Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Journal of Solid State Chemistry 179 (2006) 49–55

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Synthesis, characterisation and anion exchange properties of copper, magnesium, zinc and nickel hydroxy nitrates

Timothy Biswick[a], William Jones[a,*], Aleksandra Pacuła[b], Ewa Serwicka[b]

[a]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[b]*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-329 Krakow, Poland*

Received 4 August 2005; received in revised form 23 September 2005; accepted 24 September 2005
Available online 26 October 2005

Abstract

Anion exchange reactions of four structurally related hydroxy salts, $Cu_2(OH)_3NO_3$, $Mg_2(OH)_3NO_3$, $Ni_2(OH)_3NO_3$ and $Zn_3(OH)_4(NO_3)_2$ are compared and trends rationalised in terms of the strength of the covalent bond between the nitrate group and the matrix cation. Powder X-ray diffraction (PXRD), Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and elemental analysis are used to characterise the materials. Replacement of the nitrate anions in the zinc and copper salts with benzoate anions is possible although exchange of the zinc salt is accompanied by modification of the layer structure from one where zinc is exclusively six-fold coordinated to a structure where there is both six- and four-fold zinc coordination. Magnesium and nickel hydroxy nitrates, on the other hand, hydrolyse to their respective metal hydroxides.

Keywords: Inorganic compounds; X-ray diffraction; Infrared spectroscopy; Thermogravimetric analysis

1. Introduction

Layered double hydroxides (LDHs) and hydroxy double salts (HDSs) form a family of inorganic layered solids attracting ever-increasing attention. The unique structural and physicochemical properties of these compounds render them excellent substrates for advanced materials design. Their reported applications include the preparation of anion exchangers, complex hybrid materials, and slow-releasing drug delivery agents [1–6]. The structures of both families of compounds may be considered as deriving from the layered lattice of brucite, ($Mg(OH)_2$). In the case of LDHs a layer charge develops as a result of partial substitution of divalent cations by trivalent, thereby necessitating the presence of charge balancing anions within the interlayer [1]. In HDSs, since the cation composition of the brucite-like layers is confined to cations of the same valency (usually divalent), the existence of potentially exchangeable anions may be created by two mechanisms. In the first, a surplus layer charge is created by the occurrence of octahedral vacant sites that are capped above and below by two tetrahedrally coordinated divalent cations [7]. In the second, whilst there is complete occupancy of octahedral cationic positions, part of the framework hydroxyl groups are substituted by structure forming anions (e.g. NO_3^- [2]).

Four zinc-containing layered HDSs with nitrate as the anion are known and are: $Zn_3(OH)_4(NO_3)_2$, $Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and its anhydrous form $Zn_5(OH)_8(NO_3)_2$. The structure of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ belongs to type IIb according to the classification of Louër et al. [8]. It consists of infinite brucite-like layers, where one-quarter of the octahedrally coordinated zinc atom sites are vacant and on either side of the empty octahedra there are Zn atoms tetrahedrally coordinated by OH groups (forming the base of a tetrahedron), with a water molecule occupying the apex. Unbound nitrate groups are located between the sheets [9]. In the anhydrous form, $Zn_5(OH)_8(NO_3)_2$, where the structure is classified as type IIa, the water molecules are now replaced by nitrate anions, also directly coordinated to zinc centres via M–O bonds [10]. The structure of $Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$ is similar to that of $Zn_5(OH)_8$

---

*Corresponding author. Fax: +44 1223 336 362.
E-mail address: wj10@cam.ac.uk (W. Jones).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.09.040

$(NO_3)_2 \cdot 2H_2O$ but with NH_3 replacing H_2O on the apex of the tetrahedral zinc atoms [11]. $Zn_3(OH)_4(NO_3)_2$ has a layer structure with fully occupied octahedral sites and as such represents type I of the Louër et al classification. Nitrate anions are then bonded directly to the layers by occupying two of the six coordination positions around each zinc atom, the other four positions being taken by hydroxyl groups [12].

The structure of $Cu_2(OH)_3NO_3$ has been determined by single-crystal XRD and may be described as having brucite-like $M(OH)_2$ layers in which one quarter of the OH anions are replaced by nitrate. The nitrate anion is coordinated, through one oxygen atom, to the matrix Cu^{2+} cation. The structure consists of layers linked by hydrogen bonding between NO_3^- and hydroxyl groups. The Cu^{2+} cations occupy two non-equivalent sites consisting of a distorted $5OH + O\text{–}NO_2$ or $4OH + 2(O\text{–}NO_2)$ octahedra. Two polymorphic forms of copper hydroxy nitrate have been reported: an orthorhombic form [13] which is the most stable form of the two constitutes the mineral gerhardite, whereas the monoclinic modification [14] represents a metastable phase obtainable synthetically. The main difference between the two phases is a shift of every second layer in the orthorhombic phase; this causes the *b*-axis to double in length [14].

The structures of the hydroxide layers in $Ni_2(OH)_3NO_3$ and $Mg_2(OH)_3NO_3$ are generally considered to be similar to that of $Cu_2(OH)_3NO_3$ [15].

HDSs reported in the literature have been generally prepared by precipitation, hydrolysis or anion exchange methods. The precipitation method involves nucleating and growing the metal hydroxide layers by the slow addition of a solution of a base (e.g. NaOH, ammonia, sodium carbonate) to a solution of a metal salt containing the anion to be incorporated. Unlike in the preparation of LDHs where, for synthesis of LDHs containing interlayer anions other than carbonate, there is a need to exclude carbon dioxide from the reaction mixture by purging the reactants with an inert gas, generally no purging is required in the preparation of hydroxy salts. This is most likely because the precipitation occurs at fairly low pH values (less than 7) where atmospheric carbon dioxide would not easily interfere. One inherent problem with this technique, however, is the formation of metal hydroxides through the hydrolysis of the hydroxy salts as they form. This may be avoided using an excess of the metal salt or by carrying out the precipitation in a solution saturated with NaX, where X is the anion to be incorporated [16]. In some cases the precipitation method does not lead to well-crystallized HDS phases, and therefore hydrothermal treatment of the precipitate in the mother liquor is necessary [15].

There are several variants to the hydrolysis method of preparing HDSs. The most common method involves the reaction of a metal oxide or hydroxide with an aqueous solution of a metal salt (NO_3^-, SO_4^{2-}, Cl^-, etc.). Alternatively, a hydrated metal salt may be heated either in the presence of a base (urea or ammonia) or on its own [17–19]. HDSs may also be prepared by hydrothermal treatment of metal salt solutions either in water or in the presence of polyols [20]. The anions of some hydroxy salts are exchangeable and this property serves as a method for preparing other HDSs by anion exchange. Rojas et al. have recently used this method in the preparation of pillar-like hydroxy salts by exchanging interlayer acetate anions with oxovanadates [21].

Exchange reactions of $Cu_2(OH)_3NO_3$ and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ with inorganic and organic anions have previously been reported [15,22–24]. Further, Newman and Jones [15] also reported on attempts to exchange the nitrate anion in $Ni_2(OH)_3NO_3$ with acetate, terephthalate and benzoate anions but in all cases exchange was not possible. The lack of reactivity of nickel hydroxy nitrate was attributed to the strong bonding of the nitrate anion to the layers. However, to our knowledge, there are no reports in the literature of any studies on the exchange reactions of either zinc hydroxy nitrate, $Zn_3(OH)_4(NO_3)_2$ or magnesium hydroxy nitrate. In this paper, attempts are made to replace the nitrate with benzoate anions in copper, nickel, zinc and magnesium hydroxy nitrates.

2. Experimental

2.1. Materials

The parent hydroxy nitrates were prepared from their respective hydrated metal nitrates via the hydrolysis method. The metal nitrates were heated for approximately 12 h in an oven at 150, 170, 220, and 330 °C for copper, zinc, nickel, and magnesium hydroxy nitrates, respectively.

Exchange reactions were attempted by suspending 0.2 g of the parent material in 20 ml of 1 M solution of sodium benzoate for 24 h at room temperature with stirring. The products were filtered, washed and dried.

2.2. Methods

PXRD data were collected on a Philips X'Pert MPD diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.540$ Å) operating at 40 kV and 40 mA. The patterns were recorded from 5° to 60° 2θ with a scan step time of 19.7 s and a step size of 0.02°.The cell parameters were calculated using X'Pert Plus software. Literature values of the cell parameters for the materials were initially used and refined with respect to the observed peak positions.

FTIR spectra were recorded on a ThermoNicolet Smart Golden Gate MKII single reflection ATR spectrometer from 4000 to 500 cm^{-1}. Elemental analysis of C, H, and N was performed using a CE-440 Exeter Analytical Inc. elemental analyser.

3. Results and discussion

3.1. Characterisation of parent hydroxide nitrates

The results of elemental chemical analysis for the parent materials are presented in Table 1. The amount of nitrogen is significantly less than expected, indicating that the extent of nitrate incorporation is lower than would be expected from the ideal formula. This shows that the products formed in this case are probably non-stoichiometric, as has been observed before for some hydroxy salts of divalent metals incorporating halide anions [25].

The PXRD diagrams of the parent copper, magnesium, zinc and nickel hydroxy nitrates are presented in Fig. 1. The PXRD patterns could be indexed using previously reported cell parameter data [14–16,26] yielding the following monoclinic cell parameters: $a = 5.60(2)$ Å, $b = 6.07(3)$ Å, $c = 6.92(8)$ Å and $\beta = 94.02(3)^\circ$ for copper hydroxy nitrate, $a = 7.04(5)$ Å, $b = 9.63(2)$ Å, $c = 11.22(2)$ Å and $\beta = 100.75(1)^{o}$ for zinc hydroxy nitrate and hexagonal parameters $a = 3.13(1)$ Å, $c = 6.94(5)$ and $a = 3.13(6)$ Å, $c = 6.93(6)$ Å for magnesium and nickel hydroxy nitrates, respectively. It should be noted that the PXRD pattern of the copper hydroxy nitrate shows the presence of a small amount of the orthorhombic phase.

The values of the interlayer spacing, given by $c \sin \beta$ and $a \sin \beta$, for the copper and zinc salts respectively and corresponding to **c** for the magnesium and nickel salts, are similar and equal to ca. 6.9 Å for the four hydroxy nitrates under investigation.

The FTIR spectra and spectral assignments of the parent hydroxy nitrates are presented in Fig. 2 and Table 2, respectively. In all four hydroxy nitrates, the nitrate group is coordinated (through one oxygen atom) to the matrix cation. It is well known that the number and positions of the absorption bands of the NO_3^- depend on the NO_3^- coordination [27,28]. Comparison of the observed infrared absorptions with previously reported frequencies for coordinated NO_3 [15,29] allows us to assign the absorptions at 1418–1520 (labelled b), 1277–1325 (labelled c) and 968–1046 cm^{-1} (labelled d) to the ν_4, ν_1 and ν_2 fundamentals, respectively.

The frequency of the N–O stretching vibration, ν_2, has been shown to vary considerably in going from an

Table 1
Elemental analysis of the copper, magnesium, zinc and nickel hydroxy nitrates

Ideal formula	Theoretical values (wt%)			Experimental values (wt%)		
	N	C	H	N	C	H
$Cu_2(OH)_3NO_3$	5.8	0.0	1.3	4.2	0.0	1.1
$Mg_2(OH)_3NO_3$	8.7	0.0	1.9	6.5	0.0	1.5
$Zn_3(OH)_4(NO_3)_2$	7.2	0.0	1.0	4.5	0.0	0.9
$Ni_2(OH)_3NO_3$	6.1	0.0	1.3	5.4	0.0	1.2

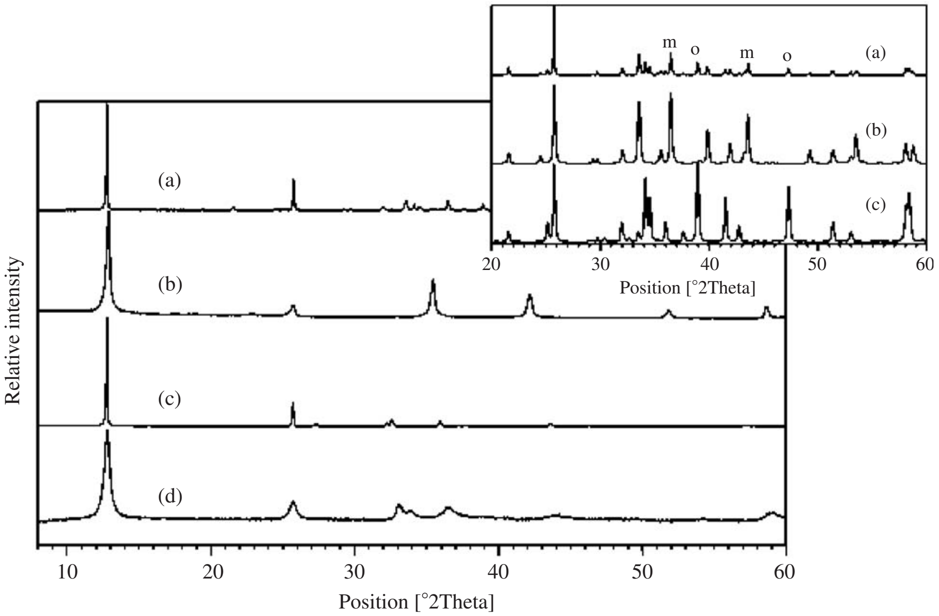

Fig. 1. PXRD patterns of (a) copper (b) magnesium (c) zinc and (d) nickel hydroxy nitrates. (Inset) PXRD patterns of the $Cu_2(OH)_3NO_3$ sample (a) compared with simulated patterns for monoclinic (b) and orthorhombic (c) phases from ICDD® (International Centre for Diffraction Data®) database.

electrostatically to a covalently bound nitrato group. The frequency of this absorption band lies between ca. 1050 cm^{-1} for an ionic nitrate, observed in some metal nitrates, and 854 cm^{-1} for covalent $O–NO_2$ observed in methyl nitrate [28]. Therefore, in the present study, using the frequency of this absorption band as an indicator of the degree of covalent character of the $M–ONO_2$ bond, we obtain the following trend: Cu < Mg < Zn < Ni. The splitting $\Delta = \nu_4 - \nu_1$, induced by the change of polarisation of the nitrate groups upon coordination, would also be expected to depend on the strength of the bonding interaction of the NO_3 with the matrix cation. The values of the splitting observed in the investigated samples range from 101 cm^{-1} for the copper hydroxy salt to 243 cm^{-1} for the nickel salt and follow the same trend as the values for the frequency of the N–O stretching vibration.

The OH stretch of the hydroxyls appear between 3400 and 3700 cm^{-1} with the magnesium hydroxy salt showing the highest frequency, reflecting a lower level of hydrogen bonding in the hydroxy salt.

Thermogravimetric data presented in Fig. 3 show that the dehydroxylation of the hydroxide layers and loss of the nitrate anion occur within a very close temperature range for the hydroxy nitrates of copper, magnesium and nickel such that the two processes are essentially inseparable under these conditions.

The copper salt decomposes from 220 to 300 °C. The expected mass loss for the decomposition of the basic salt to give CuO is 33.8% while the experimentally observed value is 33.3%. For the magnesium salt, decomposition to MgO occurs between 380 and 500 °C. The observed mass loss, 49.4%, agrees closely with the expected value of 50.1%. The nickel salt decomposes to NiO from 290 to 420 °C. The observed mass loss, 36.6%, also agrees closely with the expected value of 35.2%.

Zinc hydroxy nitrate, however, decomposes to ZnO in two highly overlapped steps between 200 and 320 °C. The total expected mass loss of 37.2% agrees well with the observed value of 36.4%. The first step of mass loss is attributed to the decomposition of the basic salt to give ZnO and an amorphous anhydrous zinc nitrate. The amorphous anhydrous zinc nitrate decomposes in the next stage to give additional ZnO.

It is interesting to note that the general trend in the decomposition temperature of the parent materials correlates well with the charge densities of the cations. Thermal decomposition of the anion and formation of the metal oxide may be initiated through breaking of the N–O bond in $M–O–NO_2$. Yuvaraj et al. have recently reported a detailed study of the thermal decomposition of metal nitrates and related decomposition temperatures to the charge densities of the metal cations [31]. The decomposi-

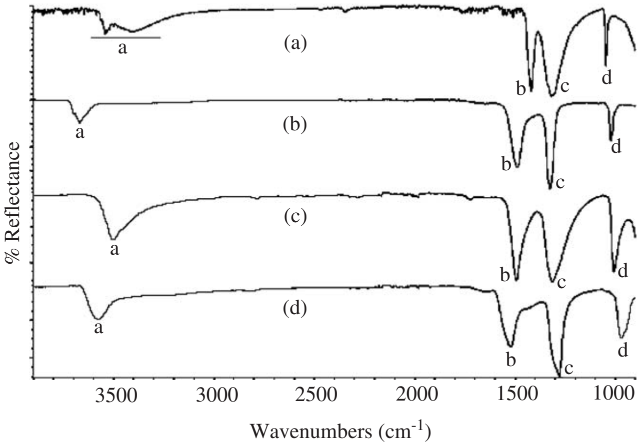

Fig. 2. FTIR spectra of (a) copper (b) magnesium (c) zinc and (d) nickel hydroxy nitrates.

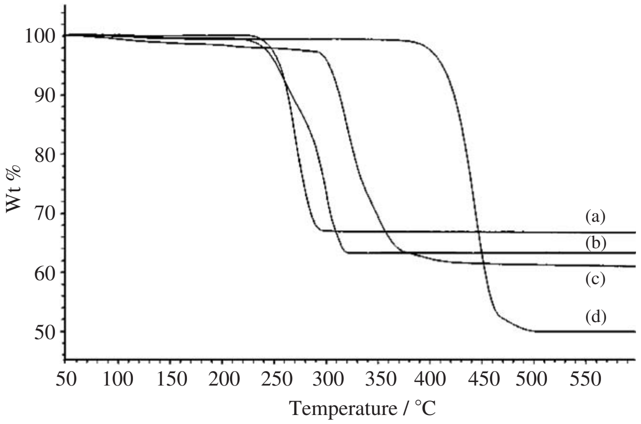

Fig. 3. TGA profiles for (a) copper (b) zinc (c) nickel, and (d) magnesium hydroxy nitrates.

Table 2
FTIR data for the parent hydroxy nitrates

Peak label	Wave number (cm^{-1})				Assignment
	$Cu_2(OH)_3NO_3$	$Mg_2(OH)_3NO_3$	$Zn_3(OH)_4(NO_3)_2$	$Ni_2(OH)_3NO_3$	
a	3545, 3400	3608	3503	3584	OH stretch
b	1418	1487	1491	1520	$O–NO_2$ asymmetric stretch ν_4
c	1317	1325	1310	1277	$O–NO_2$ symmetric stretch ν_1
d	1046	1020	1004	968	N–O stretch, ν_2
Δ	101	162	180	243	ν_4–ν_1

Table 3
Comparison of charge densities of the cations and the decomposition temperature of their hydroxy nitrates [31]

Metal cation	10^3 Charge density (e/nm^3)	Decomposition temperature of HDS (°C)
Zn^{2+}	2.21	200–320
Cu^{2+}	1.33	220–300
Ni^{2+}	0.83	290–420
Mg^{2+}	0.75	380–500

tion temperature should, therefore, decrease as the strength of the bond decreases. The strength of this bond may be reduced by two main factors: (1) through polarisation of the electron cloud of the nitrate anion by the charge density on the metal cation and (2) through back-donation of nitrate electron cloud to a vacant *d*-orbital of the metal ion [31]. Zinc has the highest charge density of the metals under investigation (Table 3) followed by copper. However, copper has empty *d*-orbitals and therefore can accept electron density from the nitrate to further weaken the N–O bond. For this reason, the decomposition temperatures of the copper and zinc hydroxy salts are not very different despite the large differences in charge density. This influence of vacant *d*-orbitals is also shown by the magnesium and nickel hydroxy nitrates. Nickel and magnesium have similar charge densities but nickel hydroxy nitrate decomposes at a much lower temperature than magnesium hydroxy nitrate because nickel has available low-energy *d*-orbitals.

3.2. Anion exchange reactions

Fig. 4 presents the PXRD patterns of the products obtained when the parent hydroxy nitrates were suspended at room temperature in aqueous solutions of sodium benzoate. It is clear from the patterns that incorporation of the benzoate anion has been achieved for both the zinc and copper hydroxy salts as evidenced by the shift of basal reflections to lower angles. No reflections from the parent material are observed in the PXRD pattern of the exchange product of the zinc salt, showing that there is complete replacement of the nitrate by benzoate anions. However, in the PXRD pattern of the exchange product of the copper salt, reflections assigned to the parent material are still present after 24 h of exchange, which shows that replacement of the nitrate for benzoate has not gone to completion. CHN elemental analysis (C = 12.71%, H = 1.71% and N = 3.09%) of this product also confirms the presence of both nitrogen- and carbon-containing species in the sample. However, complete exchange was possible for longer reaction time (48 h) as shown in Fig. 4c where reflections of the parent material are absent. Observed values from CHN analysis of the exchange material (C = 28.4%, H = 2.45% and N = 0.0%) were also similar to those expected from the ideal formula, $Cu_2(OH)_3BA$ (C = 28.1%, H = 2.68% and N = 0.0%).

The observed interlayer spacing of 15.34 Å for $Cu_2(OH)_3BA$ is similar to that previously reported for copper basic salts intercalated with benzoate anions where the anions form an approximately perpendicular bilayer between adjacent hydroxide layers [15]. The observed interlayer spacing for the benzoate derivative of $Zn_3(OH)_4(NO_3)_2$ is also similar to that previously reported for benzoate derivative of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ in which the anions also occupy the interlayer space in bilayers [15].

The FTIR spectra of the benzoate derivatives of $Cu_2(OH)_3NO_3$ and $Zn_3(OH)_4(NO_3)_2$ (fully exchanged material) are presented in Fig. 5. In both cases three

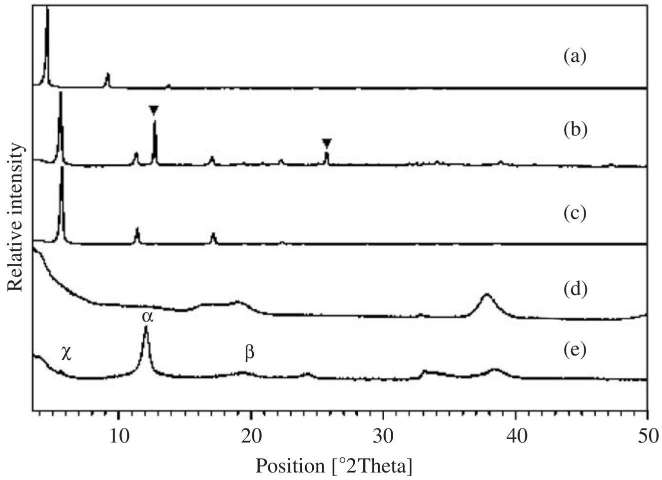

Fig. 4. Fig. 4 PXRD patterns of (a) zinc, (b) copper (after 24 h), (c) copper (after 48 h at 60 °C), (d) magnesium and (e) nickel hydroxy nitrates (after 48 h at 60 °C) after treatment with sodium benzoate solution. ▼ Represents unreacted parent copper hydroxide nitrate; χ represents benzoate derivative of nickel hydroxy nitrate; **α** and **β** refer to α-$Ni(OH)_2$ and β-$Ni(OH)_2$, respectively.

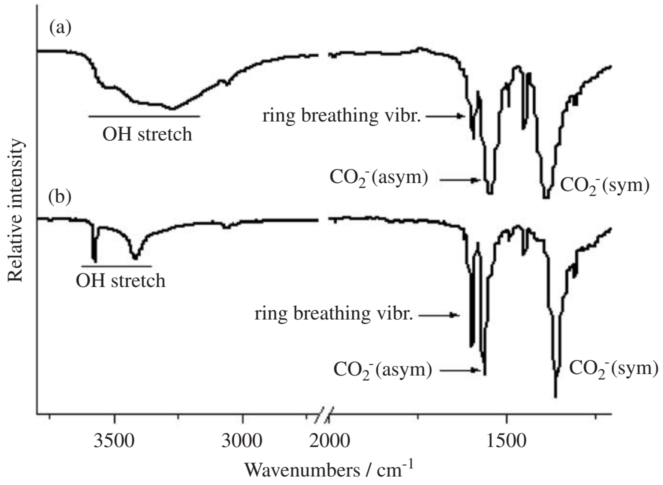

Fig. 5. FTIR spectra of benzoate derivatives of (a) $Zn_3(OH)_4(NO_3)_2$ and (b) $Cu_2(OH)_3NO_3$.

strong absorptions are observed in the region from 1200 to 1600 cm^{-1} which may be assigned to the asymmetric and symmetric vibrations of the carboxylate group and ring breathing vibrations of the benzene ring. The difference between the asymmetric and symmetric stretch in the benzoate derivative of $Cu_2(OH)_3NO_3$, 201 cm^{-1}, is characteristic of a unidentate carboxylate coordination [19]. In the benzoate derivative of $Zn_3(OH)_4(NO_3)_2$, the difference of 159 cm^{-1} is close to that for sodium benzoate (143 cm^{-1}) and therefore an ionic interaction of the carboxylate with the cation matrix may be inferred [32].

Attempts to replace the nitrate anions in the nickel and magnesium salts under the same conditions were unsuccessful. In the case of the magnesium salt, hydrolysis occurs to give a phase identified as poorly crystallised brucite, $Mg(OH)_2$, Fig. 4(d). For the nickel salt, no change was observed in the PXRD pattern after 24 h. However, after 48 h, three different phases were identified. The dominant reflections in the PXRD pattern are identified as being associated with α-$Ni(OH)_2$ (12.13°, 24.4° 2θ) and β-$Ni(OH)_2$ (19.4° 2θ) [33]. A very low-intensity reflection at ca. 5.71° 2θ (15.49 Å) may be assigned to a benzoate intercalated nickel basic salt with a similar interlayer spacing to that observed for the copper salt as would be expected from their similar structures. The presence of both nitrogen- and carbon-containing species is also confirmed from elemental analysis ($C = 6.17\%$, $H = 2.42\%$, $N = 1.17\%$). Attempts to carry out the exchange reaction at higher temperature (60 °C, 48 h) did not result in significant improvement in the amount of exchange product obtained with the dominant phase identified as β-$Ni(OH)_2$, along with small amounts of benzoate-containing nickel basic salt.

Nickel hydroxide crystallises in layered brucite-like hexagonal structure and exists in two polymorphic forms known as α- and β- forms [33]. The β-form is the thermodynamically more stable of the two and is isostructural with brucite, $Mg(OH)_2$. The α-form is a hydroxyl-deficient phase that contains intercalated anions and water molecules in the gallery. Therefore, the α-form is essentially a hydroxy salt with a higher OH to anion ratio. FTIR confirmed the presence of both benzoate anions (from the benzoate intercalated phase) and nitrate anions (from the α-$Ni(OH)_2$ phase) in the nickel sample treated at room temperature.

Two important observations on the structure of the exchange products of copper and zinc hydroxy nitrates are worth noting. Firstly, although the nitrate anions are more strongly bound to the matrix cation (as shown from FTIR) in the zinc salt than in the copper salt, under the similar reaction conditions, exchange goes to completion for the zinc salt but is only partial for the copper salt. Secondly, the interlayer spacing for the exchange product from $Zn_3(OH)_4(NO_3)_2$ is different from that of the copper and nickel salts despite the similarities in the basal spacing of their parent materials. In fact, the basal spacing for the benzoate derivative of $Zn_3(OH)_4(NO_3)_2$ (i.e. 19.1 Å) is similar to that previously reported for the benzoate derivative of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (19.3 Å) [15]. Further, the CHN elemental analysis indicates that the carbon and hydrogen content of the exchange product from $Zn_3(OH)_4(NO_3)_2$ ($C = 22.37\%$, $H = 2.77\%$) is very similar to that of the product obtained from the exchange reaction of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ with benzoate ($C = 22.14\%$, $H = 2.62\%$). These observations may suggest that during the exchange process, the $Zn_3(OH)_4X_2$ structure undergoes hydrolysis to the more basic $Zn_5(OH)_8X_2 \cdot 2H_2O$ structure. Indeed it was observed that when a sample of $Zn_3(OH)_4(NO_3)_2$ was dispersed in deionised water, it readily converted to $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$. For example, noticeable reflections of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ present in the PXRD after about 20 min in water at room temperature. It is probably this lack of stability of the $Zn_3(OH)_4X_2$ structure towards hydrolysis to the $Zn_5(OH)_8X_2 \cdot 2H_2O$ structure that facilitates easier replacement of the nitrate by other anions.

The observed trends in the exchange reactions of the four hydroxy nitrates are not specific to benzoate anions. Several other organic and inorganic anions have been attempted and similar trends were in general observed. Results from theses studies will be presented elsewhere.

4. Conclusions

The exchange reaction of $Zn_3(OH)_4(NO_3)_2$ with benzoate anions has been investigated and compared with those of structurally related hydroxy salts of copper, magnesium and nickel. It has been observed that while exchange is possible for both the zinc and copper hydroxy nitrates, the nickel and magnesium hydroxy nitrates hydrolyse to their respective hydroxides. The interlayer spacings of the exchange products of zinc and copper basic salts are different despite similarities in the interlayer spacing of the parent materials. This phenomenon has been shown to be due to the hydrolysis of the zinc salt during the reaction. Therefore, although the nitrate in $Zn_3(OH)_4(NO_3)_2$ may be readily replaced by other anions, this is not a genuine anion exchange reaction as there is substantial modification of the structure.

Acknowledgments

We are grateful to Cambridge Commonwealth Trust, Churchill College, and the Royal Society of London for financial support.

References

[1] V. Rives (Ed.), Layered Double Hydroxides: Present and Future, Nova Science Publishers, Inc., New York, 2001.

[2] S.P. Newman, W. Jones, in: W. Jones, C.N.R. Rao (Eds.), Supramolecular Organization and Materials Design, Cambridge University Press, Cambridge, 2002.

[3] D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, Wiley, New York, 1996.

[4] T.J. Pinnavaia, G.W. Beall (Eds.), Polymer–Clay Nanocomposites, Wiley, New York, 2000.

[5] M. Del Arco, E. Cebadera, S. Gutierrez, C. Martin, M.J. Montero, V. Rives, J. Rocha, M.A. Sevilla, J. Pharm. Sci. 93 (2004) 1649.

[6] S. Aisawa, H. Kudo, T. Hoshi, S. Takahashi, H. Hirahara, Y. Umetsu, E. Narita, J. Solid State Chem. 177 (2004) 3987.

[7] S. Ghose, Acta Crystallogr. 17 (1964) 1051.

[8] M. Louer, D. Louer, D. Grandjean, Acta Crystallogr. Sect. B: Struct. Sci. B 29 (1973) 1693.

[9] W. Stahlin, H. Oswald, Acta. Crystallogr. Sect. B: Struct. Sci. B 26 (1970) 860.

[10] W. Stahlin, H. Oswald, J. Solid State Chem. 2 (1971) 252.

[11] P. Benard, J.P. Auffredic, D. Louer, Powder Diffr. 10 (1995) 20.

[12] M. Louer, D. Louer, D. Weigel, C.R. Hebd. Acad. Sci. 270 (1970) 881.

[13] B. Bovio, S. Locchi, J. Crystallogr. Spectrosc. 12 (1982) 507.

[14] N. Guillou, M. Louer, D. Louer, J. Solid State Chem. 109 (1994) 307.

[15] S.P. Newman, W. Jones, J. Solid State Chem. 148 (1999) 26.

[16] K. Petrov, A. Lyubchova, L. Markov, Polyhedron 8 (1989) 1061.

[17] L. Eriksson, D. Louer, P.E. Werner, J. Solid State Chem. 81 (1989) 9.

[18] A.J. Kozak, K. Wieczorek-Ciurowa, A. Kozak, J. Therm. Anal. Calorim. 74 (2003) 497.

[19] N. Masciocchi, E. Corradi, A. Sironi, G. Moretti, G. Minelli, P. Porta, J. Solid State Chem. 131 (1997) 252.

[20] L. Poul, N. Jouini, F. Fievet, Chem. Mater. 12 (2000) 3123.

[21] R. Rojas, C. Barriga, M.A. Ulibarri, V. Rives, J. Solid State Chem. 177 (2004) 3392.

[22] H. Morioka, H. Tagaya, M. Karasu, J. Kadokawa, K. Chiba, J. Mater. Res. 13 (1998) 848.

[23] W. Stahlin, H. Oswald, J. Solid State Chem. 3 (1971) 256.

[24] F. Wypych, G.G.C. Arizaga, J. Gardolinski, J. Colloid Interface Sci. 283 (2005) 130.

[25] H.R. Oswald, W. Feitknecht, Helv. Chim. Acta 47 (1963) 272.

[26] M. Louer, D. Grandjean, D. Weigel, Acta Crystallogr. Sect. B: Struct. Sci. B 29 (1973) 1703.

[27] C.C. Addison, B.M. Gatehouse, J. Chem. Soc. (1960) 613.

[28] B.M. Gatehouse, S.E. Livingstone, R.S. Nyholm, J. Chem. Soc. (1957) 4222.

[29] C. Chouillet, J.M. Krafft, C. Louis, H. Lauron-Pernot, Spectrochim. Acta Part A 60 (2004) 505.

[31] S. Yuvaraj, F.Y. Lin, T.H. Chang, C.T. Yeh, J. Phys. Chem. B 107 (2003) 1044.

[32] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.

[33] M. Rajamathi, P.V. Kamath, J. Power Sources 70 (1998) 118.