and rubidium systems, while the largest difference is exhibited by the potassium systems. *The cesium systems are analogous but at different temperatures*, e.g., CsCl-CuCl₂-H₂O at 50°C and CsBr-CuBr₂-H₂O at 25°C.

The lithium– and sodium–halide systems are beyond the scope of our consideration since important differences originate from the significantly smaller ionic radii of lithium and sodium ions. The system NaCl-CuCl₂-H₂O at 18 and 30°C is of a simple eutonic type (4, 5). In the system LiCl-CuCl₂-H₂O only one double salt LiCl · CuCl₂ · 2H₂O is established at 0 to 99°C (1–3). In its crystal structure (space group $P2_1/c$) each cation is in octahedrical coordination, [Li⁺Cl₃(H₂O)₃], [Cu²⁺Cl₅(H₂O)], and the structure contains the linear cation arrangement

TABLE 4
Solubility in the NH_4Br-$CuBr_2$-H_2O System at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		Solid phase calculated as thoroughly suction dried (mass%)			
(1)	(2)	(1)	(2)	(1)		(2)	D_{Cu^{2+}/NH_4^+}
44.1	0.0	97.4	—	NH₄Br			
40.1	7.33	93.6	2.02	98.3		1.56	0.09
38.9	10.1	91.8	4.78	95.2		4.44	0.18
36.4	15.5	89.9	8.03	91.5		7.80	0.20
35.2	17.9	69.6	21.6	Eutonic			
35.2	18.4	70.7	23.9	Eutonic			
34.4	17.6	54.6	37.2	Eutonic			
34.1	18.5	43.0	47.9	2NH₄Br · CuBr₂ · 2H₂O			
32.7	20.0	42.2	47.3	2NH₄Br · CuBr₂ · 2H₂O			
30.8	21.4	42.0	47.0	2NH₄Br · CuBr₂ · 2H₂O			
27.2	24.3	41.0	46.8	2NH₄Br · CuBr₂ · 2H₂O			
16.5	39.2	39.3	47.5	2NH₄Br · CuBr₂ · 2H₂O			
11.7	47.6	34.4	48.9	2NH₄Br · CuBr₂ · 2H₂O			
9.13	54.8	29.0	64.4	Eutonic			
8.79	55.2	3.37	84.4	Eutonic			
5.70	55.9	0.98	94.1	CuBr₂			
—	55.8	—	—	CuBr₂			

Note. (1) is NH₄Br; (2) is CuBr₂.

FIG. 3. Powder X-ray diffraction patterns of solid phases from the $NH_4Br–CuBr_2–H_2O$ system at 25°C; 1, NH_4Br; 2, $(NH_4)_xCu_{1-x}Br$ (98.31% NH_4Br; 1.56%$CuBr_2$); 3, $(NH_4)_xCu_{1-x}Br$ (91.53% NH_4Br; 7.80%$CuBr_2$); 4, $2NH_4Br \cdot CuBr_2 \cdot 2H_2O$.

$Li^+–Cu^{2+}–Cu^{2+}–Li^+$ and planar $[Li_2^+Cu_2^{2+}Cl_6]$ dimer groups (27, 28).

The appearance of a double salt crystallization field in the solubility diagram depends on the lower solubility of the double salt (within certain limits of the solution composition) as compared with the solubilities of the respective simple salts. The lower the relative solubility of the double salt, the broader its crystallization field. The solubility and the width of the crystallization field of the double salt in the corresponding three-component system are related to the crystal chemistry stability of the double salt.

The crystallization of different double salts from the systems under consideration is determined by the formation of different Cu^{2+}-ligand complexes in the solution (e.g., $[Cu^{2+}(H_2O)_2X_4]^{2-}$, $[Cu^{2+}(H_2O)X_5]^{3-}$, $[Cu_2^{2+}(H_2O)_4X_6]^{2-}$, $[Cu^{2+}X_6]^{4-}$, $[Cu^{2+}X_4]^{2-}$, and $[Cu_2^{2+}X_6]^{2-}$) and by appropriate stacking of one type of these complexes in a crystal lattice together with the Me^+ ions. There the metal–ligand interactions and the metal ions sizes are important (24). The metal–ligand interactions define the activities of the different complexes in the solution. When the activity of a given complex is high enough to reach and exceed the activity product in the saturated solution of a salt, in the crystal structure of which this complex participates as a structural unit, then the crystallization

field of this salt appears in the solubility diagram. The Me^+ ion size determines the kind of stacking of the structural units in the crystal lattice, i.e., their most probable spacial situation, at which the minimum of free energy is reached.

Beside the Cu^{2+}-ligand complexes, complex Me^+-ligand associates also exist in the ternary solutions. These interactions affect each other because the different metal ions compete for the coordination with halide ions or with water molecules. The activity of each of the different complexes in the solution is influenced by the whole composition of the system. The interactions in which all these ions participate can be discussed on the basis of Pearson's concept of hard and soft Lewis acids and bases (22) and the Klopman scale of hardness and softness of cations and anions (23). According to Pearson, the hard Lewis acids are preferentially coordinated with hard Lewis bases, and soft Lewis acids with soft Lewis bases. The large size of the ions considered as Lewis acids or bases favors, according to Pearson, their softness. Using the method of Klopman (23), we calculated the hardness of the Me^+ ions (Table 8). The difference in hardness of the Li^+ and Cs^+ ions is the reason for their different behaviors in an aqua-halide medium. The hardness of the Li^+ ions requires an aqua-halide or solely aqueous coordination. The soft Cs^+ ions are coordinated preferentially with the
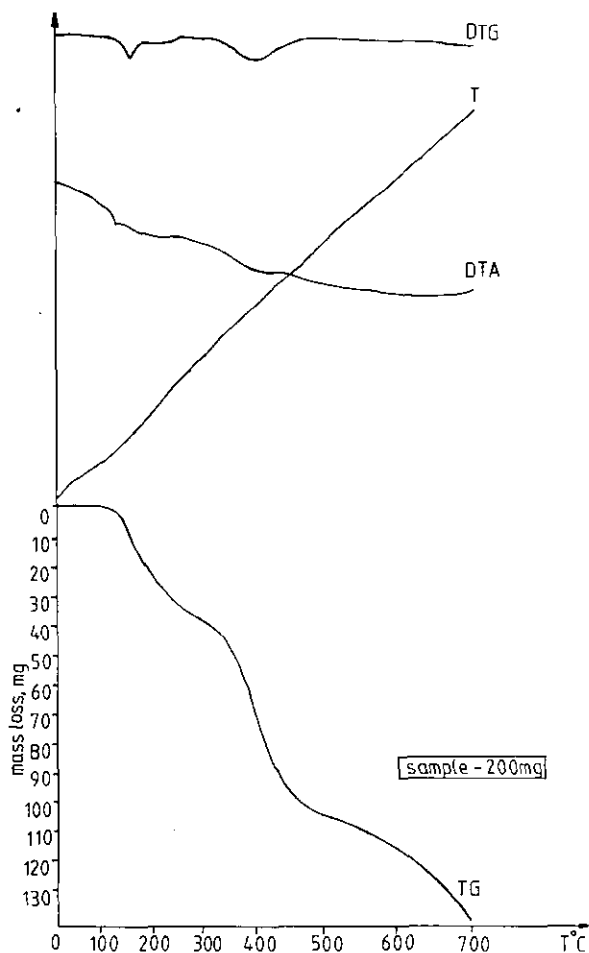
FIG. 4. DTA and TG data on the double salt $2NH_4Br \cdot CuBr_2 \cdot 2H_2O$. Paulik–Paulik–Erdey 1500 apparatus, Type 3427; heating rate, $10°C \cdot min^{-1}$; sample, 200 mg.
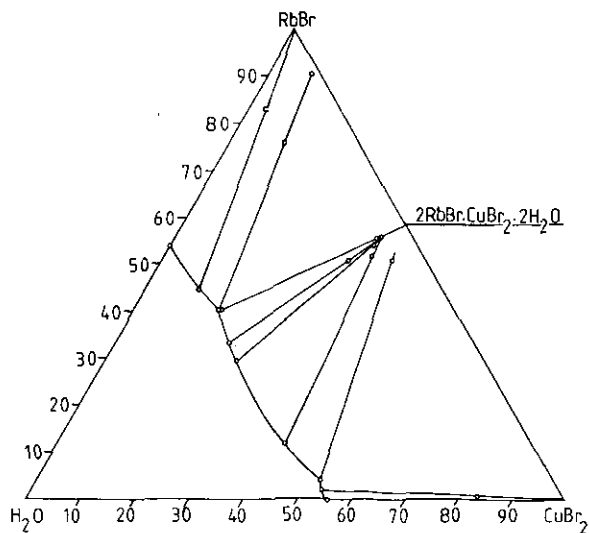
TABLE 5
Solubility in the RbBr–CuBr₂–H₂O System at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		
RbBr	CuBr₂	RbBr	CuBr₂	Solid phase
53.7	0.0	—	—	RbBr
40.1	15.9	76.0	9.90	Eutonic
40.7	16.2	56.0	37.2	$2RbBr \cdot CuBr_2 \cdot 2H_2O$
33.4	21.0	51.1	34.2	$2RbBr \cdot CuBr_2 \cdot 2H_2O$
29.7	24.1	54.6	37.1	$2RbBr \cdot CuBr_2 \cdot 2H_2O$
12.0	42.0	52.2	38.0	$2RbBr \cdot CuBr_2 \cdot 2H_2O$
4.04	52.4	51.4	41.2	Eutonic
2.55	53.3	0.98	83.4	CuBr₂
0.0	55.8	—	—	CuBr₂

softer X^- ions. For that reason, the latter have purely halide or mixed coordination environment. This is the reason for the existence of hydrated double salts in the solubility diagrams of the lithium systems, while in cesium systems mainly anhydrous double salts appear.
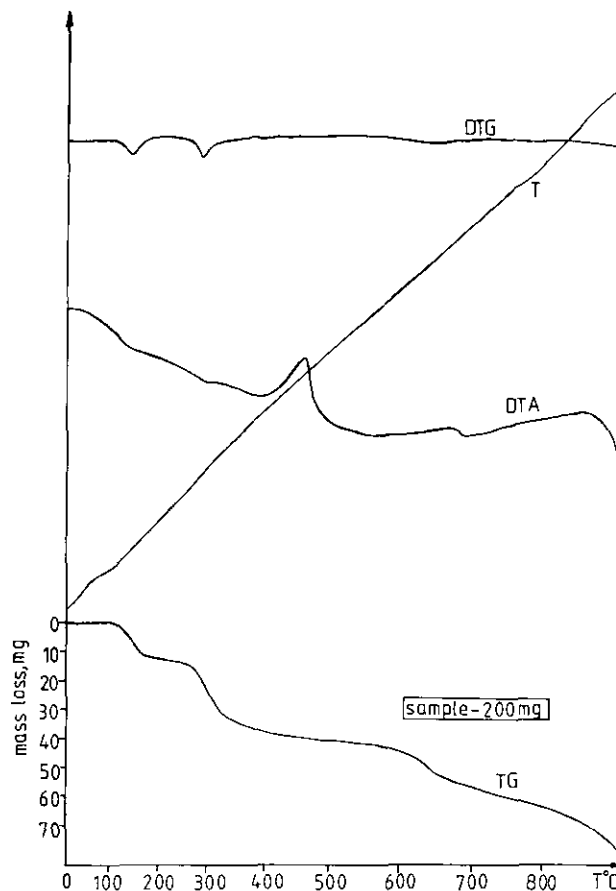

FIG. 5. Solubility diagram of the RbBr–CuBr₂–H₂O system at 25°C (in mass%).

FIG. 6. DTA and TG data on the double salt $2RbBr \cdot CuBr_2 \cdot 2H_2O$. Paulik–Paulik–Erdey 1500 apparatus, Type 3427; heating rate, $10°C \cdot min^{-1}$; sample, 200 mg.
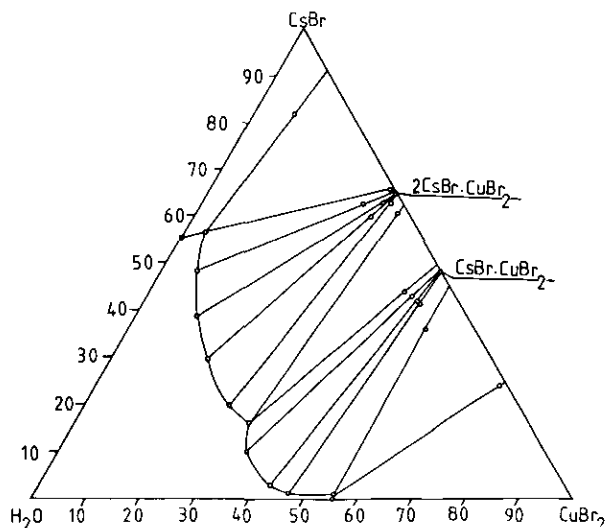
FIG. 7. Solubility diagram of the $CsBr-CuBr_2-H_2O$ system at 25°C (in mass%).

By analogy with the Cs^+ ions, the soft Cu^{2+} ions in an aqua-halide medium may have mixed or halide coordination. The purely halide coordination is more typical of bromides than of chlorides because of the larger difference in hardness of H_2O molecules and Br^- ions than is the case of H_2O molecules and Cl^- ions. In cases of combinations of the soft Cs^+, Cu^{2+}, and Br^- ions, the purely halide environment is strongly preferred. For that reason, only fields of anhydrous double salts appear in the $CsBr-CuBr_2-H_2O$ system at 25°C.

When Me^+ ions of a moderate hardness participate in

TABLE 6
Solubility in the $CsBr-CuBr_2-H_2O$ System at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		
CsBr	CuBr₂	CsBr	CuBr₂	Solid phase
55.2	0.0	—	—	CsBr
56.5	3.70	82.0	7.62	Eutonic
56.8	3.86	66.3	33.0	Eutonic
48.7	6.52	63.0	29.8	$2CsBr \cdot CuBr_2$
38.7	11.3	63.3	33.3	$2CsBr \cdot CuBr_2$
30.0	17.7	60.0	32.1	$2CsBr \cdot CuBr_2$
20.0	26.7	63.3	34.9	$2CsBr \cdot CuBr_2$
16.1	32.0	61.0	37.0	Eutonic
16.3	32.0	44.1	46.7	Eutonic
10.1	34.8	43.5	48.8	$CsBr \cdot CuBr_2$
2.99	42.4	42.3	50.4	$CsBr \cdot CuBr_2$
1.29	46.8	41.9	51.0	$CsBr \cdot CuBr_2$
1.16	55.3	36.2	54.8	Eutonic
1.58	55.3	24.3	74.6	Eutonic
0.0	55.8	—	—	CuBr₂

TABLE 7
Double Salts Obtained from $MeX-CuX_2-H_2O$ Systems[a]

KCl-CuCl₂-H₂O (6)			KBr-CuBr₂-H₂O
25°C	60-75°C	100°C	10-75°C
2:1:2	2:1:2	1:1:0	No double salts
1:1:2	1:1:0		

NH₄Cl-CuCl₂-H₂O		NH₄Br-CuBr₂-H₂O
25-30°C (9-11)	40-70°C (7, 8)	25°C
2:1:2	2:1:2	2:1:2
MC[b]	3:1:6	MC[b]

RbCl-CuCl₂-H₂O (12)	RbBr-CuBr₂-H₂O
25°C	25°C
2:1:2	2:1:2

CsCl-CuCl₂-H₂O (13, 14)			CsBr-CuBr₂-H₂O
5-18°C	25°C	50°C	25°C
2:1:2	2:1:0	2:1:0	2:1:0
3:2:2	3:2:2	1:1:0	1:1:0
4:3:2	4:3:2		
1:1:0	1:1:0		

[a] The ratio between the digits denotes the molar ratio $MeX : CuX_2 : H_2O$ in the double salts.

[b] MC, mixed crystals.

the systems under consideration, the mixed aqua-halide surroundings prevail and the presence of hydrated double salts is observed in their solubility diagrams at room temperatures.

In all $Me^+X-CuX_2-H_2O$ ($Me^+ = K^+$, NH_4^+, Rb^+, Cs^+; $X^- = Cl^-$, Br^-) systems, double salts with the formula type $2Me^+X \cdot CuX_2 \cdot 2H_2O$ (2:1:2) are formed. On the basis of crystal chemistry considerations (24), the existence and stability of these salts depend on

(i) the condition for an octahedral coordination environment of Cu^{2+} ions by $4X^-$ and $2O_w$,

$$6r_{Cu^{2+}}/(4r_{X^-} + 2r_{O_w}) = 0.41-0.73, \quad \text{and} \qquad [1]$$

(ii) the ratio between the Me^+ and X^- ionic radii in the limits

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

$$(Me^+ \text{ coordination of } 8X^- \text{ ions}). \qquad [2]$$

The Ahrens' ionic radii are denoted by r.

These salts are isostructural (including the newly established $2RbBr \cdot CuBr_2 \cdot 2H_2O$ salt) and crystallize in the

TABLE 8
Hardness Values for Me^+ Cations

X^z	$X^z \leftrightarrow X^{z-1}$ energy (ev)[a]	$X^{z-1} \leftrightarrow X^{z-2}$ energy (ev)[b]	Orbital energy (ev)[a]	Pauling's r (Å)	$r + 0.82$ (Å)	Desolvation (ev)[b]	$E_n^{\neq} = H_{acid}$ (ev)
Li^+	5.39	0.59	4.18	0.60	1.42	5.01	0.83
Na^+	5.14	0.54	4.00	0.95	1.77	4.02	0.02
K^+	4.34	0.51	3.38	1.33	2.15	3.31	−0.07
Rb^+	4.18	0.48	3.26	1.48	2.30	3.09	−0.18
Cs^+	3.89	0.40	3.02	1.69	2.51	2.83	−0.19

[a] Ref. (25).
[b] Ref. (26).

tetragonal system, space group $P4_2/mnm$, due to the Jahn–Teller effect as explained earlier (24).

The high stability of $2NH_4X \cdot CuX_2 \cdot 2H_2O$ and $2RbX \cdot CuX_2 \cdot 2H_2O$ determines their large crystallization fields in the solubility diagrams of the respective systems. The lower stability of $2KCl \cdot CuCl_2 \cdot 2H_2O$ crystals (located at the stability boundary of this crystal structure type) determines their comparatively narrow crystallization field in the KCl–$CuCl_2$–H_2O system at 25°C (6). The double salt $2KBr \cdot CuBr_2 \cdot 2H_2O$ does not exist, because the condition required by Eq. [2] is not fulfilled. As a result, the KBr–$CuBr_2$–H_2O system is of a simple eutonic type.

ACKNOWLEDGMENT

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