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Complexation of Cu(II) and Ni(II) by nitrilotriacetate intercalated in Zn–Cr layered double hydroxides

Norbert H. Gutmann,[a]† **Leone Spiccia***[a] **and Terence W. Turney**[b]

[a]*Department of Chemistry, Monash University, Victoria, 3800, Australia.*
E-mail: leone.spiccia@sci.monash.edu.au; Fax: 61 3 9905 4597; Tel: 61 3 9905 4526
[b]*CSIRO, Division of Manufacturing Science and Technology, Clayton, Victoria, 3168, Australia*

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Direct and indirect anion exchange methods have been used to intercalate a [$Zn^{II}{}_2$–Cr^{III}] lamellar double hydroxide (LDH), with $[Cu(nta)]^-$ and $[Ni(nta)]^-$ (nta = nitrilotriacetate). For the direct method, a solution of the pre-formed complexes was used to intercalate the LDH while for the indirect method the anionic nta ligand was intercalated, the product was isolated and then reacted with a solution of the metal ion to produce the intercalated complex. LDH phases with vertical and tilted orientations of the complex are proposed to account for the formation of products with basal spacings of 14 and 12 Å, respectively. The preferred arrangement varies with the metal ion, temperature and synthetic method. For the indirect method, two metal salt counter anions, *viz.*, sulfate and tosylate, displaced the metal complex from the interlayer while chloride and nitrate competed poorly for the interlayer positions.

Introduction

Among the compounds designated as layered structures, lamellar double hydroxides (LDH) represent an important class of materials.[1] Interest in such layered structures is increasing because their properties are such that nanocomposite materials can be produced.[1–3] LDH's of general formula $[M^{II}{}_{1-x}M^{III}{}_x(OH)_2]^{x+}[X^{z-}{}_{x/z}\cdot nH_2O]^{x-}$, where M^{II} and M^{III} are divalent and trivalent metal ions, respectively and x is the ratio $M^{II}/(M^{II}+M^{III})$, possess a structure in which sheets of positively charged hydroxyl layers are separated by layers of intercalated anions, X^{z-}, and additional water molecules. Desired material properties may therefore be created either by specific chemical and structural modification of the anionic interlayer or by controlled alteration of the chemical composition of the host.[1,3] There has been considerable interest in the application of porous materials, formed by intercalation of polyoxometallates and other molecules into LDH's, as sorbents, molecular sieves and catalysts and hosts for various chemical, electrochemical and photochemical reactions.[4–17]

Investigations on the intercalation of metal complexes into layered materials have shown that guest–host interactions can affect the geometric, chemical and electronic properties and stability of the intercalated complexes.[11,15,18] In order to further elucidate the nature of such interactions we have examined the intercalation of the Cu^{II} and Ni^{II} complexes of nitrilotriacetate (nta), $[Cu(nta)]^-$ and $[Ni(nta)]^-$, into a [Zn–Cr] LDH with $Zn^{II}/Cr^{III} = 2$ in aqueous solution. This was achieved by direct intercalation of the metal complex or indirectly by forming the metal complex within the hydrotalcite layers following intercalation of the nta ligand. LDH phases are named employing the nomenclature: [Zn_2–Cr–X] where 2 indicates a 2 : 1 Zn^{II}/Cr^{III} ratio and X the intercalated anion, *e.g.*, $[M(nta)]^-$. The products were analysed by X-ray powder diffraction, thermogravimetry (TG), FT-IR and diffuse reflectance UV-Vis spectroscopy. The orientations of $[M(nta)]^-$ within the interlayer are discussed, together with variations resulting from changes in the method of intercalation.

Results and discussion

Direct intercalation of $[M(nta)]^-$ ($M = Cu^{2+}$, Ni^{2+})

Throughout this study, a nitrate LDH precursor, *viz.* [Zn_2–Cr–NO_3], was the starting material for exchange reactions. The completeness of exchange of the nitrate by the anionic complexes $[M(nta)]^-$ ($M = Cu^{II}$, Ni^{II}) was confirmed by chemical analysis, X-ray powder diffraction and FTIR spectroscopy. Chemical and thermogravimetric analyses further indicated that the products had compositions corresponding to: $[Zn_2Cr(OH)_6][M(nta)(H_2O)_2]\cdot 2H_2O$.

Since the Ni^{II} and Cu^{II} intercalates have the same water content, and it is unlikely that intercalation of the Ni^{II} complex will result in loss of coordinated aqua ligands, we propose that both the Cu and Ni intercalated complexes are six-coordinate with two water molecules completing the metal coordination sphere. The other two water molecules occupy available space within the interlayer.

The X-ray powder patterns (Fig. 1) indicate that, depending on the temperature and metal ion, the nta complexes can intercalate in two different orientations, which correspond to basal spacings of ≈14.2 and ≈12.0 Å, respectively. The absence of (*hkl*) reflections where $l \neq 0$ indicated a turbostratic layered structure, attributable to strongly separated hydroxyl layers and weak bonding interactions between intercalated species and hydroxyl layers.

In the case of [Zn_2–Cr–Cu(nta)], the powder XRD pattern (Fig. 1(a)) indicates a mixture of the two orientations when exchange is performed at ambient temperature. An increase in the exchange temperature to 60 °C leads exclusively to the orientation with a basal spacing of 12 Å (Fig. 1(b)). In contrast, for [Zn_2–Cr–Ni(nta)], only the orientation producing a basal spacing of 14.2 Å is formed at 25 °C. Formation of the phase with a basal spacing of 12 Å is apparent after heating at elevated temperatures (≈100 °C). Notably, intercalation of tris(oxalato)aluminate(III) produces a more compact arrangement and lower basal spacing (9.9 Å)[19] than found here.

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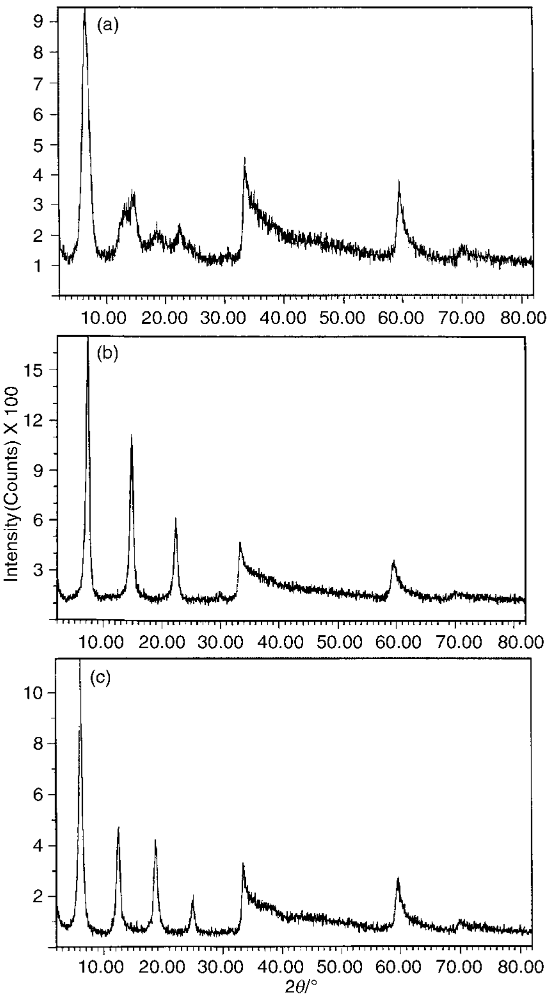

Fig. 1 X-Ray powder diffractograms of [Zn_2–Cr–Cu(nta)] prepared at: (a) 22 °C; (b) 60 °C; and (c) [Zn_2–Cr–Ni(nta)] prepared at 22 °C.

The stereochemistry of the nta ligand in such metal complexes has been described as the so-called 'butterfly' conformation[20] shown in different perspectives in Fig. 2. The structure consists of three five-atom rings, two in envelope conformation and a third flat ring defining a pseudo-mirror plane between the former two. In contrast to $[Ni(nta)]^-$, the intercalated $[Cu(nta)]^-$ complex is expected to deviate from the regular octahedral geometry due to Jahn–Teller distortion. However, comparisons of the structures of $KCu(nta)\cdot 3H_2O$,[21] $LiCu(nta)\cdot 3H_2O$,[22] $NaCu(nta)\cdot H_2O$,[23] and the related $Cu(H_2edta)\cdot H_2O$[24] (edta = ethylenediaminetetraacetate), indicate that the distortion from octahedral coordination is not systematic and is sometimes contrary to expectations deriving from the spectrochemical series. In the lithium salt[22] the Cu–O bonds are shorter whereas in the sodium[23] and potassium salt[21] they are longer than that forming part of the flat ring. Nevertheless, for the copper(II) nta intercalates, we propose that H-bonding interactions with the hydroxyl layers result in two slightly elongated Cu–O bonds within each twisted five-membered ring which occupy the apical position of an octahedron. The equatorial sites around the Cu^{II} centres are occupied by a NO_3 donor set comprising two O donors from aqua ligands, and one N and one O donor from the nta ligand.

The basal spacings of 14.2 and 12.0 Å can be rationalised by proposing that the intercalated nta complexes can adopt one of two orientations: a tilted orientation (Fig. 2(a)) responsible for the lower basal spacing and a vertical orientation (Fig. 2(b)) giving rise to the higher spacing. These two arrangements can be interchanged by adjusting the twisted five-membered rings parallel to the *c*-direction for the vertical and at an angle of nearly 45° for the tilted orientation. Notably the difference in the approximate dimensions of the vertical and tilted intercalated complex of 7.5 and 5 Å, respectively, matches the observed difference in basal spacings of ≈ 2.2 Å. The energetically favoured tilted orientation is better achieved at higher exchange temperatures and could involve additional host–guest interactions (or a greater number of H-bonds) which are not present for the vertical orientation. For the tilted orientation, the non-coordinated oxygens on two of the three carboxylates (*viz.*, both COO of one twisted ring and the COO of the flat ring) could adopt a linear arrangement which runs parallel to the plane of close-packed oxygen atoms orthogonal to the *c*-direction (Fig. 2(a)). This form could be stabilised by H-bonding interactions between these carboxylate oxygens and the OH groups. The O···O distance between the mentioned oxygen atoms of *ca.* 5.0 Å expected for a regular octahedron is comparable to the distance $a\sqrt{3} = 5.38$ A within the sheets of ideally packed OH groups. The small difference, however, should give rise to an energy barrier for the intercalated complex to overcome in order to adopt a tilted conformation. The tetragonally elongated octahedral geometry of $[Cu(nta)]^-$ allows some expansion of the O···O distance between the relevant carboxylate oxygen. This would better match the requirements of the OH matrix than the more regular octahedral geometry of $[Ni(nta)]^-$ and results in a different temperature intercalation behaviour. Experiments conducted on a [Zn–Al] host lattice, which has the same M^{II}/M^{III} ratio within the hydroxyl layers, but a slightly lower lattice constant ($a\sqrt{3} = 5.30$ A) support this proposal. For the [Zn–Al] host lattice, intercalation of both the Cu^{II} and Ni^{II} complexes gave rise to a tilted orientation (basal spacing of 12.0 Å) at ambient temperature,[25] even though the lattice constant is only slightly smaller than that for the Zn–Cr lattice.

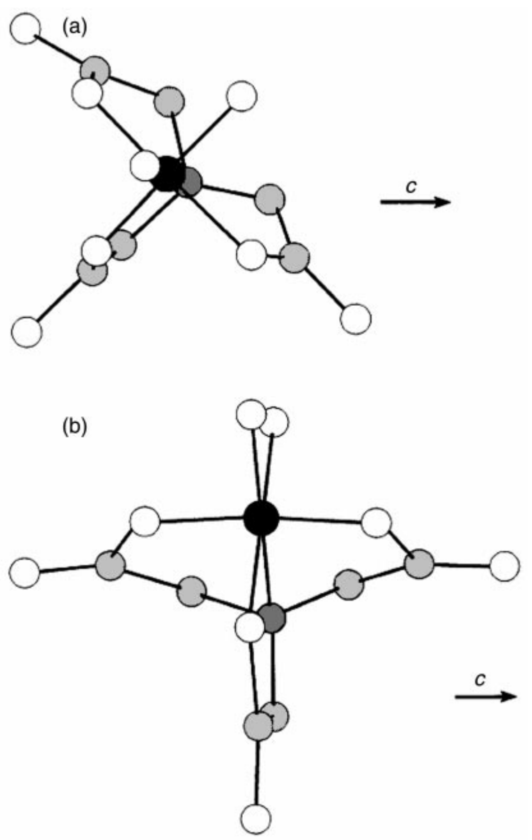

Fig. 2 Perspective view of an octahedral $[M(nta)]^-$ complex showing the chelate in tilted (a) and vertical (b) orientations relative to the *c*-direction.

The TG and DTG profiles for [Zn_2–Cr–Cu(nta)] and [Zn_2–Cr–Ni(nta)] having the intercalated complexes in tilted and vertical orientations, respectively, recorded under argon were in agreement with previously reported thermal decomposition profiles for [Zn–Cr] LDH.[26] Such compounds decompose in two main stages: removal of the interlayer water followed by dehydroxylation and removal of interlayer anions. Dehydration of interlayer water is complete at *ca.* 120 °C and is probably accompanied by the loss of water coordinated to the [Cu(nta)]$^-$ and [Ni(nta)]$^-$ complexes. Notably, salts of these complexes dehydrate fully below 150 °C.[27] Isothermal heating of the samples at 100 °C causes collapse of the structure, in a manner that is not typical of the thermal behaviour of LDH,[28] and results in the almost complete disappearance of (00*l*) reflections from the diffractograms. Thus, the coordinated water molecules play a role in preserving interlayer order. The second more complex decomposition stage probably involves partial dehydroxylation, which is indicated by a small weight loss at 210 °C in the TG profile of [Zn$_2$–Cr–Cu(nta)].

The FT-IR spectra of [Zn$_2$–Cr–Cu(nta)] and [Zn$_2$–Cr–Ni(nta)] revealed characteristic vibrations originating from the nta ligand (see Table 1), *i.e.*, the asymmetric (ν_{as}(COO) $\approx 1620\ \mathrm{cm^{-1}}$) and symmetric COO ($\nu_s(\mathrm{COO}) \approx 1400\ \mathrm{cm^{-1}}$) vibrations and the C–N stretch ($\nu(\mathrm{CN}) \approx 1120\ \mathrm{cm^{-1}}$). The ν_{as}(COO) band, which can be obscured by $\delta(H_2O)$ vibrations at $1620\ \mathrm{cm^{-1}}$, is normally more sensitive to chemical environment and binding effects than ν_s(COO) and ν(CN).[29] In these systems, the reduction in ν_{as}(COO) caused by coordination can be partially offset by the effects of H-bonding between the intercalated complex and the hydroxyl layers.[30] Nevertheless, the lowering of ν_{as}(COO) for both [Zn$_2$–Cr–M(nta)] materials by $\approx 20\ \mathrm{cm^{-1}}$ relative to that of the Na$^+$ salt, NaCu(nta)·H$_2$O,[29] matches that observed for the complex in aqueous solution.[29,31] Moreover, the position of ν(CN) (1115 and $1123\ \mathrm{cm^{-1}}$) is in agreement with that for NaCu(nta)·H$_2$O ($1115\ \mathrm{cm^{-1}}$) but is shifted from that for the anhydrous Na$_3$nta salt ($1138\ \mathrm{cm^{-1}}$). Although nta coordination can be established from the IR spectra, the orientation of the complexes within the interlayer (vertical *vs.* tilted) cannot be distinguished since differences in H-bonding interactions are not reflected in systematic changes in the IR spectrum.

Fig. 3 shows the UV-Vis-NIR reflectance spectra of the LDH's including the reference spectra of the initial [Zn$_2$–Cr–NO$_3$]. The assignment of d–d transitions due to Ni^{II} and Cu^{II} in the [M(nta)]$^-$ complexes is facilitated by the fact that the d–d transitions of the Cr^{III} present in the host layers are not affected by intercalation but are broadened because of a lowering of the symmetry (D_{3d}) caused by compression of the Cr(OH)$_6$ octahedra within the brucite-like layer along the C_3 axis.[26]

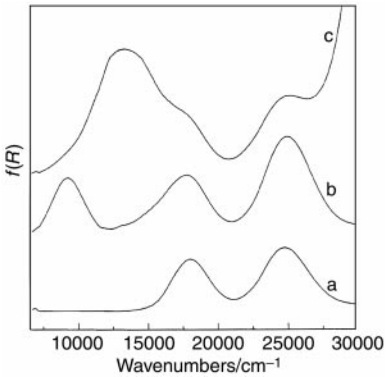

Fig. 3 UV-Vis-NIR reflection spectra of: (a) [Zn$_2$–Cr–NO$_3$], (b) [Zn$_2$–Cr–Ni(nta)] and (c) [Zn$_2$–Cr–Cu(nta)].

For [Zn$_2$–Cr–Ni(nta)], the bands at 9300 and $13\,300\ \mathrm{cm^{-1}}$ can be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions, respectively, from their correspondence with those observed for [Ni(nta)]$^-$ in aqueous solution.[32] The unusually high intensity of the first spin-forbidden transition, $^3A_{2g} \rightarrow {}^1E_g$ is a feature of high-spin Ni^{II} spectra observed when $Dq/B \approx 1$, it gains intensity by "borrowing" from the second spin-allowed transition, $^3A_{2g} \rightarrow {}^3T_{1g}$ (^{3}F) *via* spin–orbit coupling. The other spin-allowed transitions, $^3A_{2g} \rightarrow {}^3T_{1g}$ (^{3}F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (^{3}P) normally found at *ca.* 16 000 and $25\,000\ \mathrm{cm^{-1}}$, respectively, are obscured by the Cr^{III} transitions. Applying Tsuchida's rule, $10\,Dq = \nu_1$ (octahedral ligand field),[33] a reduction of $200\ \mathrm{cm^{-1}}$ in $10\,Dq$ is found for [Zn$_2$–Cr–Ni(nta)] relative to the complex in solution. H-Bonding interactions between the carboxylate oxygen and the hydroxyl layers therefore cause only a slight reduction in the electron density on the donating carboxylates, which consequently has little effect on the electronic structure of Ni^{II}.

For tetragonally distorted octahedral or square pyramidal Cu(II) complexes, two d–d transitions are usually observed, originating from d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, *cf.*, single-crystal spectrum of rhombically elongated CuH$_2$edta·H$_2$O.[34] The diffuse reflectance spectrum of [Zn$_2$–Cr–Cu(nta)] shows just one broad band at *ca.* $13\,400\ \mathrm{cm^{-1}}$ ascribed to a d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition with some contribution from the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. In comparison, the diffuse reflectance spectrum of NaCu(nta)·H$_2$O shows broad bands at 12 600 and $8300\ \mathrm{cm^{-1}}$ typical of Cu(II) in SP or distorted octahedral geometry. In aqueous solution, [Cu(nta)]$^-$ exhibits a single broad band at $11\,800\ \mathrm{cm^{-1}}$ which is the average of bands in the solid state spectrum. The shift of this band to $13\,400\ \mathrm{cm^{-1}}$ on intercalation indicates that interactions with the brucite-like layers (*e.g.*, H-bonding) cause an increase in ligand field strength. In contrast to [Ni(nta)]$^-$, intercalation of [Cu(nta)]$^-$ stabilises the complex.

Table 1 Comparison of selected nta IR bands of [Zn$_2$–Cr–M(nta)] phases prepared by direct and indirect anion exchange methods with those of reference compounds

	ν_{as}(COO)/cm^{-1}	ν_s(COO)/cm^{-1}	ν(CN)/cm^{-1}
Direct intercalation			
[Zn$_2$–Cr–Cu(nta)]^a	1615	1400	1114
[Zn$_2$–Cr–Ni(nta)]^b	1598	1404	1123
NaCu(nta)·H$_2$O^c	1635	1418	1115
Indirect intercalation			
[Zn$_2$–Cr–nta]^d	1602	1406	1130
[Zn$_2$–Cr–nta], treated with Cu^{2+} solution^e	1613	1401	1115
[Zn$_2$–Cr–nta], treated with Ni^{2+} solution^f	1598	1404	1123
Reference compounds			
[Cu(nta)]$^-$ (in aqueous solution)^g	1615		
Na$_3$(nta)^h	1580	1411	1138
nta^{3-} (in aqueous solution)^h	1588		

^{a}Intercalate with tilted orientation. ^{b}Intercalate with vertical orientation. ^{c}Ref. 29. ^{d}Prepared at pH $\approx$ 11.0. ^{e}Obtained from a 0.05 M CuCl$_2$ solution. ^{f}Obtained from a 0.005 M Ni(NO$_3$)$_2$ solution. ^{g}Ref. 31. ^{h}Ref. 37.

Indirect intercalation of $[M(nta)]^-$

Intercalation of the ligand. The intercalation of nta will be favoured at high pH, since under these conditions the ligand exists as deprotonated anionic forms. Under these circumstances, [Zn–Cr] LDH's are preferred to other $M^{II}–M^{III}$ combinations since their lower affinity for CO_2 minimises the incorporation of carbonate in preference to the desired anion.[30] Even when the exchange was carried out in air, the CO_3^{2-} content of the end product did not exceed 10%. LDH dissolution, resulting from Zn^{2+} and Cr^{3+} complexation by nta, was minimised by using low ligand concentrations (0.01 M) while still maintaining effective nta intercalation.

In keeping with the acid–base behaviour of nitrilotriacetic acid, $pK_{a,1} = 1.80$, $pK_{a,2} = 2.48$ and $pK_{a,3} = 9.65$,[35] anionic exchange on the nitrate precursor, $[Zn_2–Cr–NO_3]$, at $pH \approx 6.7$ afforded an LDH that mainly contained the monoprotonated ligand, $Hnta^{2-}$, having a basal spacing of *ca.* 14.2 Å (Fig. 4). Consequently, the C and N contents are higher than those expected for intercalation of the fully deprotonated ligand nta^{3-}.

At pH = 11, the ligand is fully deprotonated and exchanges in the nta^{3-} form, giving a product with elemental analysis corresponding to $[Zn_2Cr(OH)_6](nta)_{1/3}\cdot 2H_2O$ and a basal spacing of 12.1 Å (Fig. 4(b)). There is evidence for the presence of this phase in the XRD pattern of the product obtained at pH = 6.7 (Fig. 4(a)). The basal spacings of 14.2 and 12.1 Å for intercalated $Hnta^{2-}$ and nta^{3-}, respectively, suggest that the anion orientations between the hydroxyl layers are similar to those found for the respective metal complex intercalates, $[Zn_2–Cr–Ni(nta)]$ and $[Zn_2–Cr–Cu(nta)]$. The protonation state of the nta nitrogen has a major influence on the orientation of the intercalated ligand. In the case of $Hnta^{2-}$, the ability of its carboxylates to act as H-bonding acceptors with the brucite-like layers is reduced relative to the fully deprotonated ligand since intraligand H-bonding is likely between the N–H proton and any of the three carboxylate groups.[36] Both forms of the nta ligand give basal spacings that are substantially greater than found recently for the intercalation of oxalate, an anion which adopts flat and vertical orientations when introduced into the LDH.[19]

The $\nu_{as}(COO)$ and $\nu_s(COO)$ stretching vibrations $[Zn_2–Cr–nta]$ prepared at $pH \approx 11.0$ found at 1602 and 1406 cm^{-1} (Table 1) differ only slightly from the values found for the ionic Na^+ and K^+ salts of the ligand in the solid state and also in aqueous solution.[29,37] H-Bonding interactions between the three carboxylate groups and the main hydroxyl layer could be responsible for these small variations.[38] The UV-Vis reflectance spectrum of the $pH \approx 11.0$ $[Zn_2–Cr–nta]$ phase indicates that the anion exchange reaction causes small changes in the brucite-like hydroxyl layers. The spin-allowed $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (^4F) transitions, originating from Cr^{3+}, undergo a slight red shift (17 700 and 24 600 cm^{-1} compared to 18 000 and 24 800 cm^{-1} for $[Zn_2–Cr–NO_3]$). CEC analysis of a solution obtained by dissolution of $[Zn_2–Cr–nta]$ in 1 M perchloric acid reveals small amounts of dinuclear complex $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ as well as monomeric $[Cr(H_2O)_6]^{3+}$, the product expected from [Zn–Cr] LDH ($x = 1/3$) dissolution in acid.[26] This result points to a partial conversion of isolated $Cr(OH)_6$ entities, which are normally separated by ZnO_6 octahedra in the hydroxyl layer, into pairs of OH-bridged $Cr(OH)_6$ octahedra on nta^{3-} intercalation. However, the reactivity of the $[Zn_2–Cr–nta]$ phase towards M^{2+} insertion (M = Cu, Ni) does not appear to be influenced by these slight changes in host structure.

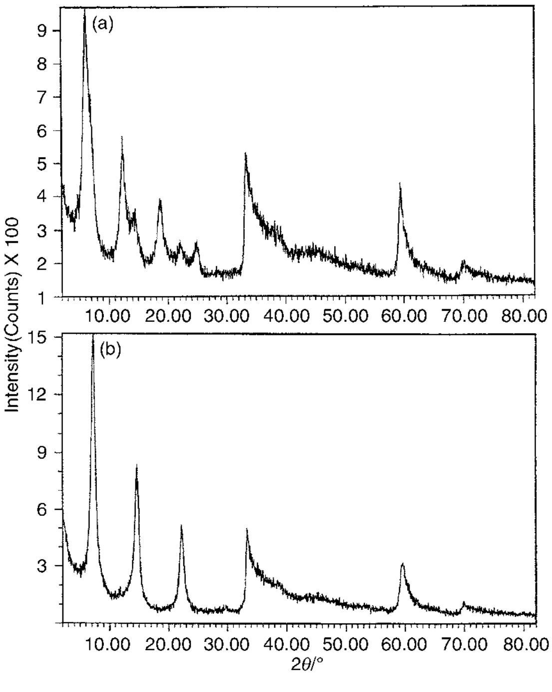

Fig. 4 X-Ray powder diffractograms of $[Zn_2–Cr–nta]$ prepared at: (a) $pH \approx 6.7$ and (b) $pH \approx 11.0$.

Cu^{2+} insertion into $[Zn_2–Cr–nta]$ interlayer. Attempts to coordinate Cu^{2+} to the intercalated nta ligand thereby incorporating the metal ion into the LDH host structure involved reaction of aqueous solutions of the Cu(II) chloride, nitrate, tosylate and sulfate salts with $[Zn_2–Cr–nta]$ samples prepared at $pH \approx 11.0$.

The degree of Cu^{2+} coordination by intercalated nta was >90% when $Cu(NO_3)_2$ and $CuCl_2$ solutions were used. The incorporation of additional anions, NO_3^- and Cl^-, within the interlayer could be confirmed by either an intense $\nu_{as}(NO_3)$ vibration at 1385 cm^{-1} in the FTIR spectrum or by precipitation of AgCl from acidic solution, respectively. In the latter case, metal uptake was also determined by argentometric titration and Cu analysis. The presence of these anions, however, had little effect on the X-ray powder patterns, apart from a slight broadening of the reflections. In order to maintain electroneutrality, the LDH precursor is forced to accommodate two NO_3^- or Cl^- anions per inserted metal ion, which must be located in 'holes' between the pillars of the LDH since the basal spacing is determined by the $[M(nta)]^-$ intercalate. The basal spacing of ≈12.0 Å, exhibited by both salts indicates that, in contrast to direct intercalation, the tilted is formed exclusively. The preferred orientation adopted by the free ligand prior to the metal insertion is preserved on incorporation of the metal, as was observed in Ni^{2+} salt insertion experiments discussed below. The fact that the UV-Vis-NIR reflectance and IR spectra match those for the intercalation compound obtained by direct exchange confirms the formation of Cu–nta intercalates.

For the sulfate salt, the anion was incorporated into the product in preference to the $[Cu(nta)]^-$ complex, despite the lower concentrations used (0.005–0.05 M for sulfate salt *cf.* 0.01–0.1 M for the others). A similar result was obtained when $[Zn_2–Cr–nta]$ was treated with $Cu(tos)_2$ solutions, except for the solution with the lowest concentration. The analysis of the Cu^{2+} and Ni^{2+} intercalated products, which made use of the facile replacement of the complexes by sulfate (see Experimental), indicated some exchange of Cu^{2+} for Zn^{2+} within the hydroxyl layers ($\leqslant 5\%$ in the case of $CuSO_4$ solutions). Stählin and Oswald observed the replacement of Zn^{2+} by Cu^{2+} in $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$, which is also a layered structure.[39]

Ni^{2+} insertion into $[Zn_2–Cr–nta]$ interlayer. The tendency of Ni^{2+} to complex with nta intercalated in the LDH is appreciably lower than Cu^{2+}. For Ni^{2+}, even anions that are normally exchanged easily, *e.g.*, NO_3^- and Cl^-, compete strongly for sites in the interlayer. The data for Ni^{II} incorporation in [Zn_2–Cr–nta] indicate that Cl^- is a stronger competitor than NO_3^-, in good agreement with the selectivity sequence reported by Mendiboure and Schöllhorn[40] and Miyata.[41] Again, the presence of these anions in the final product was proved by the strong $\nu_{as}(NO_3)$ IR band at 1385 cm^{-1} and AgCl precipitation. The powder patterns of the LDH's, generated when solutions of relatively high nickel(II) concentrations were used, exhibit two different series of (001) reflections belonging to the nitrate/chloride and Ni^{II}–nta intercalated phases. The Ni^{II} containing LDH phase, almost free of the [Zn_2–Cr–X] phase ($X = NO_3^-$, Cl^-), could be obtained using low concentration intercalating solutions. The fact that the UV-Vis-NIR and FTIR (Table 1) spectra of the products of indirect intercalation are in good agreement with those for products obtained by the direct method provides strong evidence for the incorporation of Ni^{II}. The XRD patterns of such products indicate that the [Zn_2–Cr–Ni(nta)] phases produced by the indirect method all possess a basal spacing of $\approx$12.0 Å and that the complex adopts the tilted orientation within the interlayer. In contrast, for direct intercalation this orientation was achieved only when intercalation was carried out at high temperatures. The changed orientation of $[Ni(nta)]^-$, observed when the complex is assembled within the interlayer, demonstrates that the orientation of the ligand, adopted in the absence of the metal, can determine the arrangement of the complex formed by subsequent metal insertion.

The lower affinity of [Zn_2–Cr–nta] for Ni^{2+} could be due to the lower stability of the Ni–nta complex, *cf.*, Cu–nta complex, since in aqueous solution it has a slightly lower formation constant than the Cu(II) complex (*viz.*, $pK_{[Cu(nta)]} = 12.94$ and $pK_{[Ni(nta)]} = 11.50$).[35] Since these stability constants are not vastly different, the considerably greater uptake of Cu^{2+} *versus* Ni^{2+} points to increased selectivity being conferred on the system by host–guest interactions between the complex and the hydroxyl layers.

Thus, for the tilted orientation, the Cu^{II} complex adjusts itself to the spatial demands of the OH matrix in the host structure in a better manner than the corresponding nickel complex. For indirect intercalation, $[Ni(nta)]^-$ is forced to adopt a more unfavourable tilted orientation which reduces appreciably its exchange selectivity even against supposedly weaker anions.

Experimental

Preparation

The initial LDH, [Zn_2–Cr–NO_3], used in anion exchange reactions, was obtained by adding slowly a 1 M $Cr(NO_3)_3$ solution to a ZnO suspension (5% by weight) according to published methodologies.[42] NaCu(nta)·H_2O was prepared by mixing appropriate molar equivalents of aqueous solutions of $Cu(NO_3)_2$, H_3nta, and Na_2CO_3 and evaporating slowly to dryness.[23] KNi(nta)·$3H_2O$ was synthesized in a similar way reacting basic nickel(II) carbonate with solutions of H_3nta and KOH.[27]

Synthesis of [Zn_2–Cr–M(nta)]. The exchange of NO_3^- by anionic $[M(nta)(OH_2)_2]^-$ complexes was achieved by suspending about 1 g of the precursor in 20 ml of a 0.1 M aqueous solution of the complex salt. These suspensions were kept for two days at several temperatures with occasional shaking. The supernatant solution was decanted and the solid material was again reacted with a fresh complex salt solution for a further two days at the same temperature as before. The solid was filtered, washed with distilled water and dried at room temperature. *Elemental analysis*: Calc. for $[Zn_2Cr(OH)_6][Cu(nta)(OH_2)_2]\cdot 2H_2O$: Cu 10.4, C 11.8, H 2.3, N 2.3, H_2O 11.8%; Found: Cu 10.1, C 11.7, H 2.7, N 2.2, H_2O 10.7%. Calc. for $[Zn_2Cr(OH)_6][Ni(nta)(OH_2)_2]\cdot 2H_2O$: Ni 9.7, C 11.9, H 2.3, N 2.3, H_2O 11.9%; Found: Ni 9.4, C 11.7, H 2.6, N 2.1, H_2O 10.4% (% H_2O was determined by thermogravimetry).

Synthesis of [Zn_2–Cr–nta]. In this case, 12 g of the nitrate precursor were suspended in 1 L of 0.01 M solution of the nta ligand. Two ligand solutions prepared by mixing solutions of H_3nta and KOH with acid/base ratios of either 1 : 3 or 1 : 2 giving pH $\approx$ 11.0 and pH $\approx$ 6.7, respectively, were used. The suspension was stirred for 24 h at 60 °C. For the exchange reaction carried out at pH $\approx$ 11.0, nitrogen was bubbled through the suspension to avoid competing carbonate intercalation. The supernatant solution was decanted, replaced by fresh nta solution and the reaction continued for a further 24 h under the same conditions. The product was filtered and air-dried at room temperature. IR spectroscopy was used to check the completeness of anion exchange. *Elemental analysis*: pH 6.7 product, calc. for $[Zn_2Cr(OH)_6][Hnta]_{0.5}\cdot 2H_2O$: Zn 32.2, Cr 12.7, C 7.6, H 3.3, N 1.6%; Found: Zn 31.4, Cr 12.5, C 7.7, H 3.3, N 1.7%. pH = 11.0 product, calc. for $[Zn_2Cr(OH)_6][nta]_{0.33}\cdot 2H_2O$: Zn 34.0, Cr 13.2, C 6.2, H 3.0, N 1.3%; Found: Zn 34.1, Cr 13.6, C 6.3, H 3.2, N 1.2%.

Cu^{2+} and Ni^{2+} insertion in [Zn_2–Cr–nta]. In a typical preparation, 2 g of [Zn_2–Cr–nta] prepared at pH $\approx$ 11.0 were suspended in 50 mL of either a Cu^{II} or a Ni^{II} salt solution. The concentration of such solutions varied between 0.005 and 0.05 M. Nitrate, chloride, tosylate and sulfate salts were used in the case of Cu^{2+} insertion whilst nitrate and chloride salts were used in the case of Ni^{2+} insertion. The suspensions were kept at room temperature with occasional shaking. After two days the solid was filtered, washed with distilled water and dried in air at room temperature. The completeness of insertion, defined as the ratio of the moles of Ni inserted to the moles of intercalated ligand, for Ni^{II} intercalation, was as follows: 0.80 for 0.05 M $Ni(NO_3)_2$ solution; 0.92 for 0.005 M $Ni(NO_3)_2$ solution; 0.66 for 0.05 M $NiCl_2$ solution; and 0.86 for 0.005 M $NiCl_2$ solution.

Chemical analysis. The quantitative analysis of Zn^{2+} and Cr^{3+} applied a recently described separation procedure on a strong basic anion exchanger.[30] For phases intercalated with M–nta complexes, which might interfere with the Zn^{2+} and Cr^{3+} analysis, the intercalated complexes were removed from the interlayer by treating the solid with saturated hot $(NH_4)_2SO_4$ solution prior to the separation of Zn^{2+} and Cr^{3+} ions. The solutions containing the extracted complexes were used to determine the amount of intercalated $[M(nta)]^-$ by complexometric metal titration. For this purpose, the chelate ligand present in these solutions was oxidized in a 1 : 1 mixture of 62% nitric acid and 30% hydrogen peroxide[43] before titrating. Samples of [Zn_2–Cr–nta] were subjected to the same procedure in order to remove the interfering nta.

Instrumentation. Thermogravimetric analysis (TG) was performed on a home-built optomagnetically compensating thermobalance. Samples were measured under argon stream (20 mL h^{-1}) at a heating rate of 5 °C min^{-1}. CHN analyses on complex and ligand intercalated materials were carried out on a LECO CHNS-932 analyzer. IR spectra were recorded as KBr pellets on a Perkin Elmer 1600 series IR spectrometer with a 4 cm^{-1} resolution. UV-Vis-NIR diffuse reflectance spectra were recorded on a Cary 5 spectrometer (Varian) using a $BaSO_4$ white standard. Powder X-Ray diffraction patterns were recorded on either a Siemens D-500 or a SCINTAG PAD 5 X-ray powder diffractometer using solid germanium detectors. Ni filtered CuKα radiation with a wavelength of 0.15418 nm was used in both cases and the instruments were calibrated with a Si powder reference supplied by the National Bureau of Standards.

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References

1 A. de Roy, C. Forano, K. El Malki and J.-P. Besse, in *Anionic Clays: Trends in Pillaring Chemistry in Synthesis of Microporous Materials*, ed. M. L. Occelli and H. E. Robson, Van Nostrand Reinhold, New York, 1992, vol. 2, p. 108.

2 I. V. Mitchell, *Pillared Layered Structures: Current Trends and Applications*, Elsevier Science Publishers, Amsterdam, 1990.

3 F. Cavani, F. Trifirò and A. Vaccari, *Catal. Today*, 1991, **11**, 173.

4 M. A. Drezdzon, *Inorg. Chem.*, 1988, **27**, 4628.

5 C. Hu, Q. He and E. Wang, *Prog. Nat. Sci.*, 1996, **6**, 524.

6 R. S. Weber, P. Gallezot, F. Lefebvre and S. L. Suib, *Microporous Mater.*, 1993, **1**, 223.

7 J. Wang, Y. Tian, R.-C. Wang and A. Clearfield, *Chem. Mater.*, 1992, **4**, 1276.

8 F. Kooli and W. Jones, *Inorg. Chem*, 1995, **34**, 51145122; 6237.

9 C. Depège, L. Bigey, C. Forano, A. de Roy and J. P. Besse, *J. Solid State Chem.*, 1996, **126**, 314.

10 S. K. Yun and T. J. Pinnavaia, *Inorg. Chem.*, 1996, **35**, 6853.

11 M. D. Newsham, E. P. Giannelis, T. J. Pinnavaia and D. G. Nocera, *J. Am. Chem. Soc.*, 1988, **110**, 3885.

12 T. Sichi, K. Takagi and Y. Sawaki, *Chem. Lett.*, 1996, 781; *Chem. Commun.*, 1996, 2027.

13 K. Itaya, H.-C. Chang and I. Uchida, *Inorg. Chem.*, 1987, **26**, 624.

14 C. Mousty, S. Therias, C. Forano and J.-P. Besse, *J. Electroanal. Chem.*, 1994, **374**, 63.

15 L. Ikrainczyk, M. Chibwe, T. J. Pinnavaia and S. A. Boyd, *J. Phys. Chem.*, 1994, **98**, 2668.

16 S. Bonnet, C. Forano, A. de Roy and J. P. Besse, *Chem. Mater.*, 1996, **8**, 1962.

17 T. J. Pinnavaia, M. Chibwe, V. R. L. Constantino and S. K. Yun, *Appl. Clay Sci.*, 1995, **10**, 117.

18 F. Kooli, I. C. Chisem, M. Vucelic and W. Jones, *Chem. Mater.*, 1996, **8**, 1969; J.-H. Choy, D.-K. Kim, J.-C. Park, S.-N. Choi and Y.-J. Kim, *Inorg. Chem.*, 1997, **25**, 375; J. Breu and K.-J. Range, *Monatsh. Chem.*, 1994, **125**, 141; J. Breu and C. R. A. Catlow, *Inorg. Chem.*, 1995, **34**, 4504.

19 V. Prevot, C. Forano and J. P. Besse, *J. Mater. Chem.*, 1999, **9**, 155.

20 J. D. Olivier, B. L. Barnett and L. C. Strickland, *Acta Crystallogr.*, 1984, **40**, 377.

21 V. V. Fomenko, T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1975, **16**, 649.

22 V. V. Fomenko, M. A. Kopaneva, M. A. Porai-Koshits and T. N. Polynova, *Zh. Strukt. Khim.*, 1974, **13**, 268.

23 S. H. Whitlow, *Inorg. Chem.*, 1973, **12**, 2286.

24 F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 1723.

25 L. Spiccia, N. H. Gutmann and T. W. Turney, unpublished results.

26 N. H. Gutmann and B. Müller, *J. Solid State Chem.*, 1996, **122**, 214.

27 N. D. Mitrofanova, L. I. Martynenko and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, **10**, 2115.

28 R. Allmann, *Chimia*, 1970, **24**, 99.

29 Y. Tomita and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 1069.

30 N. Gutmann, B. Müller and H.-J. Tiller, *J. Solid State Chem.*, 1995, **119**, 331.

31 Y. Tomita, A. Takeshi and K. Ueno, *J. Phys. Chem.*, 1965, **69**, 404.

32 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.

33 Y. Dou, *J. Chem. Educ.*, 1990, **67**, 134.

34 B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley and P. Nicholls, *J. Chem. Soc. (A)*, 1969, 2312.

35 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum Press, London, 1976, vol. III, p. 139.

36 A. P. Pisarevski, A. I. Yanovskij, Yu. T. Struchkov and Ya. G. Kesel'man, *Koord. Chim.*, 1994, **20**, 35; E. Skrzypczak-Jankun, D. A. Smith and H. Maluszynska, *Acta Crystallogr., Sect. C*, 1994, **50**, 1097.

37 K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, 1962, **84**, 2081; A. I. Grior'ev, N. D. Mitrofanova and L. I. Martynenko, *Zh. Neorg. Khim.*, 1965, **10**, 1409.

38 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

39 W. Stählin and H. R. Oswald, *J. Solid State Chem.*, 1971, **3**, 256.

40 A. Mendiboure and R. Schöllhorn, *Rev. Chim. Miner.*, 1986, **23**, 819.

41 S. Miyata, *Clays Clay Miner.*, 1983, **31**, 305.

42 H.-P. Boehm, J. Steinle and C. Vieweger, *Angew Chem.*, 1977, **89**, 259; H. Kopka, K. Beneke and G. Lagaly, *J. Colloid Interface Sci.*, 1988, **123**, 427; K. El Malki, A. de Roy and J.-P. Besse, *Eur. J. Solid State Inorg. Chem.*, 1989, **26**, 339.

43 Y. Tsuchitani, Y. Tomita and K. Ueno, *Talanta*, 1962, **9**, 1023.