The intercalation of bis-iminodiacetatochromium(III) ion, \([\text{Cr(ida)}_2]^2–\), in the interlayer of ZnAl-layered double hydroxide (LDH) through rehydration of ZnAl(O) mixed oxide and its characterization by XRD, TG-DTA, FT-IR and UV-vis-DRS is described. X-ray diffraction studies reveal the increase of basal spacing in the ZnAl-LDH–Cr(ida) hybrid from 7.69 Å to 12.55 Å due to intercalation of \([\text{Cr(ida)}_2]^2–\), which is also evident from FT-IR and UV-vis-DR spectra. Thermogravimetric analyses show a marginal increase in the decomposition temperature for the \([\text{Cr(ida)}_2]^2–\) moiety with exothermic peaks in the LDH–Cr(ida) hybrid, indicating enhanced thermal stability of the \([\text{Cr(ida)}_2]^2–\) ion in the LDH interlayer. This method may be useful for intercalation of other anionic Cr(III) complexes of biological importance.

**Keywords:** Intercalation, Layered double hydroxides, Layered double hydroxide hybrids, Chromium, Iminodiacetate

Biomolecules, the building block of life, perform a variety of important functions in living organisms. The storage and transfer of various bioactive molecules including drugs at desired biological sites without decomposition or secondary effects have attracted increasing attention in recent years. The biomolecule, introduced as a part of the inert matrix, is released in a controlled way reducing side effects. Despite the improvement experienced in recent years, search for efficient biomolecules containers for their transport and delivery is challenging and continues to be an exciting area of research. In this context, layered double hydroxides (LDHs), synthetic clays with positive layers and interlayer anions, have attracted much attention as the hosts for biomolecules. Bioactive molecules bearing negatively charged ions like antiviral drug molecules, antihistamines, nucleotides, amino acids and peptides, pharmaceutically important anionic metal complexes, etc., can be easily intercalated into the interlayer to form Bio-LDH-nanohybrids. The bio-nanohybrids are electrically neutral and can be transported to the desired sites.

Chromium(III) is an essential trace element for mammalian carbohydrate and lipid metabolism. Several Cr(III) complexes with aminocarboxylate as primary ligand have shown high insulin mimetic activity. Iminodiacetic acid (IDA) and its derivatives are well known chelating agents and have many biological applications. Therefore, intercalation of Cr(III) with iminodiacetic acid as primary ligand in biocompatible hosts like LDH would be interesting. The present study is in continuation of our previous report on in situ intercalation of anionic Cr(III) ascorbate complex in the interlayer of LDH and pertains to intercalation of (iminodiacetato)-chromium(III) in the interlayer of ZnAl-LDH and its characterization by various physicochemical methods.

**Experimental**

ZnAl-LDH with Zn:Al molar ratio 3:1 was prepared by coprecipitation of metal nitrates at pH ~ 10.0 under low supersaturating condition using a mixture of NaOH (2.0 M) and Na$_2$CO$_3$ (0.02 M) solution as the precipitating agent. The small amount of NO$_3$– ion present in the interlayer of as-synthesized ZnAl-LDH precursor was exchanged with CO$_3^{2–}$ ion by treatment with Na$_2$CO$_3$ (0.2 M) solution to ensure that the LDH precursor is free from nitrate ion. The carbonate exchanged LDH precursor, dried in air at 100 °C overnight, was calcined at 450 °C for 6 h to yield the ZnAl(O) mixed oxide and used for intercalation of Cr(III) complex in the interlayer through rehydration. The calcined LDH was used for intercalation of the mono-anionic complex instead of the LDH-NO$_3$– ion and also for easy intercalation of Cr(ida)$_2$– ion.

K[Cr(ida)$_2$].3H$_2$O was prepared by following the method reported earlier. The purity of the complex was checked by elemental and spectral (UV-vis) analyses which agreed well with the theoretically calculated value and that reported in literature, respectively. For intercalation of [Cr(ida)$_2$] in the interlayer, a slight excess of the stoichiometric amount of Cr(III) complex, required as the sole interlayer charge balancing anion in LDH-Cr(ida) hybrid, was dissolved in a minimum volume of
carbonate-free distilled water. A weighed amount of ZnAl(O) was dispersed in to it and pH of the resulting slurry was checked. The pH was found to be ~ 5.89 and hence the pH was not adjusted by addition of either dilute NaOH or HCl. The suspension was aged at room temperature with continuous stirring under N\textsubscript{2} atmosphere for 10 h. The red colour of the solution slowly faded away indicating intercalation of [Cr(ida)\textsubscript{2}]\textsuperscript{−} complex in the interlayer. The solid was finally separated by centrifugation, washed thoroughly with distilled water, dried in vacuum and stored in a desiccator over silica gel.

All the chemicals and reagents used were of analytical grade.

Zn, Al, Cr contents were determined by conventional wet chemical analysis and also by atomic absorption spectrometer (Avanta, GBC) using appropriate flames. C and N was analysed by Euro EA Vector elemental analyser.

Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex II X-ray diffractometer at a scanning speed of 1°(2\texttheta)/min with step 0.02° using Ni filtered Cu-K\textalpha\ radiation. Thermogravimetric measurements under N\textsubscript{2} flow (40 mL/min) were performed on a Shimadzu DT 60 thermal analyser at a heating rate of 10 °C/min. FT-IR spectra of different samples in KBr pellets were collected using a Shimadzu (IR Affinity 1) FT-IR spectrophotometer in absorption mode averaging 44 scans and at a resolution of 4 cm\textsuperscript{-1}. The UV-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a Shimadzu UV-visible spectrophotometer using BaSO\textsubscript{4} white standard.

Results and discussion

The molar ratio of Zn: Al: Cr in the LDH-Cr(ida) hybrid, derived from chemical analyses, is found to be 0.748: 0.251: 0.212. Assuming that the nitrogen content in LDH-Cr(ida) hybrid results solely from the ida moiety of intercalated Cr(III) complex, the observed molar ratio of nitrogen and Cr contents (2:1) agrees well with that expected from [Cr(ida)\textsubscript{2}]\textsuperscript{−} ion. Slightly lower value of Cr in the molar ratio of Cr:Al indicates that the entire interlayer negative charge is not balanced by the monoanionic Cr(III) complex; rather a small amount is compensated by CO\textsubscript{3}\textsuperscript{2−} or hydroxide ions. In fact, the value of carbon content in LDH-Cr(ida) hybrid is also found to be higher than that expected from the intercalated Cr(III) ida complex alone.

The powder XRD patterns of ZnAl-LDH precursor, its calcined product and LDH-Cr(ida) hybrid are shown in Fig. 1. The XRD pattern of the ZnAl-LDH precursor exhibits the typical reflection of a pure LDH phase (LDH: JCPDS file no. 38-487) with basal spacing (d\textsubscript{003}) value 7.69 Å, which is very similar to that reported earlier\textsuperscript{12,13}. On calcination at moderate temperature (450 °C), the layered structure of LDH precursor is destroyed leading to formation of ZnAl(O) mixed oxides of ZnO type structure. The lattice 'a' parameter of the mixed oxide is slightly smaller than that of pure ZnO\textsuperscript{13} (a = 2.093 Å), indicating isomorphous substitution of Al\textsuperscript{3+}. As expected the peak positions corresponding to (003), (006) and (009) reflections are clearly shifted to lower 2\texttheta values in the rehydrated LDH intercalated with Cr(III) complex. Accordingly the basal spacing (d\textsubscript{003}) is increased to 12.55 Å. This increase of basal spacing from 7.69 Å in ZnAl-LDH to 12.55 Å in LDH-Cr(ida) hybrid indicates the intercalation Cr(ida)\textsubscript{2−} in the interlayer of rehydrated ZnAl-LDH. Taking into account the thickness of brucite-like layer of ZnAl-LDH to be 4.8 Å as reported by Cavani et al.\textsuperscript{12}, the gallery height (interlayer spacing) of LDH-Cr(ida) was found to be 7.75 Å, which is slightly more than that obtained (7.5 Å) on intercalation of iminodiacetate dianion in the interlayer of MgAl-LDH\textsuperscript{6}. On the other hand, the gallery height in the present case is relatively higher than that obtained (5.72 Å) by \textit{in situ} intercalation of anionic Cr(III) ascorbate complex in the interlayer of...
MgAl-LDH\textsuperscript{11}. Moreover, the crystallinity of rehydrated sample intercalated with Cr(ida)\textsubscript{2}\textsuperscript{−} ion is less than that of parent ZnAl-LDH precursor, as also observed by in a previous study on intercalation of Cr(III) ascorbate complex\textsuperscript{11}.

The TG-DTA curves of both K[Cr(ida)\textsubscript{2}] and LDH-Cr(ida) hybrid are shown in Fig. 2. The neat Cr(III) complex primarily exhibits two stage weight loss in the temperature range 30-290 and 300-450 °C. The first stage weight loss (~ 14.1 %) with endothermic peaks centered at 90 °C and 190 °C corresponds to loss of three structural water molecule while the second stage loss (~ 44.6 %) may be attributed to the decomposition of ida moiety leading to formation of K\textsubscript{2}O and Cr\textsubscript{2}O\textsubscript{3} as the final products. The total weight loss agrees well the theoretically calculated value according to the following transformation:

\[
2K[Cr(ida)\textsubscript{2}].3H\textsubscript{2}O \rightarrow 6H\textsubscript{2}O + K\textsubscript{2}O + Cr\textsubscript{2}O\textsubscript{3} + \text{product from ida} \quad (1)
\]

The LDH-Cr(ida) hybrid also exhibit two stage weight loss in the temperature range 25-200 °C and 250-450 °C, which is similar to those shown by ZnAl-LDH precursors\textsuperscript{11}. However, the total weight loss is about 8.0 % more than that normally observed with ZnAl-LDH precursor with Zn:Al ratio 3:1 (~ 32 %) due to intercalation of [Cr(ida)\textsubscript{2}]\textsuperscript{−} in the interlayer\textsuperscript{12,13}. The first weight loss (3.5 %) accompanied by a broad endothermic peak centred at 120 °C is as usual attributed to removal of physisorbed water molecules of LDH. The second weight loss in overlapping stages (~ 37.16 %) with endothermic peak at ~ 250 °C followed by multiple exothermic peaks is attributed to dehydroxylation of brucite-like layer and decomposition of the ida moiety of Cr(III) complex. It may be noted that ZnAl-LDH precursor primarily exhibits two stage weight loss with only endothermic peaks\textsuperscript{13}. The multiple exothermic peaks in the case of LDH-Cr(ida) is due to predominance of the large exothermic peaks during decomposition of Cr(III) complex over relatively less prominent endothermic peak arising out of dehydroxylation of brucite-like layer. Marginal shift (~ 10 °C) towards higher temperature in exothermic peak positions in the case of LDH-Cr(ida) hybrid from that of neat [Cr(ida)\textsubscript{2}]\textsuperscript{−} is indicative of the higher stability of [Cr(ida)\textsubscript{2}]\textsuperscript{−} in LDH-Cr(ida) hybrid, presumably due to further coordination of free oxygen end or hydroxide of brucite layer, respectively\textsuperscript{14}.

Intercalation of [Cr(ida)\textsubscript{2}]\textsuperscript{−} in the interlayer is further evident from the UV-vis-DR and FT-IR spectra. The UV-vis-DRS of LDH-Cr(ida) hybrid along with that of K[Cr(ida)\textsubscript{2}] is presented in Fig. 3. The K[Cr(ida)\textsubscript{2}] complex exhibits three characteristic absorption maxima at 230, 400 and 540 nm, corresponding to spin allowed, Laporte forbidden transitions from the fundamental state \( ^4T\textsubscript{2g} \rightarrow ^4T\textsubscript{2g} \) (F), \( ^4T\textsubscript{2g} \rightarrow ^4T\textsubscript{1g} \) (F) and \( ^4T\textsubscript{2g} \) (P) respectively\textsuperscript{11,15}. On intercalation in the interlayer of ZnAl-LDH, the absorption maxima of all the peaks are shifted to higher wavelengths by 5 – 40 nm. The FT-IR spectra of K[Cr(ida)\textsubscript{2}] and LDH-Cr(ida) hybrid...
are shown in Fig. 4. The observed bands in the range 3550-3400 cm\(^{-1}\) in both K[Cr(ida)\(_2\)] and LDH-Cr(ida) hybrid correspond to –OH stretching mode of H\(_2\)O/structural –OH group. Appearance of absorption band at 3250-3100 cm\(^{-1}\) in K[Cr(ida)\(_2\)] is attributed to \(\nu\)N-H stretching of ida\(^5\), while the peaks in the same range in the case of LDH-Cr(ida) hybrid is merged with the broad peak due to hydrogen bonding of –OH group with carboxylate of ida moiety or due to the small amount of carbonate ion in the interlayer. The bands at 1607 and 1393 cm\(^{-1}\) in K[Cr(ida)\(_2\)] are mainly attributed to asymmetric and symmetric stretching vibrations of COO\(^-\) (\(\nu\)COO\(^-\)) of ida moiety, respectively. Appearance of both these peaks in the case of LDH-Cr(ida) hybrid with marginal shift (~10 cm\(^{-1}\)) toward lower frequencies, due to hydrogen bonding with free oxygen end of coordinated ida, provides further evidence in favour of intercalation of [Cr(ida)\(_2\)] in the interlayer of ZnAl-LDH.

A preliminary study on the release profile of intercalated ida complex shows that the exchange of ida complex is reversible. Treatment of LDH-Cr(ida) hybrid with phosphate buffer saline (pH ~ 7.4) at 35 °C for 2 h followed by estimation of the Cr(III) complex released by AAS indicates that about 90 % of the intercalated [Cr(ida)\(_2\)] is released. Further study is required for detailed release profile of [Cr(ida)\(_2\)] from the interlayer.

**Acknowledgement**

Financial assistance for infrastructural development in the Department of Chemistry, North Orissa University, Baripada, Orissa, India, from DST (FIST) and UGC (SAP) are gratefully acknowledged.

**References**