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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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Abstract

Synthesis of single crystals of Cd(OH)Cl and Cu(OH)Cl allowed to revisit the structure of these hydroxychlorides and confirm their space group: $P6_3mc$ ($R = 0.041$; $R_w = 0.050$) for Cd(OH)Cl and $P2_1/c$ ($R = 0.051$; $R_w = 0.072$) for Cu(OH)Cl. Positions of hydrogen atoms were determined and an hypothesis of hydrogen bonds is discussed in relation with 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.

Key words

Crystal structure, cadmium, copper, hydroxychloride.

INTRODUCTION

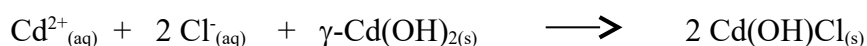
Many studies have been published on divalent metal hydroxychlorides, $M(OH)Cl$, which structures are related to the brucite type (1-5). To our knowledge, few structural studies were carried out on single crystals, excepted for $Cd(OH)Cl$ but the crystal structure was determined in 1934 (6) and for $Cu(OH)Cl$, 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: $\gamma-Cd(OH)_2$. Single crystals of $\beta-Cd_2(OH)_3Cl$ 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, $Cu_2(OH)_3Cl$. This was a surprising result, by reason of the peculiar surrounding of copper, due to 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 to explain why the isomorphism between copper and cadmium compounds is possible only in the case of $M_2(OH)_3Cl$ 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 $CdCl_2$, 2.5 H_2O , 0.1 mole of $\gamma-Cd(OH)_2$ and 100 moles of H_2O is gradually heated from room temperature to 323K, during four weeks. In the presence of Cl^- ions, crystals of $\gamma-Cd(OH)_2$ are slowly transformed into $Cd(OH)Cl$ according to the following scheme:



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 Iiatka and 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 the Mo-K α radiation. The lattice parameters were refined by least squares from 25 reflections. The structural determination, using the XTAL and MOLEN package, confirmed the space groups, P6₃mc for Cd(OH)Cl (6) and P2₁/c for Cu(OH)Cl (1). Lorentz-polarisation and absorption corrections have been applied to the data.

TABLE I
Single crystal X-ray data and structure refinement results

Crystal data	Cd(OH)Cl	Cu(OH)Cl
Crystal dimensions (mm)	0.15 x 0.15 x 0.3	0.1 x 0.25 x 0.35
Crystal system	Hexagonal	Monoclinic
Space group	P6 ₃ mc	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
<i>hkl</i> (min., max.)	<i>h</i> (0,2) <i>k</i> (0,4) <i>l</i> (0,14)	<i>h</i> (-10,8) <i>k</i> (0,10) <i>l</i> (0,8)
μ (Mo-K α) (cm ⁻¹)	98.8	115.7
Transmission factors	0.699 to 1.478	0.733 to 1.536
Total measured reflections	225	1040
Unique reflections	87	889
Reflections: $I > 3\sigma(I)$	84	799
Variable parameters	10	28
R, Rw	0.041, 0.050	0.051, 0.072
G.O.F.	1.918	1.925

The structure of the two compounds is composed of one independent atom of M²⁺, chloride, oxygen and hydrogen. The non-hydrogen atoms were refined anisotropically. Hydrogen

atoms were included but atomic parameters were not refined. Details on X-ray data collection and results of structure refinements are given in Table 1 and atomic coordinates with displacement parameters, in Table 2.

TABLE II
Atomic coordinates and displacement parameters

Atom	x	y	z	Ueq x 100
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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*	0.700	0.165	0.420	3.5

H atom coordinates were not refined.*

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	2.05(14)	2.05(14)	0.9(2)	1.03	0.0	0.0
O	2.8(5)	2.8(5)	0.1(6)	1.39	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)

General displacement anisotropic parameters : $U_{(i,j)} \times 100$

Structural comparison and relationship to the brucite type

The two structures display parallel sheets of $M(OH)Cl$ formula, which could be only linked together by hydrogen bonds. The cadmium ion is surrounded by 3 oxygen atoms at 0.2273 nm and 3 chloride atoms at 0.2704 nm. Oxygen atoms are situated in cis-positions in the same half-space defined by cadmium atoms belonging to the sheet, all chloride atoms being located in the other half-space.

TABLE III
Interatomic bond distances and angles

Cd O₃ Cl₃ Polyhedron

<u>Bond lengths (nm)</u>	<u>Angles (°)</u>	<u>Hydrogen bond hypothesis</u> (bonds: nm and angles (°))
(x3) Cd – O : 0.2273(5)	(x3) O – Cd – O' : 107.4(3)	O – H : 0.093
(x3) Cd – Cl : 0.2704(3)	(x3) O – Cd – Cl : 162.9(4)	(x3) O.....Cl : 0.3352(12)
	(x6) O – Cd – Cl' : 82.2(3)	(x3) H.....Cl : 0.270
	(x3) Cl – Cd – Cl' : 85.32(8)	(x3) O – H.....Cl : 128.3
		(x3) Cd – O – H : 111.5

Cu O₃ Cl₃ Polyhedron

<u>Bond lengths (nm)</u>	<u>Angles (°)</u>	<u>Hydrogen bond hypothesis</u> (bonds: nm and angles (°))
Cu – O : 0.1984(3)	O – Cu – O' : 81.22(11)	O – H : 0.101
Cu – O' : 0.2012(4)	O – Cu – O'' : 166.82(8)	O.....Cl : 0.3226(3)
Cu – O'' : 0.2018(3)	O – Cu – Cl : 92.46(9)	H.....Cl : 0.226
Cu – Cl : 0.22915(11)	O – Cu – Cl' : 84.15(6)	O – H.....Cl : 159.7
Cu – Cl' : 0.26985(8)	O – Cu – Cl'' : 110.11(6)	Cu – O – H : 111.4
Cu – Cl'' : 0.27201(8)	O' – Cu – O'' : 100.35(11)	Cu' – O – H : 110.4
	O' – Cu – Cl : 162.07(6)	Cu'' – O – H : 112.0
	O' – Cu – Cl' : 101.22(6)	
	O' – Cu – Cl'' : 78.52(6)	
	O'' – Cu – Cl : 89.64(9)	
	O'' – Cu – Cl' : 82.71(6)	
	O'' – Cu – Cl'' : 82.96(6)	
	Cl – Cu – Cl' : 94.75(3)	
	Cl – Cu – Cl'' : 88.08(3)	
	Cl' – Cu – Cl'' : 165.37(3)	

(Atoms noted (') or ('') correspond to equivalent positions)

The polyhedron $\text{Cd}(\text{O})_3(\text{Cl})_3$ thus obtained, is very distorted as shown in Fig 1, where are drawn surroundings of M^{2+} , Cl and O in $\beta\text{-Cd}(\text{OH})_2$ (1a) (brucite type), $\text{Cd}(\text{OH})\text{Cl}$ (1b) and $\text{Cu}(\text{OH})\text{Cl}$ (1c). Values of interatomic distances and angles are reported in Table 3. On the other hand, the polyhedron $\text{Cu}(\text{O})_3(\text{Cl})_3$ 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 one 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 (d^9 , here). Therefore, chloride atoms are found alternatively with oxygen atoms in each half-space defined as above (see Fig.1c and 4). Jahn-Teller effect is straightforwardly the reason which explains why the two compounds $\text{Cd}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{OH})\text{Cl}$ cannot have isomorphous structures. In a recent publication (5), we have determined the crystal structure of $\beta\text{-Cd}_2(\text{OH})_3\text{Cl}$ and surprisingly it was isomorphous with atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$ (11). In contrast to the $\text{M}(\text{OH})\text{Cl}$ type, an isomorphism is possible between cadmium and copper in the case of $\text{M}_2(\text{OH})_3\text{Cl}$. In fact, in the structure of $\text{M}_2(\text{OH})_3\text{Cl}$ two types of polyhedra exist which contain one or two chloride atoms instead of three in $\text{M}(\text{OH})\text{Cl}$ polyhedra : $\text{M}(\text{O})_5\text{Cl}$ and $\text{M}(\text{O})_4(\text{Cl})_2$. In the structure of atacamite, chloride atoms are always placed at a long distance of copper, 0.2750 and (x2) 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 (x2) 0.2829 nm. The same phenomenon can be noticed for the oxygen located at the opposite side of chloride in the polyhedron $\text{M}(\text{O})_5\text{Cl}$; 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 $\text{Cu}_2(\text{OH})_3\text{Cl}$ and $\beta\text{-Cd}_2(\text{OH})_3\text{Cl}$ is possible.

If we compare the structure of $\text{Cd}(\text{OH})\text{Cl}$ with $\beta\text{-Cd}(\text{OH})_2$ (space group $P\text{-}3m1$, $a = 0.3496$ nm, $c = 0.4702$ nm), there is an evident relationship. In brucite, $\text{Cd}(\text{O})_6$ polyhedra are regular and consequently, have the same orientation in the different sheets. So, the c parameter, perpendicular to the sheets, corresponds to the distance between 2 sheets. It is not the case for $\text{Cd}(\text{OH})\text{Cl}$ (space group $P6_3mc$, $a = 0.36648$ nm, $c = 1.02305$ nm), which polyhedra, $\text{Cd}(\text{O})_3\text{Cl}_3$, very distorted with the substitution of three oxygens by three chlorides, have not the same orientation in two neighboring sheets (rotation of 180° about c axis), so that the c parameter is equal to the distance corresponding to three sheets (see Fig.2 and 3).

Hydrogen bonds hypothesis

In brucite structural type, it was assumed, regarding the high value of the $\nu(\text{O-H})$ stretching vibration (near 3600 cm^{-1}) and the too long distance between hydrogen and acceptor ($\text{H}\cdots\text{O} > 0.240$ nm), that no hydrogen bonds could be considered. In a recent publication this result is widely discussed (8). The authors 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 $\text{H}\cdots\text{acceptor}$ is larger than 0.240 nm. In this hypothesis we have studied the possibilities of such hydrogen bonding in $\beta\text{-Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{OH})\text{Cl}$. In this way, IR spectra of the three compounds have been performed in Nujol, using an FTIR spectrometer (Fig.5).

The crystal structure of $\beta\text{-Cd}(\text{OH})_2$ 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 ($^\circ$) of the surrounding of H atom, issued from this last publication are : $\text{O-H} : 0.089$; (x3) $\text{O}\cdots\text{O}'$ (acceptor) : 0.324 ; (x3) $\text{H}\cdots\text{O}' : 0.260$; (x3) $\text{Cd-O-H} : 118.3$; (x3) $\text{O-H}\cdots\text{O}' : 129.1$. As shown on Fig.1a and Fig.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 ($\nu(\text{O-H}) = 3597.4 \text{ cm}^{-1}$) (Fig.5a), we think they could be mainly responsible of the crystal cohesion, because they form a close network of overlapped bonds (Fig. 2).

The corresponding values of distances and angles in the surrounding of H atom, obtained in this work, for $\text{Cd}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{OH})\text{Cl}$ are reported in Table 3. In the case of $\text{Cd}(\text{OH})\text{Cl}$, they are similar to those of $\beta\text{-Cd}(\text{OH})_2$; the main difference being due to an increase of the iono-covalent radii of the acceptor which is here, Cl atom instead of O. The strength of hydrogen bonds seems to be a little higher, in regard of the value of O-H stretching mode ($\nu(\text{O-H}) = 3514.7 \text{ cm}^{-1}$) (Fig.5b). Nevertheless the structure of $\text{Cd}(\text{OH})\text{Cl}$ 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 (Fig. 1b and 3). As for $\text{Cu}(\text{OH})\text{Cl}$, its structure is more different of the brucite type than the $\text{Cd}(\text{OH})\text{Cl}$ one. This is due to Jahn-Teller effect. Only one hydrogen bond could exist per hydrogen atom (See Fig.1c and 4), but the strength of this bond is straightforwardly more important ($\nu(\text{O-H}) = 3395.8 \text{ cm}^{-1}$ and $\text{O}\cdots\text{H} : 0.226 \text{ nm}$). In this case, 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 to conclude to the probability of existence of hydrogen bonds more or less important, in the three compounds and that hydrogen bonds could be mainly responsible of the structural cohesion between layers.

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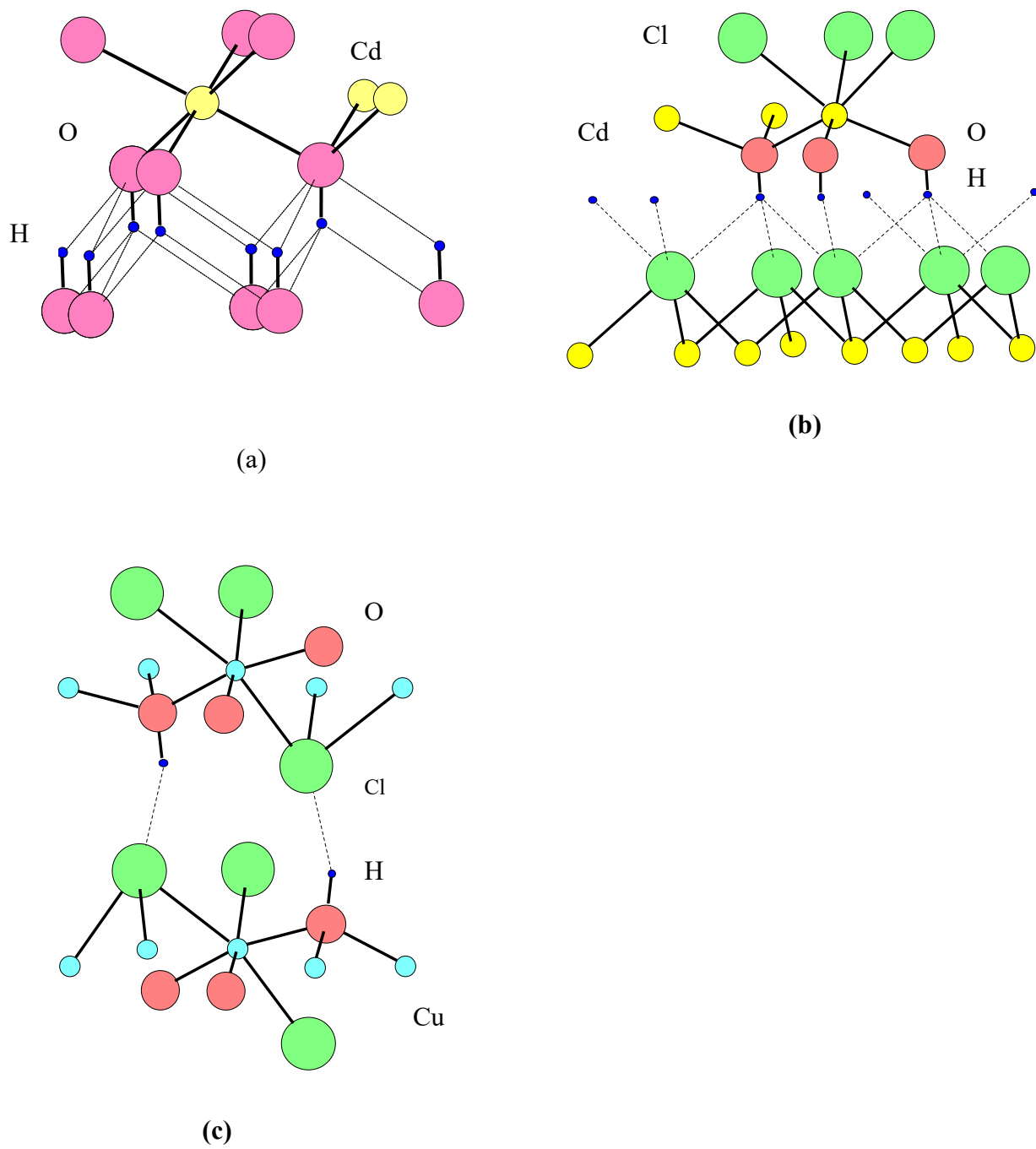


FIG. 1. Surrounding of atoms in (a) β -Cd(OH)₂, (b) Cd(OH)Cl, and (c) Cu(OH)Cl.

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

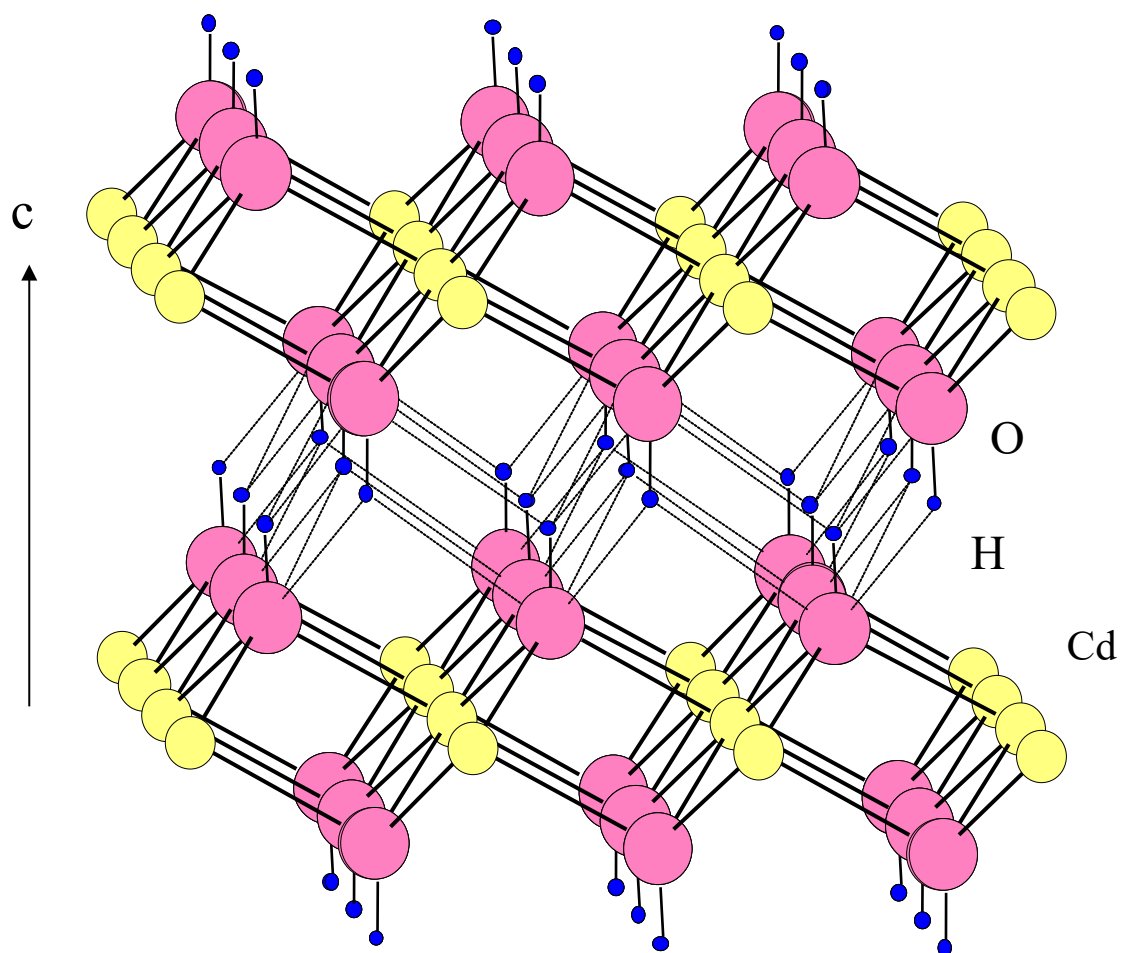


FIG. 3. $\text{Cd}(\text{OH})\text{Cl}$: crystal structure in perspective

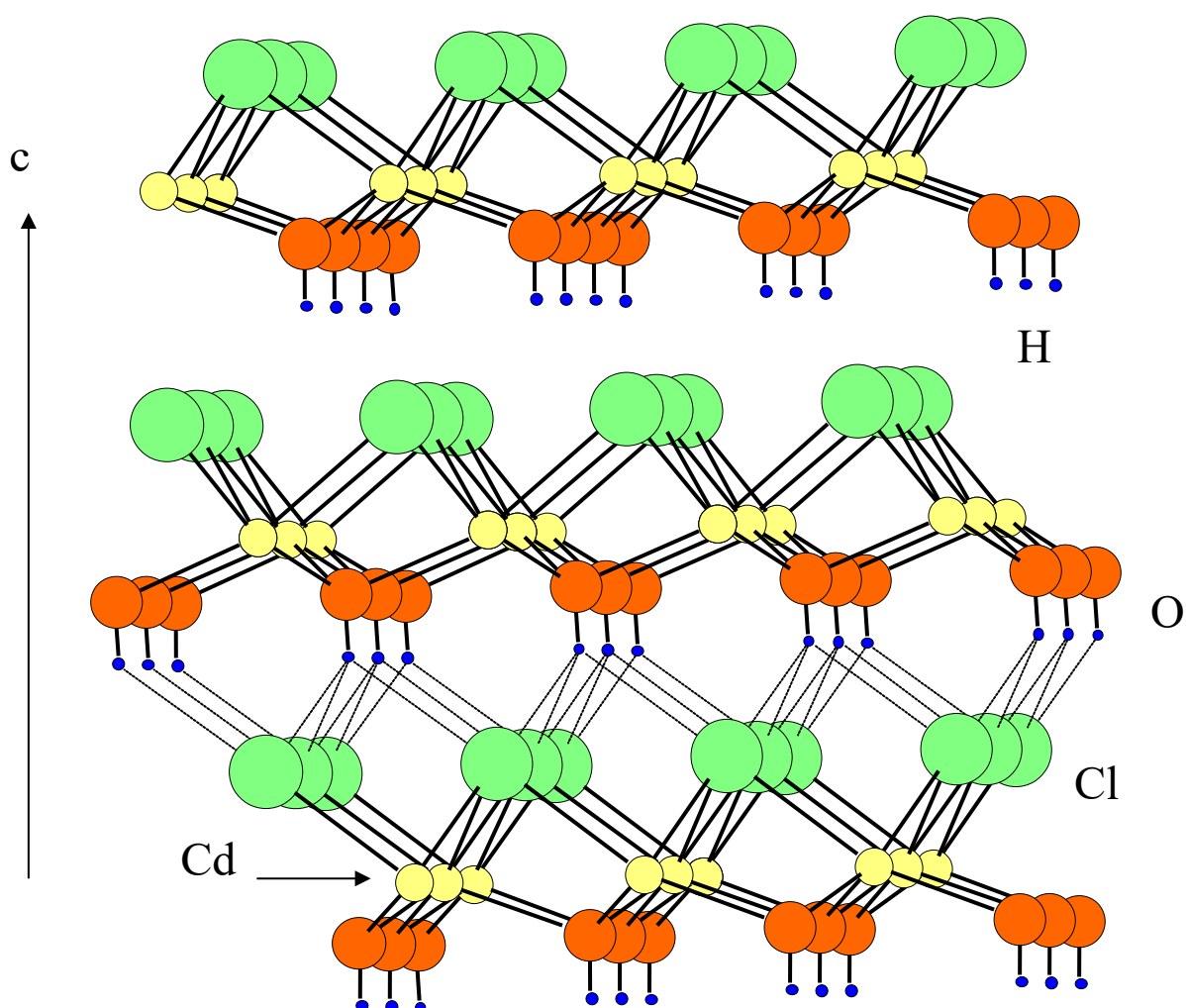
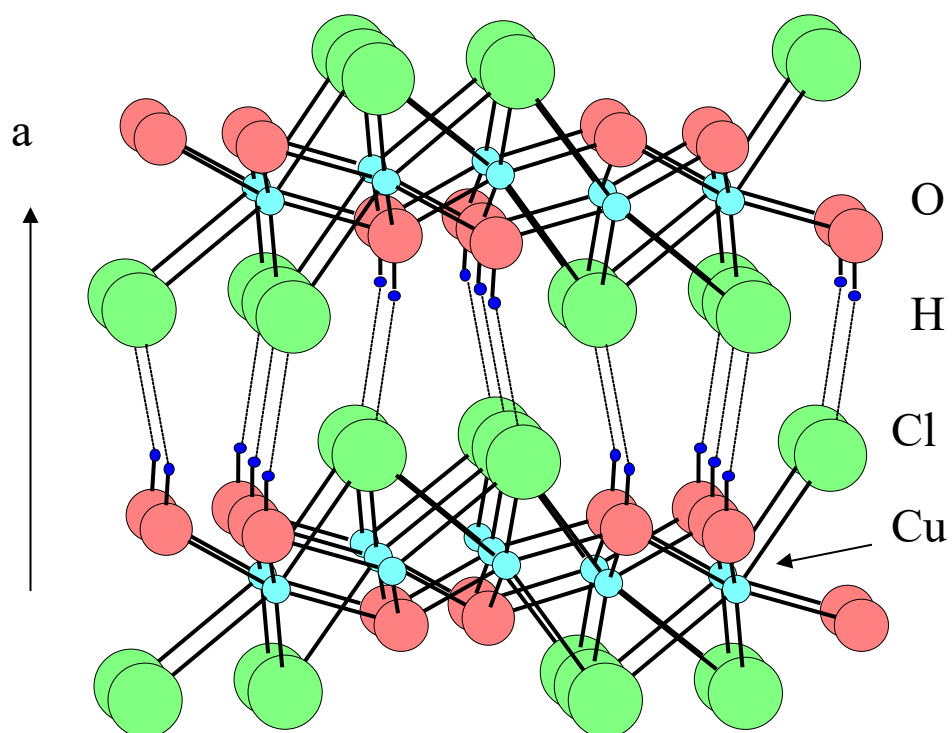


FIG. 4. $\text{Cu}(\text{OH})\text{Cl}$: crystal structure in perspective.



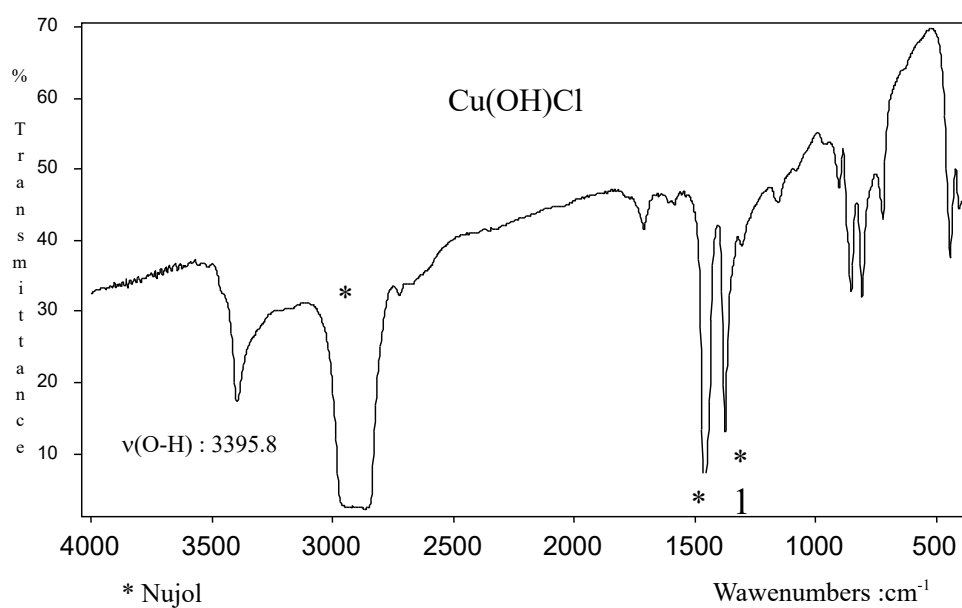
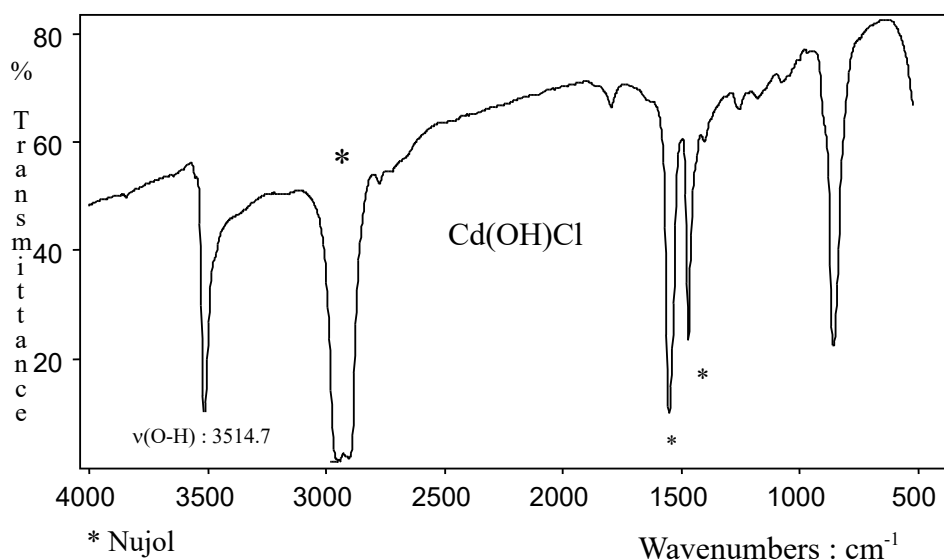
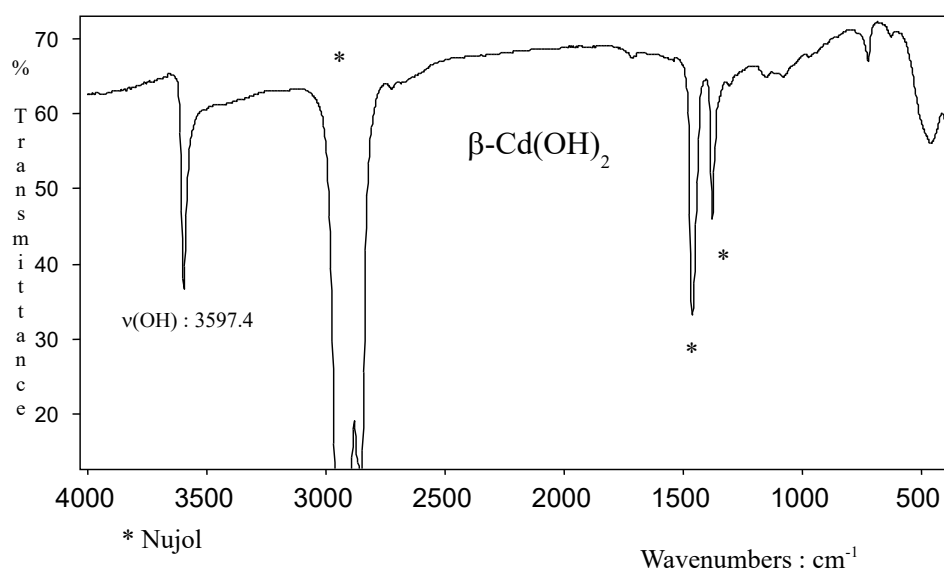


FIG. 5. IR spectra of β -Cd(OH)₂ , Cd(OH)Cl, and Cu(OH)Cl.