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Synthesis and Crystal Structures of Cd(OH)Cl and Cu(OH)Cl and Relationship to Brucite Type

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Synthesis of single crystals of Cd(OH)Cl and Cu(OH)Cl allowed us to revise the structure of these hydroxychlorides and confirm their space group: $P6_3mc$ ($R = 0.041$; $R_w = 0.050$) for Cd(OH)Cl and $P2_1/c$ ($R = 0.051$; $R_w = 0.069$) for Cu(OH)Cl. Positions of hydrogen atoms were determined and an hypothesis of hydrogen bonds is discussed in relation to the infrared spectra. A comparison of the structures shows that an isomorphism is not possible between the two compounds, due to the important Jahn–Teller effect of divalent copper. On the other hand, a structural relationship exists between Cd(OH)Cl and β-Cd(OH)$_2$, which belongs to the brucite-type family. © 2000 Academic Press

Key Words: **crystal structure; cadmium; copper; hydroxychloride.**

INTRODUCTION

Many studies have been published on divalent metal hydroxychlorides, M(OH)Cl, which structures are related to the brucite type (1–5). To our knowledge, few structural studies were carried out on single crystals, except for Cd(OH)Cl but the crystal structure was determined in 1934 (6) and for Cu(OH)Cl, which a more recent determination gives a R value near 13% (7).

In a recent publication (5), we exposed a new route for the preparation of cadmium hydroxychlorides based on using more reactive starting material: γ-Cd(OH)$_2$. Single crystals of β-Cd$_2$(OH)$_3$Cl and Cd(OH)Cl were obtained in this way. The crystal structure determination of the first one shows that it is isostructural with atacamite, the corresponding solid phase of copper, Cu$_2$(OH)$_3$Cl. This was a surprising result, by reason of the peculiar surrounding of copper due to the Jahn–Teller effect.

The aims of this paper are to propose recent data for structural studies of Cd(OH)Cl and Cu(OH)Cl, confirm their space groups, try to show a relationship to the brucite type, and explain why the isomorphism between copper and cadmium compounds is possible only in the case of M_2(OH)$_3$Cl and not for M(OH)Cl.

SYNTHESIS AND CRYSTAL STRUCTURE DETERMINATION

Crystals of Cd(OH)Cl were synthesized under hydrothermal conditions (5). A reacting system containing 0.1 mole of CdCl$_2$, 2.5H$_2$O, 0.1 mole of γ-Cd(OH)$_2$, and 100 moles of H$_2$O is gradually heated from room temperature to 323 K, during four weeks. In the presence of Cl$^-$ ions, crystals of γ-Cd(OH)$_2$ are slowly transformed into Cd(OH)Cl according to the scheme

$$\mathrm{Cd^{2+}_{(aq)} + 2\ Cl^-_{(aq)} + \gamma\text{-}Cd(OH)_{2(s)} \rightarrow 2Cd(OH)Cl_{(s)}}$$

Owing to the large grain size of the starting material γ-Cd(OH)$_2$ (around several tenths of a mm), the reaction kinetic is very slow and favors the formation of large crystals. Crystals of Cd(OH)Cl are colorless and have an hexagonal prismatic shape.

Crystals of Cu(OH)Cl were prepared according to the method used by Iiataka *et al.* (7). They appear under the shape of small olive-green plates.

Intensity data collections were performed with a MACH 3 NONIUS diffractometer operating with Mo$K\alpha$ radiation. The lattice parameters were refined by least squares from 25 reflections. The structural determination, using the XTAL (12) and MoLEN (13) package, confirmed the space groups, $P6_3mc$ for Cd(OH)Cl (6) and $P2_1/c$ for Cu(OH)Cl (1). Lorentz polarization and absorption corrections with Difabs program (14) have been applied to the data.

The structure of the two compounds is composed of one independent atom of M^{2+}, chloride, oxygen, and hydrogen. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but atomic parameters were refined isotropically only for Cu(OH)Cl. Details on X-ray data collection and results of structure refinements are given in Table 1 and atomic coordinates with displacement parameters are given in Table 2.

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TABLE 1
Single Crystal X-Ray Data and Structure Refinement Results

Crystal data	Cd(OH)Cl	Cu(OH)Cl
Crystal dimensions (mm)	$0.15 \times 0.15 \times 0.3$	$0.1 \times 0.25 \times 0.35$
Crystal system	Hexagonal	Monoclinic
Space group	$P6_3mc$	$P2_1/c$
a (nm)	0.36648(5)	0.62953(4)
b (nm)	0.36648(5)	0.66649(11)
c (nm)	1.02305(11)	0.55580(4)
γ or β (degrees)	120	118.138(11)
Z	2	4
Density calc. (g/cm^{-3})	4.592	3.762
θ (°) (min., max.)	2, 30	2, 30
hkl (min., max.)	$h(0,2)$ $k(0,4)$ $l(0,14)$	$h(-10, 8)$ $k(0, 10)$ $l(0, 8)$
μ(Mo$K\alpha$) (cm^{-1})	98.8	115.7
Absorption corrections	Difabs	Difabs
Transmission factors	0.11 to 0.22	0.18 to 0.37
Total measured reflections	225	1040
Unique reflections	87	889
Reflections: $I > 3\sigma(I)$	84	799
Variable parameters	10	32
R, Rw	0.041, 0.050	0.051, 0.069
G.O.F.	1.918	1.540

Structural Comparison and Relationship to the Brucite Type

The two structures display parallel sheets of M(OH)Cl formula, which could be linked together only by hydrogen bonds. The cadmium ion is surrounded by three oxygen atoms at 0.2273 nm and three chloride atoms at 0.2704 nm. Oxygen atoms are situated in *cis*-positions in the same half-space defined by the plane of cadmium atoms belonging to the sheet, all chloride atoms being located in the other half-space.

The polyhedron Cd(O)$_3$(Cl)$_3$ thus obtained, is very distorted as shown in Fig 1, where the surroundings of M^{2+}, Cl, and O in β-Cd(OH)$_2$ (Fig. 1a) (brucite type), Cd(OH)Cl (Fig. 1b) and Cu(OH)Cl (Fig. 1c) are shown. Values of interatomic distances and angles are reported in Table 3. The polyhedron Cu(O)$_3$(Cl)$_3$ is very different. Two chloride atoms are located in *trans*-positions at a long distance of copper, 0.26985 and 0.27201 nm and the third atom is placed at a very short distance, 0.22915 nm in the very distorted square-plane surrounding of copper. This unexpected short distance for Cu–Cl bonds is naturally due to the important Jahn–Teller effect displayed by copper (4 + 2, here). Therefore, chloride atoms are found alternatively with oxygen atoms in each half-space defined as above (see Figs. 1c and 4). The Jahn–Teller effect is straightforwardly the reason which explains why the two compounds Cd(OH)Cl and Cu(OH)Cl cannot have isomorphous structures. In a recent publication (5), we determined the crystal structure of β-Cd$_2$(OH)$_3$Cl and surprisingly it was isomorphous with atacamite Cu$_2$(OH)$_3$Cl (11). In contrast to the M(OH)Cl type, an isomorphism is possible between cadmium and copper in the case of M_2(OH)$_3$Cl. In fact, in the structure of M_2(OH)$_3$Cl two types of polyhedra exist which contain one or two chloride atoms instead of three in M(OH)Cl polyhedra: M(O)$_5$Cl and M(O)$_4$(Cl)$_2$. In the structure of atacamite, chloride atoms are always placed at a long distance of copper, 0.2750 and (× 2) 0.2776 nm (Jahn–Teller effect). These distances correspond approximately to the distances between cadmium and chloride and naturally, without Jahn–Teller effect in the case of cadmium, 0.2735 and (× 2) 0.2829 nm. The same phenomenon can be noticed for the oxygen located at the opposite side of chloride in the polyhedron M(O)$_5$Cl; Cu–O: 0.2358 nm (Jahn–Teller effect); Cd–O: 0.2328 nm (without effect). In these conditions the replacement of Cu^{2+} by Cd^{2+} ion does not lead to a great deformation of the structure. This coincidence in the values of distances M–Cl and M–O explains why the isomorphism between Cu$_2$(OH)$_3$Cl and β-Cd$_2$(OH)$_3$Cl is possible.

If we compare the structure of Cd(OH)Cl with β-Cd(OH)$_2$ (space group $P\overline{3}m1$, $a = 0.3496$, $c = 0.4702$ nm), there is an evident relationship. In brucite, Cd(O)$_6$ polyhedra are regular and, consequently, have the same orientation in the different sheets. So, the c parameter, perpendicular to the sheets, corresponds to a single interlayer distance. It is not the case for Cd(OH)Cl (space group $P6_3mc$, $a = 0.36648$, $c = 1.02305$ nm), which polyhedra,

TABLE 2
Atomic Coordinates and Displacement Parameters

Atom	x	y	z	$U_{\text{eq}} \times 100$
		Cd(OH)Cl		
Cd	1/3	2/3	0.00791	1.59(4)
Cl	1/3	2/3	0.3433(5)	1.7(2)
O	0.0	0.0	0.0892(14)	1.9(6)
H*	0.0	0.0	0.180	3.5
		Cu(OH)Cl		
Cu	0.03201(7)	0.11772(6)	0.28577(7)	0.98(2)
Cl	0.3115(1)	0.0907(1)	0.1334(2)	1.03(3)
O	0.8807(4)	0.1478(3)	0.5318(5)	0.71(7)
H*	0.674(14)	0.128(8)	0.528(12)	7(2)

Atoms	$U(1, 1)$	$U(2, 2)$	$U(3, 3)$	$U(1, 2)$	$U(1, 3)$	$U(2, 3)$
			Cd(OH)Cl			
Cd	1.49(3)	1.49(3)	1.80(5)	0.75	0.0	0.0
Cl	2.06(14)	2.06(14)	0.8(2)	1.03	0.0	0.0
O	1.9(5)	1.9(5)	1.0(6)	− 0.3	0.0	0.0
			Cu(OH)Cl			
Cu	1.16(1)	0.82(2)	0.95(1)	0.191(9)	0.60(1)	0.225(9)
Cl	0.66(2)	1.45(3)	0.99(2)	0.03(2)	0.22(2)	0.00(2)
O	0.45(6)	0.92(8)	0.75(7)	0.04(6)	0.02(5)	0.09(6)

Note. H^* atom coordinates were calculated for Cd(OH)Cl and refined isotropically for Cu(OH)Cl. Atomic displacement parameters: $U_{(i,j)} \times 100$.

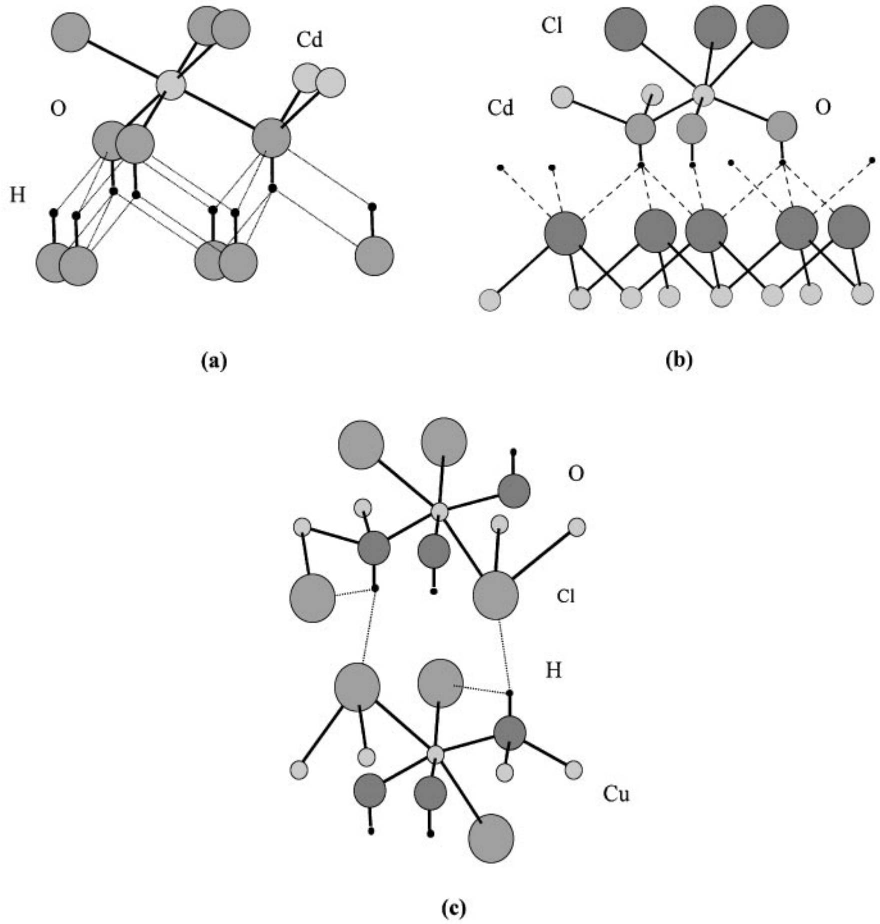

FIG. 1. Surrounding of atoms in (a) β-Cd(OH)$_2$, (b) Cd(OH)Cl, and (c) Cu(OH)Cl.

Cd(O)$_3$Cl$_3$, very distorted with the substitution of three oxygens by three chlorides, do not have the same orientation in two neighboring sheets (rotation of 180° about the *c* axis), so that the *c* parameter is equal to a double interlayer distance (see Figs. 2 and 3).

Hydrogen Bonds Hypothesis

In brucite structural type, it was assumed, regarding the high value of the ν(O–H) stretching vibration (near 3600 cm^{-1}) and the too long distance between hydrogen and acceptor (H $\cdots$ O > 0.240 nm), that no hydrogen bonds could be considered. Nevertheless, in a recent publication this result is widely discussed (8). These authors (8) give several reasons to think that in contrast to most of the literature published, hydrogen bonding in brucite type cannot be excluded in principle, even if the distance H–acceptor is larger than 0.240 nm. In this hypothesis, we have studied the possibilities of such hydrogen bonding in β-Cd(OH)$_2$, Cd(OH)Cl, and Cu(OH)Cl. In this way, IR spectra of the three compounds have been performed in Nujol, using an FTIR spectrometer (Fig. 5).

The crystal structure of β-Cd(OH)$_2$ has been determined for the first time with a single crystal in 1970 (9). Very recently the structure has been revisited and the atomic position of hydrogen atom determined (10). Distances (nm) and angles (°) of the surrounding of H atom, issued from this last publication are: O–H: 0.089; ($\times$3) O $\cdots$ O′ (acceptor): 0.324; ($\times$3) H $\cdots$ O′: 0.260; ($\times$3) Cd–O–H: 118.3; ($\times$3) O–H $\cdots$ O′: 129.1. As shown in Figs. 1a and 2, three hydrogen bonds could be possible per hydrogen atom with three different oxygen acceptors located at the same distance. Reciprocally each oxygen atom could be involved in three hydrogen bonds with three different hydrogen atoms. Although these bonds are very weak (ν(O–H) $= 3597.4$ cm^{-1}) (Fig. 5a), we think they could be mainly responsible of the crystal cohesion, because they form a close network of overlapped bonds (Fig. 2).

TABLE 3
Interatomic Bond Distances and Angles

Bond lengths (nm)	Angles (°)	Hydrogen bound hypothesis (bonds: nm and angles (°))
	CdO_3Cl_3 polyhedron	
(× 3) Cd–O : 0.2273(5)	(× 3) O–Cd–O′ : 107.4(3)	O–H : 0.093
(× 3) Cd–Cl : 0.2704(3)	(× 3) O–Cd–Cl : 162.9(4)	(× 3) O ⋯ Cl : 0.3352(12)
	(× 6) O–Cd–Cl′ : 82.2(3)	(× 3) H ⋯ Cl : 0.270
	(× 3) Cl–Cd–Cl′ : 85.32(8)	(× 3) O–H ⋯ Cl : 128.3
		(× 3) Cd–O–H : 111.5
	CuO_3Cl_3 polyhedron	
Bond lengths (nm)	Angles (°)	Hydrogen bound hypothesis (bonds: nm and angles (°))
Cu–O : 0.1984(3)	O–Cu–O′ : 81.22(11)	O–H : 0.13(1)
Cu–O′ : 0.2012(4)	O–Cu–O″ : 166.82(8)	Cu–O–H : 103(3)
Cu–O″ : 0.2018(3)	O–Cu–Cl : 92.46(9)	Cu′–O–H : 87(3)
Cu–Cl : 0.22915(11)	O–Cu–Cl′ : 84.15(6)	Cu″–O–H : 141(3)
Cu–Cl′ : 0.26985(8)	O–Cu–Cl″ : 110.11(6)	Inter-sheet H-bond
Cu–Cl″ : 0.27201(8)	O′–Cu–O″ : 100.35(11)	O ⋯ Cl : 0.3226(3)
	O′–Cu–Cl : 162.07(6)	H ⋯ Cl : 0.231(6)
	O′–Cu–Cl′ : 101.22(6)	O–H ⋯ Cl : 124(5)
	O′–Cu–Cl″ : 78.52(6)	Intra-sheet H-bond
	O″–Cu–Cl : 89.64(9)	O ⋯ Cl : 0.3095(3)
	O″–Cu–Cl′ : 82.71(6)	H ⋯ Cl : 0.235(7)
	O″–Cu–Cl″ : 82.96(6)	O–H ⋯ Cl : 113(4)
	Cl–Cu–Cl′ : 94.75(3)	
	Cl–Cu–Cl″ : 88.08(3)	
	Cl′–Cu–Cl″ : 165.37(3)	

Note. Atoms noted (′) or (″) correspond to equivalent positions.

The corresponding values of distances and angles in the surrounding of H atom, obtained in this work, for Cd(OH)Cl and Cu(OH)Cl are reported in Table 3. In the case of Cd(OH)Cl, they are similar to those of β-$Cd(OH)_2$; the main difference is due to an increase of the iono-covalent radii of the acceptor, which is a Cl atom instead of an O. The strength of hydrogen bonds seems to be a little higher, in regard of the value of the O–H stretching mode (ν(O–H) = 3514.7 cm^{-1}) (Fig. 5b). Nevertheless, the structure of Cd(OH)Cl is not so stable as the brucite type because hydrogen atoms are twice less numerous as in brucite and then, possibilities of hydrogen bonds also (Figs. 1b and 3). As for Cu(OH)Cl, its structure differs more from the brucite type than the Cd(OH)Cl structure. This is due to the Jahn–Teller effect. Only two hydrogen bonds could exist per hydrogen atom (See Figs. 1c and 4 and Table 3), but the strength of these bonds is straightforwardly more important

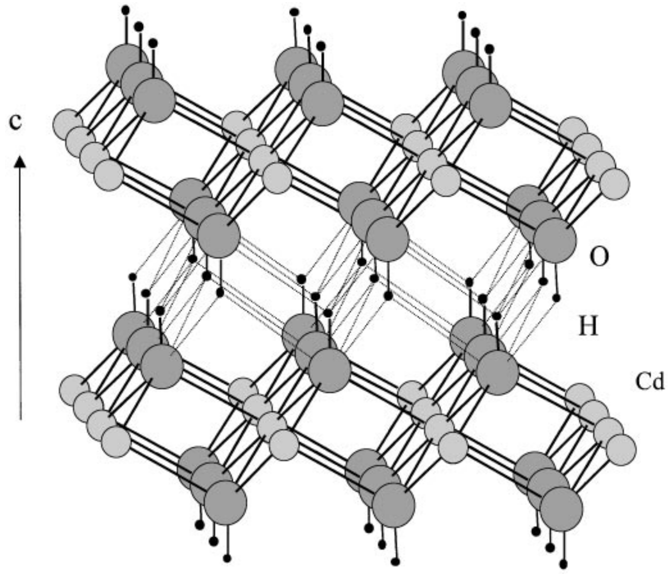

FIG. 2. β-$Cd(OH)_2$: crystal structure in perspective.

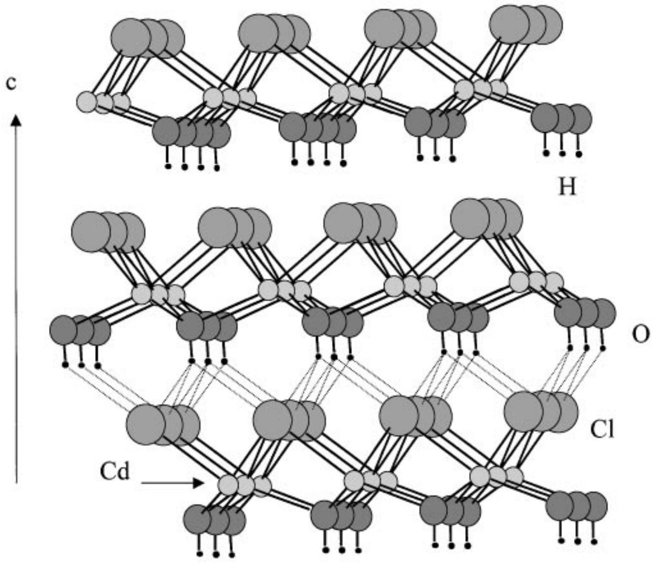

FIG. 3. Cd(OH)Cl: crystal structure in perspective.

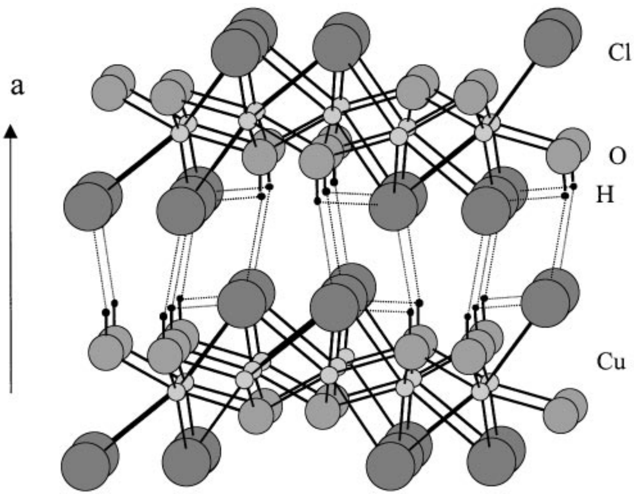

FIG. 4. Cu(OH)Cl: crystal structure in perspective.

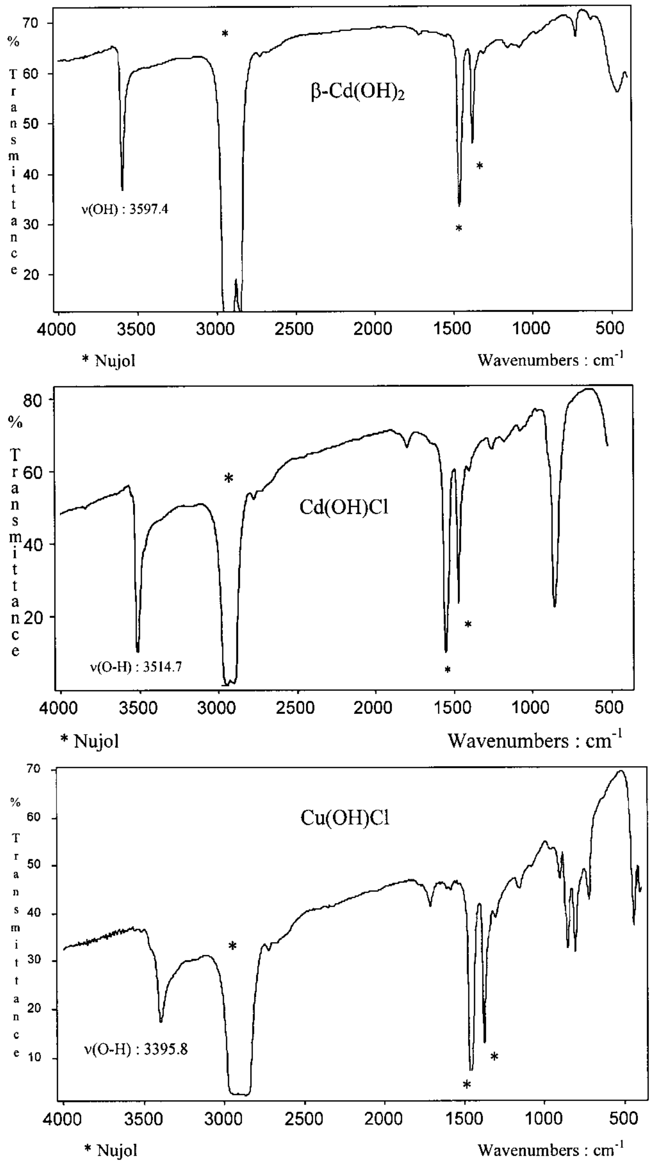

FIG. 5. IR spectra of β-Cd(OH)$_2$, Cd(OH)Cl, and Cu(OH)Cl.

(ν(O–H) = 3395.8 cm^{-1}; H $\cdots$ Cl: 0.231 and 0.235 nm). In this case, the existence of hydrogen bonding is absolutely certain.

Comparison of hydrogen bonding hypothesis in the three compounds shows that, if bonds are weak, they give rise to a dense network, but if bonds are less numerous they are strengthened. This fact may allow one to conclude the probability of existence of hydrogen bonds more or less important, in the three compounds, and that hydrogen bonds could be mainly responsible for the structural cohesion between layers.

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