CHEMISTRY LETTERS, pp. 1869-1872, 1989.

Anion-Exchange in Basic Copper Acetate

Shoji YAMANAKA,* Toshiharu SAKO, and Makoto HATTORI
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Higashi-Hiroshima 724

Basic copper acetate, $Cu_2(OH)_3(OCOCH_3)\cdot H_2O$ has the layer structure of the botallackite type. The acetate ions are located between the positively charged copper hydroxide layers and exchangeable with various anions such as NO_3^-, ClO_4^-, Cl^-, Br^-, I^- and carboxylate ions. The exchange reactions are topotactic and some are reversible.

Cation-exchangeable layer structured compounds can be interesting host structures for intercalation reactions. Examples are clay minerals with silicate layers such as smectites and vermiculites,[1,2] and transition metal oxysalts such as niobates, titanates and molybdates.[3-5] The cations are located between the negatively charged inorganic layers, and exchanged with organic as well as inorganic cations. A variety of polar solvent molecules intercalate into the interlayer spaces, co-ordinating to the cations with large polarizing powers.

Although a variety of cation-exchangeable layer structured compounds are known, anion-exchangeable layer structured compounds are very rare. At present only hydrotalcite-type double hydroxides, $[M^{II}{}_{1-x}M^{III}{}_x(OH)_2]^{x+}\ Y^{z-}{}_{x/z}\cdot nH_2O$ and $[Al_2Li(OH)_6]^+Cl^-$, are reported to be anion-exchangeable,[6,7] where the double hydroxide layers are positively charged and charge-balanced by the interlayer anions. Recently, extensive studies have been made of the anion-exchange reactions of the hydrotalcite-type compounds and revealed that anion-exchange reactions in the positively charged layers proceed in a manner very similar to that of cation-exchange reactions in negatively charged layers.[8,9]

If more kinds of host materials with positively charged layers are available, there are a number of anions which will form interesting intercalation compounds with positive layers. In this study, a new type of anion-exchangeable layer structured compound, basic copper acetate, $Cu_2(OH)_3(OCOCH_3)\cdot H_2O$ has been developed and its ion-exchange properties are investigated.

The basic copper acetate was prepared by titrating a 0.1 M (1 M = 1 mol dm^{-3}) copper acetate solution with 0.1 M NaOH up to OH/Cu $\approx$ 1. Green-colored platelet crystals of about 5 x 4 μm^2 were obtained. The composition was determined to be $Cu_2(OH)_3(OCOCH_3)\cdot H_2O$ as reported by Gauthier.[10] The X-ray powder diffraction (XRD) pattern can be indexed on the basis of a monoclinic cell, the dimensions of which are compared with those of the basic copper salts of the botallackite type in

Table 1. Lattice dimensions of the botallackite type compounds

	a	b	c/Å	β/°	Ref.
$Cu_2(OH)_3(OCOCH_3)\cdot H_2O$	5.546	6.029	9.296	94.5	This work
$Cu_2(OH)_3Cl$	5.640	6.138	5.726	94.3	12
$Cu_2(OH)_3Br$	5.640	6.139	6.056	93.5	12
$Cu_2(OH)_3NO_3$	5.576	6.050	6.896	94.5	13

Table 1. The layer structure of the botallackite is related to that of the CdI_2 type.[11] The copper ions are octahedrally co-ordinated in a distorted form by 4OH + 2X and 5OH + X, where X is halide or nitrate ion shown in the table. The X ions are located between the copper hydroxide layers. As seen from the table, the lattice dimensions of the a-b plane of the basic acetate are very similar to those of the basic salts of the botallackite structure, only the basal spacing (= csinβ) being changed in accordance with the size of the acetate ion. Although the structure of the basic acetate has not been analyzed by using the single crystal, it seems reasonable to conclude that the copper basic acetate has the botallackite type structure. On heating to 100 °C or by evacuation, the basic copper acetate loses the hydrated water and the basal spacing decreases to 7.20 Å. On exposure to a humid air, the spacing reverts to the initial 9.30 Å. It is likely that the water molecules also reside between the copper hydroxide layers together with the acetate ions as shown in Fig. 1.

The basic copper acetate crystals were dispersed in 1 M solutions of NaX (X = Cl, Br, I, NO_3,and ClO_4), respectively at room temperature. After standing for one day, the crystals were separated, washed with water, and dried in a stream of dry air. The basal spacings of the separated samples are compared with those of the corresponding basic salts in Table 2. As seen from the table, the basal

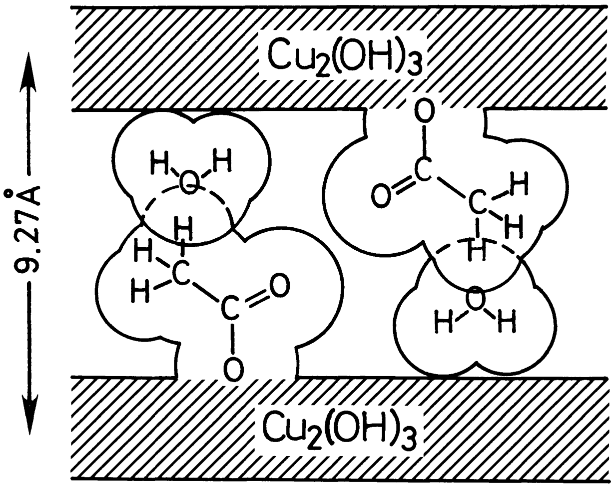

Fig. 1. Schematic structural model of $Cu_2(OH)_3(OCOCH_3)\cdot H_2O$.

Table 2. Basal spacings of the ion-exchanged products

X	Basal spacing/Å	Corresponding basic salt	
		Composition	Basal spacing/Å
Cl^-	5.71	$Cu_2(OH)_3Cl$	5.71[12)]
Br^-	6.04	$Cu_2(OH)_3Br$	6.04[12)]
I^-	6.58	$Cu_2(OH)_3I$	6.53[12)]
NO_3^-	6.90	$Cu_2(OH)_3NO_3$	6.87[13)]
ClO_4^-	7.34	$Cu_7(OH)_{12}(ClO_4)_2$	7.34[a)]

a) This study.

spacing of the basic copper acetate is changed to those of the corresponding basic salts. This finding suggests that the acetate ions in the copper basic acetate are exchanged with the corresponding anions. To our knowledge, no crystallographic data on the basic copper perchlorate has been reported.. The basic salt $Cu_7(OH)_{12}(ClO_4)_2$ was prepared by the method reported by Näsänen and Tamminen,[14)] and its basal spacing was determined to be 7.34 Å. The composition of the basic perchlorate salt is peculiar among the basic salts examined. During the exchange of the acetate with perchlorate ions, the acetate ions may be exchanged with hydroxyl as well as perchlorate ions. For further study on the mechanism of the conversion of the acetate form to the perchlorate one, structural data on the basic perchlorate are strongly required.

The exchanged products with NO_3^- and ClO_4^- anions were reversibly converted to basic copper acetate in a 1 M CH_3COONa solution. In addition, it was found that NO_3^-, ClO_4^- and CH_3COO^- were reversibly exchanged with each other, while the chloride and bromide ions were not re-exchanged with the acetate ions. A series of scanning electron micrographs of the basic copper acetate crystals were taken before and after the ion-exchanges. It was revealed that the shape of the crystals were retained by the ion-exchanges, indicating that the reactions were topotactic.

The exchanges of the interlayer acetate ions with carboxylate ions, n-$C_nH_{2n+1}COO^-$ (n = 0 - 11) were also performed. The basal spacings of the resulting crystals are shown in Fig. 2 as a function of the number of carbon atoms (n) in the alkyl chains of the carboxylate ions used. Although some exchanged compounds have more than one kind of basal spacing, apparently the spacing tends to increase linearly with the number of carbon atoms. The slope of the line is calculated to be about 2.5 Å/carbon atom, indicating that the carboxylate ions are oriented with the alkyl chains almost perpendicular to the layer. The different spacings for the products exchanged with the same kind of carboxylate ions may be attributed to the slight differences in the orientations of the chains and the exchanged amount. Further studies on the structures of the exchanged products are currently in progress.

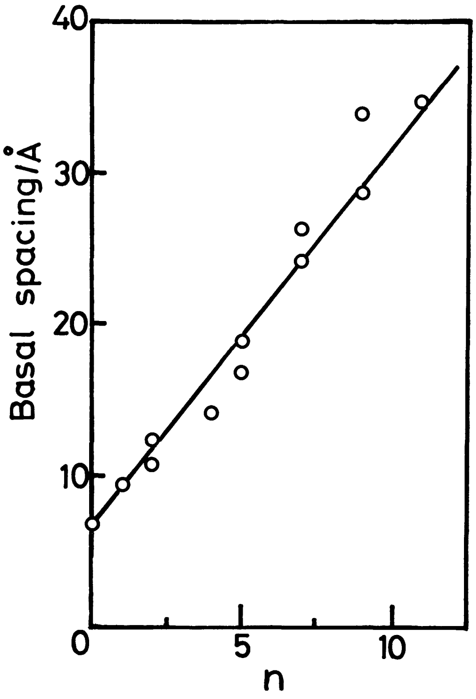

Fig. 2. Basal spacings of the basic copper salts obtained by the exchange with carboxylate ions vs. the number of carbon atoms (n) in the alkyl chains of the carboxylate ions.

This study was partly defrayed by the Grant-in-aid for Scientific Research on Priority Area of the Ministry of Education, Science and Culture.

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(Received August 3, 1989)