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**Synthesis and study of sodium hydroxi-cuprate:
Na₂Cu(OH)₄ and copper hydroxide: Cu(OH)₂**

by

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ABSTRACT - Sodium hydroxi-cuprate: Na₂Cu(OH)₄ and copper hydroxide Cu(OH)₂, have been synthesized. Chemical and thermal analysis, crystallographic and infrared studies are reported. Na₂Cu(OH)₄ is orthorhombic, space group Pna2₁. Cell parameters were determined from a single crystal; a(Å) = 6.766(4), b(Å) = 6.751(4), c(Å) = 9.003(5), z = 4.

INTRODUCTION

Ternary systems MO, Na₂O, H₂O have been studied by Scholder since 1933. In these works, sodium hydroxi-metallates, of formula type: Na₂M(OH)₄ are mentioned. More recently, a synthetical paper has been published (Scholder et al. 1966) [1].

Sodium hydroxi-metallates are not stable when exposed to the humidity and carbon dioxide of the air. Their formula have been inferred from the results of the chemical analysis only. Crystallographic studies of these compounds have never been mentioned. In the present paper the study of Na₂Cu(OH)₄ is reported. A new method of synthesis which gives rise to single crystals, is proposed. Single crystals allow a complete crystallographic study which confirms the chemical formula unambiguously.

Na₂Cu(OH)₄ is an intermediate material of great interest for the synthesis of Cu(OH)₂. Many publications [2, 3, 4, 5], mentioned the synthesis of Cu(OH)₂. All these works stress the fact that it is difficult to obtain pure solids. This is probably due to the lack of stability of Cu(OH)₂ and explains why, recently, a new mineral Cu(OH)₂, has been discovered, named Spertiniite [6]. Infrared and thermal analysis bring out some informations on the two compounds Na₂Cu(OH)₄ and Cu(OH)₂.

EXPERIMENTAL PROCEDURE

After recovering and purifying processes, chemical analysis were performed for copper and sodium with an inductively coupled plasma spectrometer "Jobin et Yvon". X-Ray diffraction powder patterns were recorded on a diffractometer " Rigaku D MAX II", using CuK α radiation. Single crystal study was carried out on an automatic diffractometer " CAD-4 Nonius ". Infrared spectra were obtained with an IR-spectrometer " PYE Unicam SP3-300 ". Finely grounded samples were dispersed in a paraffin oil (nujol) and inserted between two Kbr plates. For differential thermal analysis and thermogravimetric analysis "Adamel ATD 67 " and " Adamel TH 59 " analyzers were used at a heating rate of 300°C/H.

CHEMICAL STUDY

For the preparation of Na₂Cu(OH)₄, the use of a very active copper oxide is required. Good results have been obtained with:

- Copper oxide prepared in our laboratory from copper nitrate solutions precipitated with sodium hydroxide.

- Copper oxide "Sedema réf.: 3011406".

Starting systems containing copper oxide and sodium hydroxide have been slowly hydrated, sheltered from carbon dioxide. Several tests carried out at room temperature, in the ternary system H₂O, CuO, Na₂O permit to define approximatively the domain where the pure solid phase is in equilibrium with its saturated solution, which contains mainly, sodium hydroxide. Recovering and purifying of Na₂Cu(OH)₄ are very difficult because this compound is stable only when the sodium hydroxide solutions are very concentrated. If sodium hydroxide is diluted by washing crystals with water or with a non aqueous solvent, Na₂Cu(OH)₄ decomposes quickly giving rise to Cu(OH)₂, and then CuO.



A powder pattern of the solid phase in equilibrium with its saturated solution shows that the phase is well-crystallized and has a new pattern. In order to isolate Na₂Cu(OH)₄, it is necessary to obtain big crystals. Thus, we can take them from the solution, and dry them with filter paper. A starting system containing 10 moles of NaOH for 1 mole of CuO and 40 moles of water has been slowly dehydrated for one month, at room temperature and sheltered from carbon dioxide. Blue octahedral-shaped crystals of average size 0.1 mm, were obtained. Thus, crystal structure determination and compound analysis became possible. Copper hydroxide is obtained from sodium hydroxi-cuprate by adding water to the mixture containing Na₂Cu(OH)₄ and its mother liquor. The composition of the starting system is:

5 moles of NaOH for 1 mole of CuO and 13 moles of water. After reaction, the mixture is quickly introduced in a large quantity of water. A few minutes later, the copper hydroxide, obtained in this way, is filtered, washed out with water, dried with acetone and then, introduced into a glovebox using KOH, for several days. X-ray powder pattern agrees well

with the J.C.P.D.S. cards (files n° 13- 420 and 35-505). Chemical analysis results are reported in the table I.

Despite the purification process used and the strong hygroscopicity of $\text{Na}_2\text{Cu}(\text{OH})_4$, analytical results are in good agreement with the chemical formula. As for copper hydroxide, the shortage of copper is mainly due to adsorbed water, the amount of which has been determined by thermal analysis. The resulting material contains about 18 moles of adsorbed water for one hundred moles of $\text{Cu}(\text{OH})_2$. Unavoidable adsorbed water is explained by the very finegrained powder obtained. A stronger desorption can destroy the structure of $\text{Cu}(\text{OH})_2$, giving rise to CuO and H_2O . On the other hand, copper hydroxide prepared in this way, is free of anions adsorbed during the precipitation from copper salt solutions.

CRYSTALLOGRAPHIC STUDIES

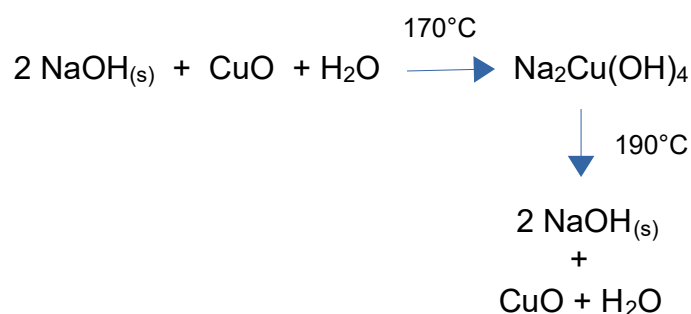
An octahedral single crystal of 0.2 mm size was used for the crystallographic study. The crystal was first quickly introduced inside a lindeman glass tube, sealed at the extremities. The unit-cell is orthorhombic and the space group $\text{Pna}2_1$. The refined lattice parameters are reported in the table II. The crystal structure is in progress and will be shortly published [7]. Copper atom has a square-plane surrounding while sodium atoms occupy octahedral sites. Among the hydrogen atoms belonging to the four independent OH, only two of them are responsible for weak hydrogen bonds. The orthorhombic cell of $\text{Cu}(\text{OH})_2$, was determined by H. Jaggi et al.[5]; space group is Cmcm .

Cell parameters, refined from the powder pattern data are reported in the table II. Indexed powder patterns are given in table III.

THERMAL ANALYSIS

In order to get a better understanding of the formation process of $\text{Na}_2\text{Cu}(\text{OH})_4$, a DTA of the mixture $2 \text{NaOH} + 1 \text{CuO} + 1 \text{H}_2\text{O}$ was carried out (Fig. 1). On the thermal curve, at first occurs an endothermic peak at 60°C . It is due to the loss of water adsorbed on sodium hydroxide. Exothermic sharp peak beginning at 170°C and centered at 180°C corresponds to the hydroxi-cuprate formation. An X-Ray pattern confirms this fact. The thermal stability domain of the compound is very narrow, because decomposition begins at 190°C . A large endothermic peak centered at 230°C corresponds to this reaction which gives rise again to the starting materials. The synthesis of the pure solid phase from a stoichiometric mixture is impossible because formation and decomposition reactions occur in the same temperature range.

This result is summarized in the following equation:



Kinetic of sodium hydroxi-cuprate formation, from a stoichiometric mixture, becomes quick enough, only when the temperature comes close to the decomposition reaction one, which corresponds to the end of the thermodynamic stability area. On the other hand, when there is an excess of water and sodium hydroxide, kinetic is fast enough to allow compound formation at room temperature.

The DTA curve of $\text{Cu}(\text{OH})_2$, (Fig. 1) is simpler. A large endothermic peak beginning at about 150°C and centered at 160°C corresponds to the decomposition reaction which gives rise to CuO . A weak exothermic peak follows, which is probably due to the CuO crystallization. Thermolysis of $\text{Cu}(\text{OH})_2$, is characterized by an experimental loss in weight of 21.0%. That loss agrees well with the expected one, 20.91%, corresponding to the mixture $\text{Cu}(\text{OH})_2$, 0.02 NaOH , 0.18 H_2O , composition of which was deduced from chemical analysis. Copper hydroxide obtained in this way, is containing about 3.2% adsorbed of water.

INFRARED STUDIES

Infrared study was limited to absorption bands corresponding to the stretching vibrations of hydroxyl groups (Fig. 2). The IR spect.um of $\text{Na}_2\text{Cu}(\text{OH})_4$ displays four bands in the $\nu(\text{OH})$ region. This is in good agreement with the results of the crystal structure determination which show that four independent OH exist. Two of them are affected by weak hydrogen bonds. Their absorption bands occur at lower frequencies, 3 525 and 3490 cm^{-1} than those of the two other ones 3600 and 3570 cm^{-1} . As previously mentioned, this result is closely confirmed by the structural study.

Copper hydroxide $\text{Cu}(\text{OH})_2$, has a simpler IR spectrum. The crystal structure is characterized by two independent OH, thus two absorption bands occur. In this case, OH groups are very different. One of them is affected by a strong hydrogen bond. The corresponding vibration takes place at 3300 cm^{-1} . The other OH absorbs at 3560 cm^{-1} . It means that hydrogen bond is, then, very weak.

CONCLUSION

The study of sodium hydroxi-cuprate $\text{Na}_2\text{Cu}(\text{OH})_4$ is decisive to confirm the existence of sodium hydroxi-metallates $\text{Na}_2\text{M}(\text{II})(\text{OH})_4$. The preparation of single crystals allows the structural determination of $\text{Na}_2\text{Cu}(\text{OH})_4$. Little is known about the structure of alkali hydroxi-metallates. Moreover, the present work shows that sodium hydroxi-cuprate is an interesting intermediate product for the preparation of copper hydroxide $\text{Cu}(\text{OH})_2$, for which common preparative methods do not appty very easily.

A similar study, carried out with cadmium, has confirmed the existence of sodium hydroxi-cadmiate $\text{Na}_2\text{Cd}(\text{OH})_4$. This work will be published shortly. sodium hydroxi-cadmiate is also an intermediate for preparing cadmium hydroxide $\text{Cd}(\text{OH})_2$. Hydroxides obtained from sodium hydroxi-metallates do not exhibit the "Brucite" structure which is commonly found among most divalent metal hydroxides. The following work will be the study of the other sodium hydroxi-metallates $\text{Na}_2\text{M}(\text{OH})_4$.

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TABLE I
Chemical analysis results.

Phases	Cu% _(Theo)	Cu% _(Exp)	Na% _(Theo)	Na% _(Exp)	$r = \frac{\text{Na}}{\text{Cu}}$
Na ₂ Cu(OH) ₄	35,79	30,6	25,91	23,2	2,1
Cu(OH) ₂	65,14	62,0	0	0,44	$2,0 \times 10^{-2}$

TABLE II
Cell parameters

Phases	Symmetry	Space group	a(Å)	b(Å)	c(Å)	z	ρ_{obs}	ρ_{calc}
Na ₂ Cu(OH) ₄		Pna2 ₁	6,766(4)	6,751(4)	9,003(5)	4	/	2,87
Cu(OH) ₂	Orthorhombic	Cmcm	2,955(2)	10,632(6)	5,273(4)	4	3,47	3,91 3,44*

* Density evaluated for the mixture Cu(OH)₂+0.02 NaOH+0.18 H₂O.

TABLE III

$\text{Na}_2\text{Cu}(\text{OH})_4$					$\text{Cu}(\text{OH})_2$				
D_{HKL}	I/I_0	H	K	L	D_{HKL}	I/I_0	H	K	L
5.458	6	0	1	1	5.356	80	0	2	0
4.522	22	0	0	2	3.760	100	0	2	1
4.246	100	1	1	1	2.853	5	1	1	0
3.391	24	{ 2	0	0	2.642	68	0	4	0
3.024	4	{ 0	2	0	2.510	37	1	1	1
2.875	12	2	1	0	2.369	19	0	4	1
2.713	20	{ 2	1	1	2.367	19	0	2	2
2.550	10	{ 1	2	1	2.274	61	1	3	0
2.509	3	{ 2	0	2	2.088	9	1	3	1
2.398	94	{ 0	2	2	1.937	3	1	1	2
2.316	4	1	1	3	1.773	3	0	6	0
2.258	29	2	1	2	1.722	40	{ 1	5	0
2.184	6	2	2	0	1.679	4	{ 1	3	2
2.137	11	2	2	1	1.670	6	0	6	1
2.111	18	0	3	1	1.643	8	1	5	1
2.083	11	{ 3	1	0	1.495	5	1	1	3
2.074	8	{ 1	3	0	1.477	13	2	0	0
1.873	11	{ 2	1	3	1.444	10	1	5	2
1.687	18	2	2	2	1.425	4	2	2	0
1.639	36	3	1	1	1.375	6	2	2	1
1.583	4	1	3	1	1.329	3	0	8	0
1.567	6	{ 2	0	4	1.288	7	2	0	2
1.549	4	{ 0	2	4	1.250	4	2	2	2
1.513	7	{ 4	0	0	1.232	2	1	5	3
1.434	10	{ 0	4	0	1.187	3	0	8	2
1.375	6	{ 1	1	5	1.139	3	1	3	4
1.351	9	2	2	4	1.107	3	2	2	3
1.271	3	{ 4	0	2	1.071	1	1	7	3
1.256	5	{ 0	4	2	1.043	3	2	6	2
1.194	6	3	3	1					
1.124	3	4	1	4					
		{ 4	2	0					
		{ 2	4	0					
		4	2	2					
		{ 3	1	5					
		{ 1	3	5					
		{ 4	0	4					
		{ 0	4	4					
		2	2	6					
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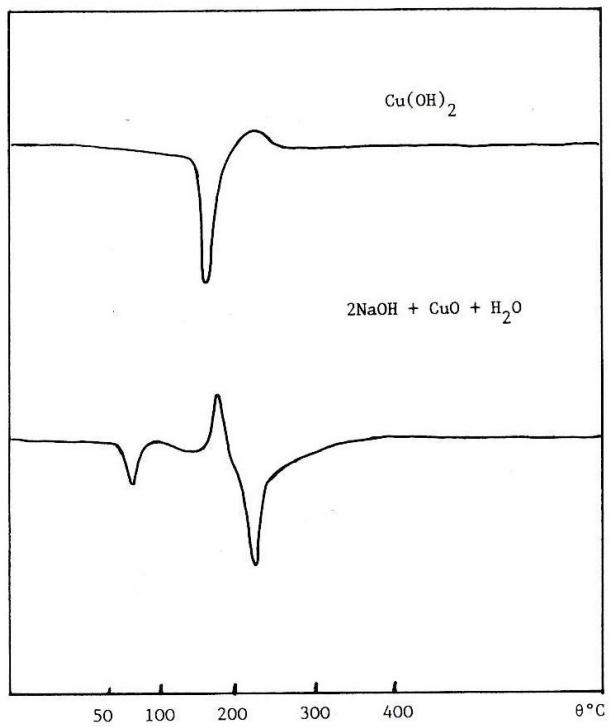


Fig. 1

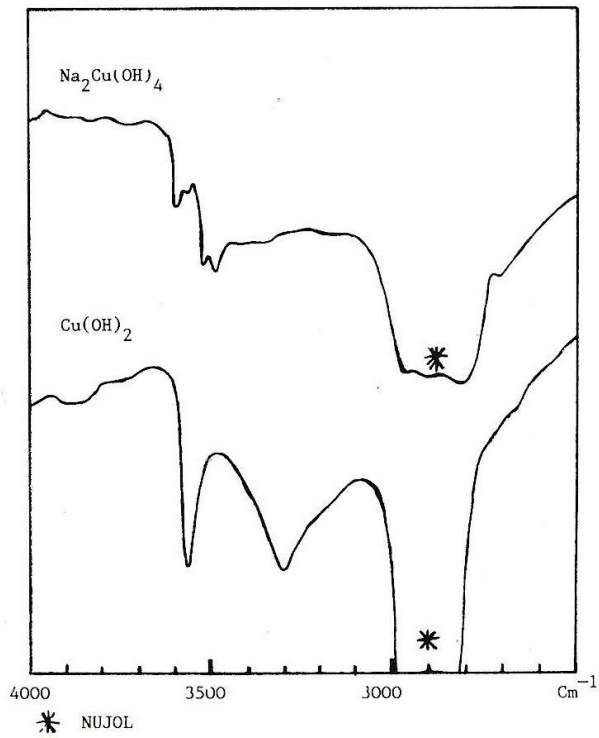


Fig. 2

Fig. 1. — DTA Curves.
Fig. 2. — Infrared spectra.