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Article

Cu^{II} Hydroxy Salts: Characterization of Layered Compounds by Vibrational Spectroscopy

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Hidroxo-sais lamelares de composição $Cu_2(OH)_3X$ ($X = NO_3^-$, CH_3COO^- e ClO_4^-) foram sintetizados através da coprecipitação (sais básicos de nitrato e acetato) e da troca iônica (sal básico de perclorato). Os sólidos cristalinos foram caracterizados por difratometria de raios X, análise termogravimétrica e espectroscopia vibracional. Bandas fracas em 336 e 345 cm^{-1} (espectro Raman) dos sais de nitrato e perclorato, respectivamente, foram tentativamente atribuídas ao νCu-O (ânion). Os ions nitrato possuem simetria C_{2v} no composto $Cu_2(OH)_3NO_3$ e, consequentemente, observa-se o desdobramento dos modos E'. A quebra da degenerescência também é observada nos modos F_2 do íon ClO_4^- livre, ocasionando o desdobramento das bandas em 630 e 1100 cm^{-1} no espectro do hidroxo-perclorato de cobre(II). A pequena diferença de energia entre os modos ν_{as}C-O e ν_sC-O (Δ=143 cm^{-1}) do sal de acetato sugere a presença de ligação de hidrogênio entre o oxigênio não coordenado do grupo carboxilato e um íon hidroxila adjacente. Os íons nitrato, acetato e perclorato estão coordenados ao cobre(II) de modo monodentado.

Copper hydroxy salts with a layer-type structure and general composition $Cu_2(OH)_3X$ ($X = NO_3^-$, CH_3COO^- and ClO_4^-) were synthesized by co-precipitation (nitrate and acetate salts) and ion exchange (perchlorate salt) methods. The isolated polycrystalline solids were characterized by X-ray diffractometry, thermogravimetric analysis and vibrational spectroscopy. A weak band at 336 and 345 cm^{-1} (Raman spectrum) of the nitrate and perchlorate salts, respectively, was tentatively assigned to the nCu-O (anion). In $Cu_2(OH)_3NO_3$ the nitrate ion has a C_{2v} symmetry and, accordingly, a splitting in the E' modes is observed. The same happens to the hydroxy perchlorate salt with the degeneracy breakdown of the F_2 modes (free ClO_4^-) at 630 and 1100 cm^{-1} leading to band splitting. For the carboxylate salt, the small difference in the energy of ν_{as}C-O and ν_sC-O (Δ=143 cm^{-1}) suggests that hydrogen bonding with neighbor OH group may be present. Nitrate, carboxylate and perchlorate are monocoordinated to copper(II) in the investigated salts.

Keywords: copper hydroxy salts, copper hydroxy nitrate, copper hydroxy acetate, layered hydroxy salts, botallakite-type compounds, Raman spectroscopy

Introduction

In recent years an increasing interest on transition metals hydroxy salts with layer-type structure and general composition $[M^{II}_2(OH)_{3(1-y)/n}]A^{n-}_{(1+3y)/n}\cdot mH_2O$ has been observed.[1] Several investigated compounds present ionic-exchange capabilities, *i.e.*, undergo topotatic reactions leading to the replacement of the A^{n-} anions coordinated to the metal by carboxylate,[2-4] sulfonate[3] and phosphonate ions.[3] Layered inorganic-organic hybrid materials of composition $M_2(OH)_3X$ (M = Cu or Co; X = organic anion) have shown very interesting magnetic properties since the ferromagnetic interaction is dependent on the interlayer distance imposed by the intercalated anion carbon chain.[5] These compounds are also very promising in nanocomposites preparation as observed, for example, in the improvement of mechanical and/or thermal stability of a polymer in which a nanoscopically sized lamellar hydroxy salt was dispersed.[6]

Layer-type hydroxy salts can be seen as divalent metal hydroxide derivatives in which some OH$^-$ ions are replaced by Cl$^-$, Br$^-$, NO_3^- or SO_4^{2-}.[7] They present the CdI_2 structure, with the cations occupying the interstices of octahedral $M(OH)_6$ units bound by the edges as shown in Figure 1a. The extension of OH$^-$ replacement varies significantly, leading to both stoichiometric and non-stoichiometric solid compounds. Examples of the former class can be found in nature as for example in minerals such as

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gerhardtite ($Cu_2(OH)_3NO_3$),[8] botallackite ($Cu_2(OH)_3Cl$),[9] langite ($Cu_4(OH)_6SO_4.2H_2O$)[10] and posnjakite ($Cu_4(OH)_6SO_4.H_2O$).[11]

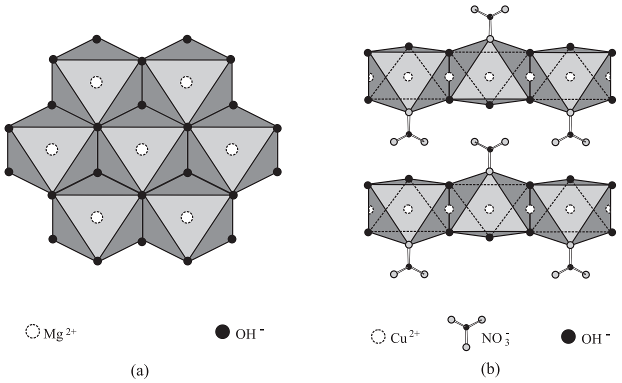

Figure 1. Schematic representations of (a) magnesium hydroxide layer (brucite), showing [$Mg(OH)_6$] octahedral units sharing edges; (b) layered structure of adjacent $Cu_2(OH)_3NO_3$ layers, where ¼ of the anionic sites are occupied by nitrate ions.

Among them, gerhardtite deserves special attention since its synthetic analog is being used in vehicle airbags.[6] Furthermore, it is considered as precursor in the preparation of CuO used as catalyst[12] and, recently, in the synthesis of one-dimensional lined up $Cu(OH)_2$ nanorods.[13]

Synthetic gerhardtite can be prepared through the direct reaction of $Cu(NO_3)_2$ and NaOH aqueous solutions[12] or by the digestion of CuO in $Cu(NO_3)_2$ concentrated aqueous solution.[14,15] The synthesis of Cu^{II} hydroxy nitrate requires very strict control of the experimental variables, especially pH, temperature and reagent concentration, in order to avoid the formation of $Cu(OH)_2$ and/or CuO.

The chemical properties presented by such layered compounds depend critically on the anions incorporated in the inorganic matrix and how they are interacting with the metal centers.[16] Hence the investigation of such properties demands techniques that are sensitive to the environment in the cation vicinity, as vibrational spectroscopy and X-ray diffraction.

The spectroscopic behavior of the anions in the interlayer environment reflects changes in symmetry upon coordination (or grafting) to the metal centers. A good example is the perchlorate ion since its T_d symmetry is lowered to C_{3v} and C_{2v} when coordinated by one or two oxygen atoms, respectively and the type of coordination can be followed by vibrational spectroscopy as a degeneracy breakdown of the F_2 modes. Thus the triply degenerated F_2 modes (T_d symmetry) split into two or three bands according to the new symmetry (C_{3v} and C_{2v} symmetry, respectively) and, therefore, according to the type of coordination.[17]

Raman spectroscopy is particularly attractive in the investigation of the layer-type compounds here reported, as the matrix contribution is less significant than in the FTIR spectrum, due to the small Raman cross section presented by OH vibrations.[18] Nevertheless, only a few studies report the use of Raman spectroscopy in the characterization of intercalated species.[16] Carbonate, nitrate and carboxylate intercalated in layered double hydroxide were studied without the interference of neither adsorbed/trapped water molecules nor OH vibrations.[19]

In the present work, the layered materials with general composition $Cu_2(OH)_3X$ ($X = NO_3^-$, CH_3COO^- and ClO_4^-) were synthesized by co-precipitation (nitrate and acetate salts) and ion exchange (perchlorate salt). The isolated materials were characterized by X-ray diffraction and thermogravimetry (except perchlorate) and the results are in full agreement with the literature.[2,3,4,20] FTIR data are available in previously reported studies[3,21,22] but, as far as the authors are concerned, Raman spectroscopy was only employed in one investigation of natural gerhardtite[23] and copper hydroxy perchlorate was not characterized by vibrational spectroscopy before.

This work aims to explore the complementary information obtained from Raman and FTIR spectroscopies, contributing to the understanding of the type of coordination of nitrate, carboxylate and perchlorate in the copper hydroxy salt structure.

Experimental

$Cu(OH)_3NO_3$ synthesis

$Cu(OH)_3NO_3$ was synthesized according to the literature.[12] A $Cu(NO_3)_2$ (Aldrich) aqueous solution with concentration 0.10 mol L^{-1} (determined by electrogravimetry) was slowly added under stirring to 10.0 mL of a 0.195 mol L^{-1} NaOH (Merck) aqueous solution, until a 1.5 OH^-/Cu^{2+} molar ratio. The bluish-green solid was isolated by filtration, washed with deionized water and dried under vacuum in a dissecator containing silica gel as drying agent.

$Cu_2(OH)_3Ac$ synthesis

Cu^{II} hydroxy acetate was synthesized according to a method already described in the literature.[20] An aqueous 0.10 mol L^{-1} NaOH solution was added dropwise and under stirring to an aqueous 0.10 mol L^{-1} Cu^{II} acetate (Aldrich) solution, until a OH^-/Cu^{2+} molar ratio of 1. The bluish-green solid was filtered, washed with deionized water and vacuum dried in a dissecator containing silica gel as drying agent.

$Cu_2(OH)_3ClO_4$ synthesis

Cu^{II} hydroxy perchlorate was prepared through an ionic exchange reaction. $Cu_2(OH)_3NO_3$ (100 mg) was suspended in 25 mL of 1.0 mol L^{-1} $NaClO_4.H_2O$ (Synth) aqueous solution and kept under stirring at room temperature for 8 days. The bluish-green solid was filtered, washed with deionized water and dried under *vacuum* in a dissecator containing silica gel as drying agent.

Instrumentation

Elemental analysis (C, H, N) was carried out in a Perkin Elmer mod. 2400 equipment. X-ray powder diffraction data (XRPD) were obtained in Rigaku diffractometer mod. Miniflex, using the Cu K_α radiation (1.541Å, 30 kV and 15 mA) and Ni filter. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 instrument under N_2 (flow rate = 30 mL min^{-1}) and a heating rate of 10 °C min^{-1} up to 900 °C. FTIR spectra were recorded from the samples diluted with KBr in the 400-4000 cm^{-1} range, with a Bomem MB-102 spectrometer, using a DRIFT accessory (Pike Technologies). The Raman spectra were obtained in Renishaw Raman Microscope (System 3000), fitted with an Olympus metallurgical microscope (BH2-UMA) and a CCD camera (Wright, 600x400 pixels); the 632.8 nm line of a He-Ne laser (Spectra Physics, mod. 127) was used and the laser power at the sample was kept below 0.4 mW in order to avoid thermal or photochemical degradation.

Results and Discussion

Mineral gerhardtite, $Cu_2(OH)_3NO_3$, has an orthorhombic cell (a = 6.087(2), b = 13.813(4), c = 5.597(2) Å)[8] but the synthetic copper hydroxy nitrate is obtained as a monoclinic metastable phase. In both polymorph structures, Cu(II) ions are in distorted octahedral sites in the layers and it is possible to distinguish two metal centers. In one site copper ions are coordinated to four hydroxide ions in the equatorial positions and to two more distant nitrate ions in the axial positions while in the other metal site copper ions are coordinated to four hydroxide ions in the equatorial positions and to one nitrate and one hydroxide ion in the more distant axial positions, as shown in Figure 1b.[8] These distorted octahedral arrangements of [4+2] and [4+1+1] types are examples of Jahn-Teller distortions related to the $3d^9$ configuration of copper(II). Oxygen atoms in the lamellae are in distorted tetrahedral sites bounded to three copper ions (μ_3-OH) and one hydrogen atom or to three metal ions and one oxygen atom from NO_3^- anion. Nitrate ligand is bounded to three copper ions (μ_3-ONO_2) and in a perpendicular orientation related to the brucite-like layer.

XRPD patterns shown in Figure 2 reveal that the three synthesized copper(II) hydroxy salts are crystalline solids free of CuO and/or $Cu(OH)_2$ crystalline phases. Copper(II) hydroxy nitrate X-ray diffraction pattern is in agreement with the synthetic $Cu(OH)_3NO_3$ monoclinic phase (d_{001}= 6.81 Å and d_{002}= 3.43 Å).[24]

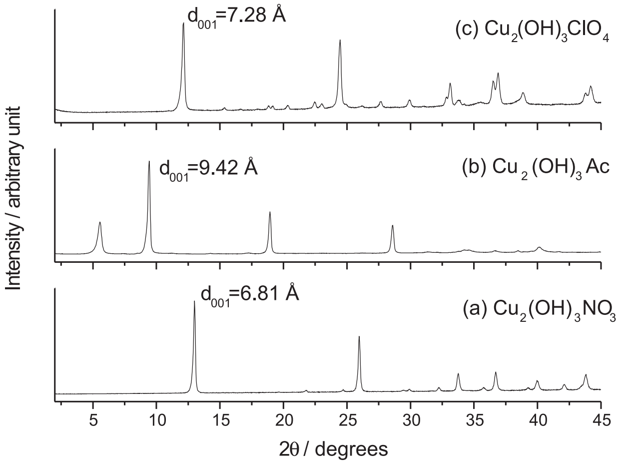

Figure 2. XRD patterns of: (a) copper hydroxy nitrate; (b) copper hydroxy acetate; (c) copper hydroxy perchlorate.

Copper(II) hydroxy acetate sample shows basal diffraction peaks at d_{001}= 9.42 Å, d_{002}= 4.69 Å and d_{003}= 3.12 Å, as reported in the literature for $Cu_2(OH)_3Ac.H_2O$.[2,3,4] The crystal structure analysis of copper basic acetate on a single crystal was not carried out up to now. However, Masciocchi *et al.*[22] have done the *ab initio* XRPD structure determination of the metal basic acetate and proposed the doubling of the *c* axis (*i.e.*, $c = 2 \times 9.33$ Å). The authors also reported that the basal spacing decreases to d = 7.22 Å for the anhydrous phase. Some authors observed an extra diffraction peak corresponding to a spacing of 15.5-16 Å in the XRPD patterns of $Cu_2(OH)_3Ac.H_2O$ that they assigned to a phase with a hydration degree higher than one.[4,22] In Figure 2, it is possible to observe a peak at $2\theta = 5.55^o$ (d = 16.2 Å). As it will be discussed ahead, the hydroxy acetate salt isolated in this work does not have a hydration degree higher than one. The appearance of the extra peak deserves a more detailed study in future works since other interpretation can be proposed besides hydration. Coincidentally, the sum of the basal spacing of monohydrated and anhydrous $Cu_2(OH)_3Ac$ phases is about 16 Å.

Copper hydroxy perchlorate was obtained by ion exchange using the nitrate salt as precursor. XRPD pattern shows the absence of peaks related to the precursor phase (Figure 2), indicating that ion exchange reaction was practically complete. The basal spacing increases from 6.81 Å to 7.28 Å when nitrate (thermochemical radii = 1.65 Å) is replaced by the larger perchlorate anion (thermochemical radii = 2.26 Å).[25] One work describes the preparation of the copper basic perchlorate salt using the layered acetate salt as precursor.[2] According to the authors, the isolated material has a basal spacing of 7.34 Å and composition $Cu_7(OH)_{12}(ClO_4)_2$ (or $Cu_2(OH)_{3.43}(ClO_4)_{0.57}$), suggesting that hydroxide and perchlorate anions are randomly distributed in the layer coordination sites.

Figure 3 shows the thermogravimetric curves (TGA and DTG) for copper(II) hydroxy nitrate and acetate under nitrogen atmosphere. The hydroxy nitrate salt is an anhydrous compound that undergoes decomposition in one step producing CuO according to the chemical equation:[14]

$$4\ Cu_2(OH)_3NO_{3(s)} \rightarrow 8\ CuO_{(s)} + 4\ NO_{2(g)} + O_{2(g)} + 6\ H_2O_{(g)}$$

Considering the TGA curve shown in Figure 3, copper(II) basic nitrate loses 33.6 wt.%, a very close value to the expected one (33.8%).

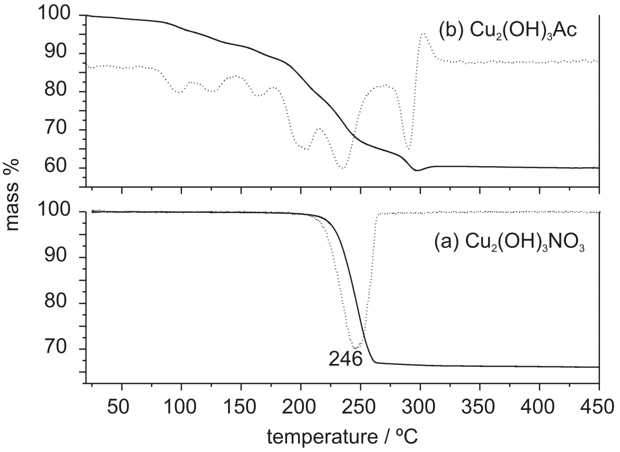

Figure 3. TGA (full lines) and DTG (dashed lines) profiles in nitrogen atmosphere for: (a) copper hydroxy nitrate; (b) copper hydroxy acetate.

Analyzing the gases evolved in the thermal composition of copper(II) hydroxy acetate, Newman and Jones[3] detected the water release below 140 °C and, at higher temperatures, acetic acid. Considering these data, it is here proposed that the sample isolated in this work loses interlayer water in two steps up to 145 °C (7.7 wt.%) and undergoes decomposition after this temperature according to the chemical equation:

$$Cu_2(OH)_3CH_3COO_{(s)} \rightarrow 2\ CuO_{(s)} + CH_3COOH_{(g)} + H_2O_{(g)}$$

Hence, the sample loses 32.3 wt.% in the temperature range 145-450 °C, while the expected valor for acetic acid and water liberation is 32.9 wt.%. Hence, XRPD patterns and thermogravimetric data confirm that the copper(II) hydroxy salts were isolated in this work with the structure and composition expected.

FTIR and Raman spectra of $Cu_2(OH)_3NO_3$ are shown in Figure 4 and the respective band positions are reported in Table 1. The Raman spectrum is in agreement with a previously reported study of natural gerhardtite.[23] The FTIR spectrum was not recorded below 600 cm^{-1} but in the Raman spectrum, the relatively weak modes at 258, 408, 455 and 505 are also observed in the spectrum of natural gerhardtite reported by Frost *et al.*[23] (258, 410, 458 and 503 cm^{-1}) and in the FTIR data for another copper basic nitrate (255, 427, 455 and 510 cm^{-1}).[21] However, the authors of these papers do not agree on the band assignment as the 258 cm^{-1} mode was assigned by Frost *et al.*[23] to a lattice vibration and by Secco and Worth to a O-H torsion; the remaining three bands were assigned in reference 23 to O-H deformation modes of the $Cu(OH)_3$ units, whereas in reference 21 these bands are described as arising from NO_3^- external modes.

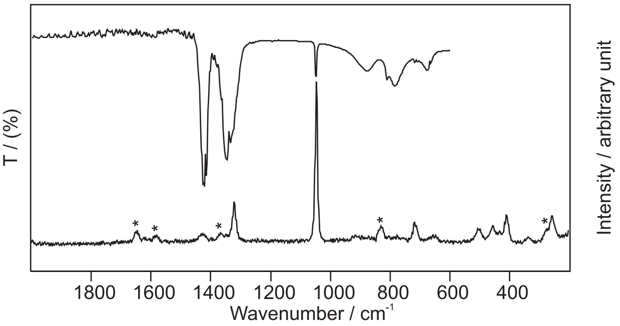

Figure 4. FTIR and Raman spectra of $Cu_2(OH)_3NO_3$. Asterisks: laser plasma lines.

Table 1. Vibrational spectroscopic data of hydroxy nitrate copper(II)

Raman	FTIR	Tentative assignment[a,b]
336 (w)	-	Cu-O-NO_2 stretching
-	675 (w,br)	Cu-O-H deformation
709	708 (vw)	ONO_2^- out-of-plane deformation (ν_5)
717 (w)	718 (vw)	ONO_2^- out-of-plane deformation (ν_3)
-	784 (m,br)	Cu-O-H deformation
-	810 (w)	ONO_2^- out-of-plane deformation (ν_6)
-	878 (m)	Cu-O-H deformation
1045 (s)	1049 (m)	ONO_2^- stretching (ν_1)
1319 (m)	-	ONO_2^- stretching (ν_2)
-	1325 (s)	ONO_2^- stretching (ν_2)
-	1334 (s)	ONO_2^- stretching (ν_2)
-	1346 (s)	ONO_2^- stretching (ν_2)
1365 (w)	1352 (sh)	ONO_2^- stretching (ν_2)
-	1415 (s)	ONO_2^- stretching (ν_4)
1427 (br)	1427 (s)	ONO_2^- stretching (ν_4)
-	1432 (sh)	ONO_2^- stretching (ν_4)

[a]reference 17; [b]reference 21.

A weaker Raman band is observed at 336 cm^{-1} and is here assigned to the Cu-ONO$_2$ stretching vibration; in natural gerhardtite,[23] this band shows up at 336 cm^{-1} and is reported as arising from a O-H—O hydrogen bond vibration. A relatively intense band is observed at 328 cm^{-1} in the FTIR spectrum of $Cu_4(OH)_6(NO_3)_2$ and was assigned as a Cu-O stretching vibration[21] but it is not clear whether the oxygen atom belongs to a OH$^-$ or NO_3^- group. Further search in the literature revealed a vibrational study of the $CuNO_3^+$ ion in acetone solution in which a polarized band at 335 cm^{-1} was assigned to the Cu-ONO$_2$ stretching vibration,[26] thus reinforcing the assignment here reported.

Of special interest are the modes relate to NO_3^- vibrations as they reveal the actual ion symmetry. In the free state, this four atom ion belongs to the molecular point group D_{3h} with irreducible representation for the internal modes $\Gamma = A'_1 + A''_2 + 2E'$, originating 4 normal modes ν_1, ν_2, ν_3 and ν_4. When the ion symmetry is lowered to C_{2v} or C_s the degeneracies of the E' representations are removed and splitting of the originally degenerade modes is observed. Accordingly, ν_1 (*ca.* 1050 cm^{-1}) mode is only Raman active, ν_2 (*ca.* 890 cm^{-1}) is only IR active whereas ν_3 (*ca.* 1370 cm^{-1}) and ν_4 (*ca.* 690 cm^{-1}) are observed both in Raman and IR spectrum. X-ray diffraction data[8] indicates that nitrate is monocoordinated to copper causing a lowering in its symmetry (from D_{3h} to C_{2v}) and, as a consequence, a breakdown in the degeneracy of the E' modes (ν_3 and ν_4).

As shown in Figure 4, there is a clear splitting of the ν_3 mode, with bands showing up at 1335, 1346, 1416 and 1421 cm^{-1}. It is expected that the larger the interaction between NO_3^- ion and the inorganic matrix, the larger the band splitting. The observed splitting (86 cm^{-1}) indicates that the interaction is weak (Δ = 187 cm^{-1} in the case of $CuNO_3^+$ and Δ = 74 cm^{-1} for $[Cu(H_2O)_6]^{2+}$),[26] what could suggest that the nitrate ion can be only intercalated and not coordinated (grafted) in the lamellae. However, it has to be considered that (*i*) TGA curves do not show water release; (*ii*) previously reported X-ray data shows that NO_3^- is grafted, not intercalated as free anion and (*iii*) NO_3^- coordination occurs in the axial position, which is longer than the equatorial ones (mean value: 2.40 Å).[8]

A similar effect is expected for the ν_4 mode, but such splitting is not evident from the Raman and IR spectrum of $Cu_2(OH)_3NO_3$; the same is observed in other studies in the literature.[21,26] A broad band centered at 660 cm^{-1} and a sharp band at 717 cm^{-1} are observed in the ν_4 mode region (Raman spectrum) and can be considered as good candidates for the two components. This assumption is not straightforward since in the 670 cm^{-1} region a Cu-O-H deformation mode is expected, as demonstrated by Secco and Worth who observed a band at 675 cm^{-1} together with the ν_2 mode of CO_2 at 667 cm^{-1} in a study involving another basic copper nitrate. As it will be discussed below, a comparison of the IR and Raman spectra of the nitrate and perchlorate copper hydroxy derivative gives support to the assignment here proposed.

In the IR spectrum in Figure 4 a sharp band is clearly observed at 1049 cm^{-1} (ν_1) thus confirming the degeneracy removal as this band is not IR active under D_{3h} symmetry. The ν_2 mode is not observed in the Raman spectrum, however, it has to be emphasized that in the same region an artifact is present in the spectrum.

Summing up, the vibrational spectra clearly show that nitrate coordinates to copper through a relatively weak interaction which do not support bidentate coordination as, in this case, the splitting of the ν_3 mode would be much larger than observed.

Previous X-ray diffraction patterns (Figure 2) showed that the copper hydroxide crystalline structure is preserved when nitrate is replaced by acetate and perchlorate, thus permitting the discussion of the vibrational spectra of these salts to be focused on the CH_3COO^- and ClO_4^- bands.

FTIR and Raman spectra of $Cu_2(OH)_3Ac.H_2O$ are shown in Figure 5. In the case of carboxylates, it is believed that an increase in ν_{as} and Δ (ν_{as} - ν_s) occurs when the C-O bonds are no equivalent, as expected in monodentate coordination. This is not always true[27] and, particularly, in some cases where Δ is less than 200 cm^{-1}, this behavior has been linked to the existence of hydrogen bond between the non-coordinated oxygen atom and water or other ligand.

Table 2 presents the vibrational spectra data obtained from the basic copper carboxylate compound. The FTIR spectrum is in full agreement with a previously reported data,[22] with the carboxylate bands showing up at 1408 cm^{-1} and 1551 cm^{-1} (Δ=143 cm^{-1}). The observed difference seems too small for a monodentate coordination, however, *ab initio* XRPD structure determination showed that the carboxylate ions coordinates to copper by only one oxygen atom[22] and, in the same study, the authors suggested the presence of hydrogen bond between the free oxygen in the grafted carboxylate and a neighbor hydroxyl group, explaining the low Δ found. The low frequency region in the Raman spectrum presents bands from the copper hydroxide matrix and acetate ion (Table 2) but it was not possible to identify the νCu-O.

The Raman and IR spectra of the basic copper perchlorate salt are shown in Figure 6 and the frequencies listed in Table 3. As already discussed in the case of the nitrate salt, FTIR spectrum showing that there is no water and the presence of a band in the low frequency region (below 400 cm^{-1}) in the Raman spectrum that can be

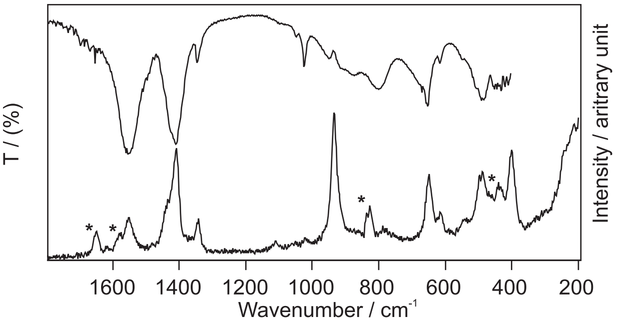

Figure 5. FTIR and Raman spectra of $Cu_2(OH)_3Ac$. Asterisks: laser plasma lines.

Table 2. Vibrational spectroscopic data of hydroxy acetate copper(II)

RAMAN	FTIR	Tentative assignment[a,b]
402 (s)		$Cu(OH)_3$ deformation
490 (m)	485 (m)	$Cu(OH)_3$ deformation
614 (w)	615 (w)	COO π deformation
650 (m)	654 (m)	OCO angular deformation
	680 (sh,br)	Cu-O-H deformation
	875 (w,br)	Cu-O-H deformation
1408 (s)	1411 (s)	ν_sCOO
	1424 (sh)	ν_sCOO
1551 (w)	1554 (br)	ν_{as} COO
1578 (w)		ν_{as} COO

[a]reference 21; [b]reference 22.

assigned to a Cu-O (anion) stretching are strong indications that the ion is grafted in the lamellae and not intercalated as free anion.

In the low frequency region of the Raman spectrum shown in Figure 6, three bands are observed at 235, 300 and 345 cm^{-1} which can not be assigned to free perchlorate modes or to copper hydroxide lattice vibrations. A study of ClO_4^- adsorption on copper electrode has shown that the Cu-O vibration shows up at 302 cm^{-1} as a weak band.[28] In the same work, the authors found that pure electrostatic interaction leads to a Cu-O stretching band at 177 cm^{-1}. It is reasonable to assume that coordination to copper in the hydroxide matrix is a stronger interaction than adsorption and, considering the three bands cited above, it also seems reasonable to assign the weak 345 cm^{-1} band to the Cu-O (perchlorate) vibration. Such frequency compares well in terms of position and intensity to the weak band at 336 cm^{-1}, present in the Raman spectrum of the nitrate salt, which is assigned in this study to the Cu-O (nitrate) vibration.

Table 3. Vibrational spectroscopic data of hydroxy perchlorate copper(II)

RAMAN	FTIR	Tentative assignment[a,b]
346 (w)	355 (m)	$Cu\text{-}O\text{-}ClO_3$ stretching
	436 (m)	$O\text{-}ClO_3^-$ (ν_6)
619 (m)	616 (m)	$OClO_3^-$ bending (ν_3)
	743 (m)	$OClO_3^-$ bending (ν_5)
927 (s)	928 (w)	ClO_4^- stretching (ν_1)
1054 w		ClO_4^- stretching (ν_2)
	1084 (s)	ClO_4^- (ν_2)
1100 (vw,br)	1111 (s)	ClO_4^- (ν_4)
1145 (vw,br)		ClO_4^- (ν_4)

[a]reference 17; [b]reference 28.

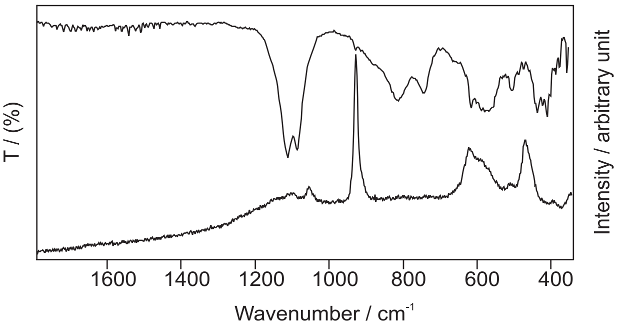

Figure 6. FTIR and Raman spectra of $Cu_2(OH)_3ClO_4$.

The ClO_4^- bands can provide very useful information concerning whether the perchlorate is inserted in a monodentate or bidentate arrangement. The free ion present T_d symmetry, which is lowered to C_{3v} when coordination occurs by one oxygen atom or to C_{2v} symmetry when coordination proceeds through two oxygen atoms. Under T_d symmetry, the four normal modes expected for ClO_4^- are $\nu_1(A_1)$ at *ca.* 935 cm^{-1}, ν_2(E) at *ca.* 460 cm^{-1}, $\nu_3(F_2)$ at *ca.* 1100 cm^{-1} and $\nu_4(F_2)$ at *ca.* 630 cm^{-1};[17] all of them are Raman active and only the two F_2 modes (triply degenerate) are IR active. Analyzing the Raman and IR spectra at *ca.* 630 cm^{-1} and 1100 cm^{-1} a band splitting is clearly observed, however, due to the band broadness of these modes it is not possible to state that the splitting led to two or three bands in the case of mono or bidentate coordination, respectively. However, it has been shown[28] that the ν_1 mode is also sensitive to the type of coordination with the C_{3v} symmetry causing a downshift to 930 cm^{-1}, whereas under C_{2v} symmetry such band shows up at 917 cm^{-1}. The ClO_4^- ν_1 band, as shown in Figure 6, appears at 928 cm^{-1} indicating a C_{3v} coordination, however, a broadening at the lower wavenumber side of such band can suggest that a small contribution from bidentate coordination can also be present.

Conclusions

Complementary information from Raman and IR spectroscopies was used in the characterization of basic copper nitrate, acetate and perchlorate salts. In such compounds, the anions are monocoordinated to copper and a tentative assignment for the Cu-O (salt) stretching vibration was proposed in the case of nitrate and perchlorate. Splitting of degenerade modes were also used to assess the actual ion symmetry in the basic copper salt, which is lowered from D_{3h} to C_{2v} symmetry (nitrate) and from T_d to C_{3v} symmetry (ClO_4^-).

The presence of water was not detected from the FTIR spectra, except for the carboxylate copper salt, in agreement with TGA information.

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