

Synthesis and anion exchange reactions of a layered copper–zinc hydroxy double salt, $\text{Cu}_{1.6}\text{Zn}_{0.4}(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$

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Abstract. A mixed-metal hydroxysalt of formula $\text{Cu}_{1.6}\text{Zn}_{0.4}(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$ has been synthesized by an acetate hydrolysis route. Acetate ions can be exchanged with simple inorganic anions such as chloride and nitrate, and organic anions such as benzoate and large surfactant anions such as dodecyl sulphate. Structures of these hydroxysalts are derived from that of $\text{Cu}_2(\text{OH})_3\text{NO}_3\cdot\text{H}_2\text{O}$ with some of the Cu^{2+} ions being replaced by Zn^{2+} .

Keywords. Copper–zinc hydroxides; Cu–Zn hydroxysalts; anion exchange.

1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays, consist of positively charged layers and charge-compensating anions loosely held in the interlayer region. These solids exhibit unique interlayer chemistry and hence find applications in varied fields such as sorption, catalysis, electrochemistry and photochemistry to cite a few.¹ These solids undergo anion exchange reactions to yield a variety of functional materials and composites.²

Layered hydroxysalts are structurally and functionally related to LDHs closely and may also be brought under the classification of anionic clays.³ These can be broadly separated into two structural types, based on the structure of either zinc hydroxynitrate⁴ with the formula $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ or copper hydroxynitrate^{5,6} with the formula $\text{Cu}_2(\text{OH})_3\text{NO}_3\cdot\text{H}_2\text{O}$. In $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$, a quarter of the octahedral sites in the brucitic layers are vacant and Zn^{2+} ions occupy the tetrahedral sites on either side of the vacant octahedral sites making the layers positively charged with the composition $[\text{Zn}_3\Box\text{Zn}'_2(\text{OH})_8]^{2+}$, where Zn is in an octahedral site, \Box is an octahedral vacancy and Zn' is in a tetrahedral site.⁴ The tetrahedral coordination of Zn^{2+} ion is satisfied by three hydroxyl ions of the brucitic layer and a water molecule. The positive charge of the layer is compensated for by

incorporating anions in the interlayer region. In $\text{Cu}_2(\text{OH})_3\text{NO}_3\cdot\text{H}_2\text{O}$ and related systems such as $\text{Ni}_2(\text{OH})_3(\text{NO}_3)\cdot\text{H}_2\text{O}$ the brucitic layers are not positively charged as in the case of zinc hydroxynitrate. Here 25% of the OH⁻ ions of the $\text{M}(\text{OH})_2$ layers are replaced by NO_3^- ions which are coordinated directly to the metal matrix.^{7,8}

Hydroxy double salts are hydroxysalts of the above-mentioned types containing two different metal ions. A number of hydroxy double salts of the zinc hydroxynitrate type have been studied in the past.^{9,10} These solids have been shown to exhibit anion exchange behaviour similar to that of hydrotalcites. In the past attempts have been made to prepare copper zinc hydroxy double salts but these materials have not been well characterised.¹⁰ Recently, Xue *et al*¹¹ have reported the synthesis of ktenasite, a copper zinc hydroxysulphate, which is formulated as $[\text{Cu}_{3.88}\text{Zn}_{0.78}(\text{OH})_{6.32}(\text{SO}_4)_2][\text{Zn}(\text{H}_2\text{O})_6]_{0.5}\cdot 0.24\text{H}_2\text{O}$. This compound comprises copper hydroxysalt-like layers of the composition $[\text{Cu}_{3.88}\text{Zn}_{0.78}(\text{OH})_{6.32}(\text{SO}_4)_2]^-$ in which copper and zinc atoms occupy octahedral sites and the sulphate ions are grafted into the layer. To compensate for the negative charge on the layer, hydrated Zn^{2+} ions are incorporated into the interlayer region.

In this paper, we report the synthesis and anion exchange behaviour of copper zinc hydroxyacetate which derives its structure from that of $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ with one fifth of the Cu^{2+} ions isomorphously substituted by Zn^{2+} ions.

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2. Experimental

Cu–Zn hydroxy acetate is prepared by adding solid ZnO (0.033 moles) to 200 ml of an aqueous solution of cupric acetate (0.050 moles) with vigorous stirring followed by heating of the resultant mixture at 65°C for 2 days with occasional stirring. It should be noted that excessive or prolonged heating results in the formation of copper oxide. The pale blue solid obtained is washed free of ions with distilled water, followed by washing with anhydrous alcohol a few times, then filtered and dried in air at 65°C. The final alcohol washing is necessary to avoid dehydration leading to copper oxide during prolonged drying. Alternatively, the sample could be dried at room temperature under vacuum.

Interlayer acetate ions are replaced by various anions. About 200 mg of Cu–Zn hydroxyacetate is dispersed in 15 ml of 0.25 M aqueous solution of sodium salt of the anion, A^{n-} ($A^{n-} = \text{Cl}^-, \text{NO}_3^-, \text{C}_6\text{H}_5\text{COO}^-, \text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$) and stirred for 24 h at room temperature. The products are washed with deionised water followed by anhydrous alcohol and dried in air at 65°C.

The materials were characterized by powder X-ray diffraction (Siemens D5005, Bragg-Brentano $q-2q$ geometry, CuK_α radiation, 4° $2q$ per minute), infrared spectroscopy (Nicolet Model Impact 400D FT-IR spectrometer, KBr pellets, 4 cm^{-1} resolution) thermogravimetry (a lab-built system, heating rate 5°C per minute) and wet chemical analysis. Copper content was estimated gravimetrically using salicylaldehyde oxime. Zinc content was estimated by complexometric titration after removing copper by precipitating it out as its sulphide.

3. Results and discussion

The powder X-ray diffraction (PXRD) pattern of the Cu–Zn hydroxy acetate is shown in figure 1a. The pattern expanded in the $2q$ region 30–70 degrees is shown in the inset. The powder pattern is similar to that of $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ reported earlier by Yamanaka *et al*⁶ which implies that the layer structure is related to that of botallackite with the acetate ions being directly coordinated to the Cu^{2+} or Zn^{2+} ions. Reflections due to ZnO are completely absent suggesting that the Zn^{2+} ions are incorporated in the hydroxysalt structure. The basal spacing is 9.465 Å indicating that the structure is not related to that of ktenasite¹¹ whose basal spacing is 11.82 Å even with

sulphate, a shorter anion. The pattern could be indexed to a monoclinic cell (similar to copper hydroxyacetate) with the cell parameters $a = 5.536 \pm 0.002$ Å, $b = 6.141 \pm 0.005$ Å, $c = 9.447 \pm 0.004$ Å and $\beta = 94.46 \pm 0.03^\circ$. The nominal changes in the cell parameters reported for copper hydroxyacetate⁶ suggest partial incorporation of Zn^{2+} ions in place of Cu^{2+} ions.

Wet chemical analysis shows the composition as Cu = 39.6% and Zn = 10.3% leading to the nominal formula $\text{Cu}_{1.6}\text{Zn}_{0.4}(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$. EDXA results are in agreement with this formula. The $[\text{Zn}]/[\text{Cu}]$ ratio is 0.25 in the product and it is less than the $[\text{Zn}]/[\text{Cu}]$ ratio of the reaction mixture which is 0.66, indicating that the reaction is not stoichiometric unlike in the case of the nickel acetate–ZnO reaction.¹⁰ Attempts to increase the zinc content by starting with higher $[\text{ZnO}]/[\text{Cu}^{2+}]$ ratio were unsuccessful as the products turned black due to the formation of CuO.

IR spectra of copper–zinc hydroxyacetate (figure 2a) confirm the presence of acetate ions in the sample.

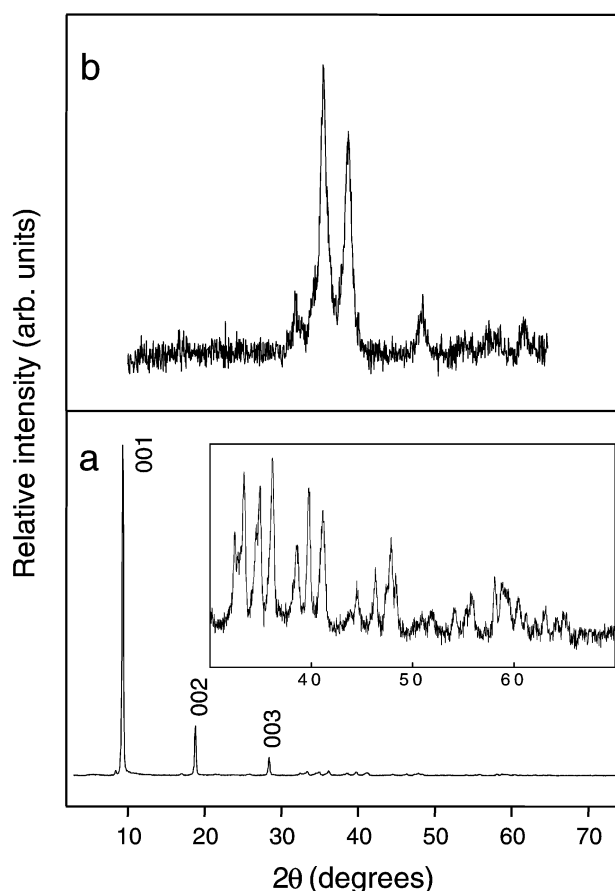


Figure 1. Powder XRD patterns of (a) copper–zinc hydroxyacetate and (b) its thermal decomposition product.

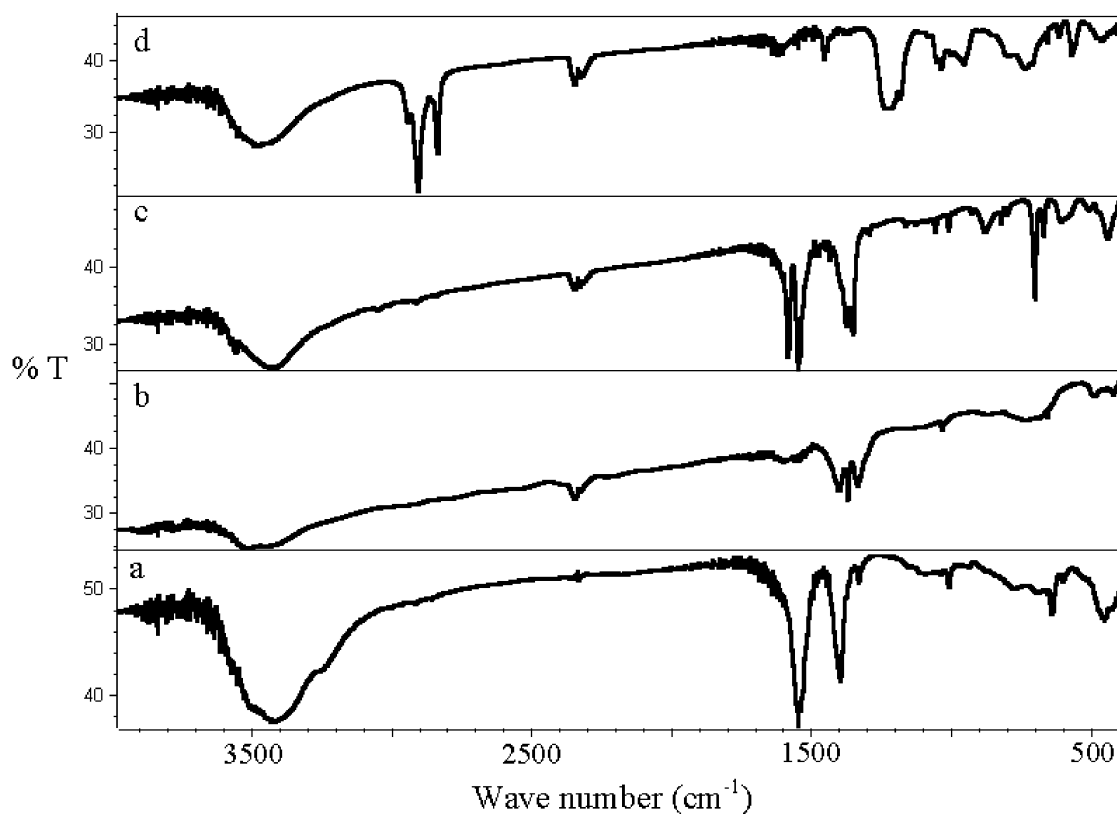


Figure 2. Infrared spectra of copper–zinc hydroxyacetate (a), and its anion-exchanged products obtained by exchanging with nitrate (b), benzoate (c) and dodecyl sulphate (d).

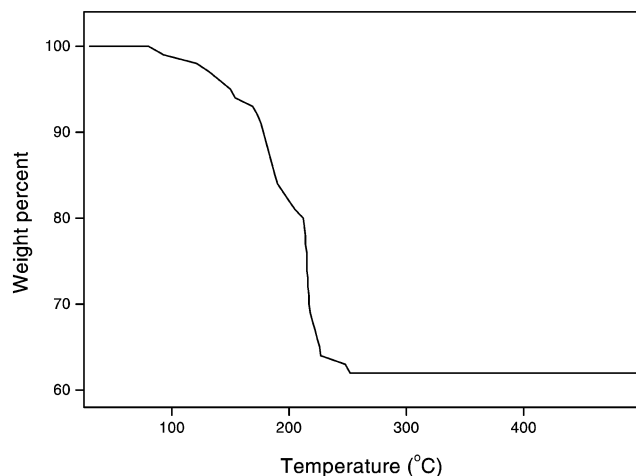


Figure 3. Thermogravimetry curve of copper–zinc hydroxyacetate.

The peaks at 1410 and 1550 cm^{-1} are due to the stretching vibrations of carboxylate ion and the strong and broad absorption at around 3500 cm^{-1} is due to the O–H stretching vibration of the hydroxyl groups of the brucitic layer and the intercalated water.

Thermogravimetric curves of copper–zinc hydroxyacetate (figure 3) show overlapping steps. The first loss ($\sim 7\%$) occurs in the range $80\text{--}170^\circ\text{C}$ and this corresponds to the loss of interlayer water molecules. The unresolved second and third losses observed in the range $170\text{--}250^\circ\text{C}$ are due to dehydroxylation and decomposition. The net loss observed is 38% , which matches with the proposed formula. The product formed upon decomposition gives a PXRD pattern (figure 1b) matching that of tenorite, while no peaks due to ZnO are observed. Possibly the oxide is a solid solution with Zn substituting a fraction of Cu atoms in the tenorite structure. Such solid solutions have been used as precursors for the syntheses of mixed metal phosphonates.¹²

The Cu–Zn hydroxyacetate exhibits anion exchange reactions. Different anions such as chloride, nitrate, benzoate and dodecyl sulphate (DS) may be exchanged for the acetate ions. The PXRD pattern shown in figure 4a indicates the incorporation of the smaller anion Cl^- with the interlayer spacing being 5.66 \AA . Figure 4b shows the PXRD pattern of nitrate-exchanged product with the interlayer spacing 6.99 \AA which

matches with that of $\text{Cu}_2(\text{OH})_3\text{NO}_3 \cdot \text{H}_2\text{O}$ reported in the literature.⁵ The d -spacing is 1.5 Å less than that of an LDH containing interlayer nitrate anions indicating that the NO_3^- anions are directly coordinated to the $\text{Cu}^{2+}/\text{Zn}^{2+}$ cations of the brucitic layers. The PXRD patterns of benzoate and DS exchanged products are shown in figure 4c and d respectively. Here the interlayer spacings are 15.5 and 29.8 Å respectively again, indicating direct grafting of the anion into the layers.

IR spectrum of the nitrate exchanged product shows that the NO_3^- group is grafted to the matrix cation. The observed bands suggest that the nitrate ion is of C_{2v} symmetry. Figure 2b shows absorption bands at 1424 and 1341 cm^{-1} , which are due to the asymmetric and symmetric NO_2 stretching and the absorption at 1052 cm^{-1} corresponds to N–O stretch of the unidentate O– NO_2 group.^{13,14} The sharp peak at 1380 cm^{-1} is due to free nitrate ions that are produced due to the interaction of the sample with KBr.¹⁵ In figure

2c we show the IR spectrum of the benzoate-exchanged product. The absorption bands around 1393 and 1595 cm^{-1} are due to the carboxylate ion and the absorptions at 1455 and 716 cm^{-1} are due to C=C skeletal in-plane vibration of the aromatic group and C–H bending vibration of a monosubstituted benzene ring respectively,¹⁶ thus confirming incorporation of the benzoate into the solid. In case of DS intercalated product (figure 2d) we observe absorptions at 2920 and 2850 cm^{-1} due to C–H stretching of the alkyl chain of DS and a band at 1260 cm^{-1} due to the sulphate group.¹⁷ In all these cases and also the chloride-exchanged product (not shown), acetate-related absorptions are totally absent confirming quantitative ion exchange.

4. Conclusions

Copper–zinc hydroxyacetate with partial isomorphous substitution of Zn^{2+} for Cu^{2+} ions are synthesized and its other anion analogues obtained through anion exchange reactions. All these solids derive their structures from that of $\text{Cu}_2(\text{OH})_3\text{NO}_3 \cdot \text{H}_2\text{O}$ with the anions grafted into the layers.

Acknowledgments

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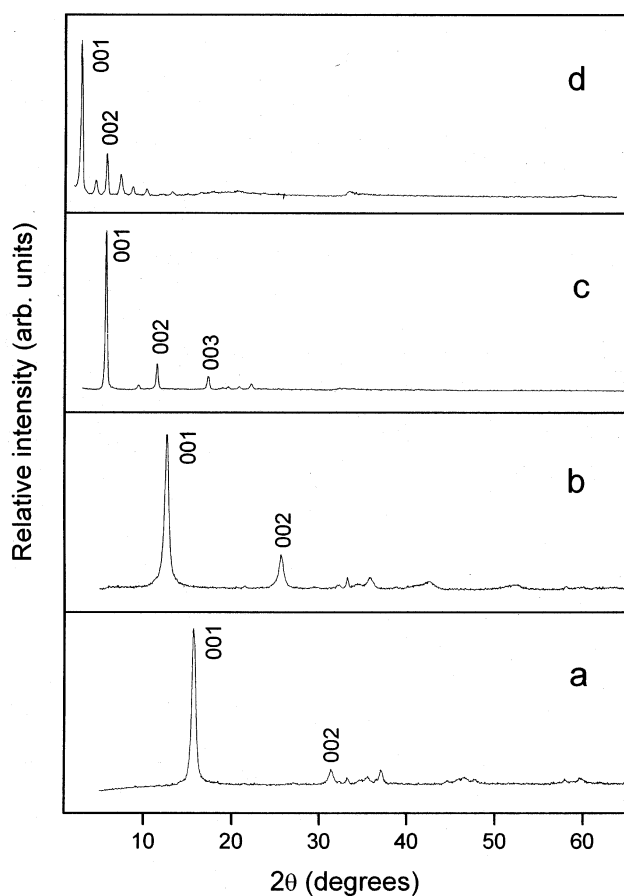


Figure 4. Powder XRD patterns of copper–zinc hydroxy-salt ion-exchanged with chloride (a), nitrate (b), benzoate (c) and dodecyl sulphate (d).

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