Inorg. Chem. **2004**, *43*, 6421–6425

Inorganic Chemistry
Article

Insertion of Iodine in a Functionalized Inorganic Layered Solid

L. Mohanambe and S. Vasudevan*

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore-560012, India

Received April 1, 2004

The galleries of a Mg–Al layered double hydroxide have been functionalized by intercalation of (carboxymethyl)-β-cyclodextrin cavities. The functionalized inorganic solid can adsorb iodine molecules from vapor as well as nonaqueous and aqueous solutions. The adsorbed iodine complexes with the grafted cyclodextrin cavities, disassociating heterolytically to form polyiodide species. Electronic and Raman spectra provide conclusive evidence for the existence of linear symmetric triodide, I_3^-, and pentaiodide, I_5^-, species within the cyclodextrin cavities confined in the layered double hydroxide.

Introduction

The ability to accommodate guest molecules in their interlamellar space is perhaps the most unique feature of the chemistry of layered inorganic solids.[1] In a majority of these solids the interaction between host and guest is Coulumbic, with the guest species compensating for the charge deficit, either positive or negative, of the inorganic layer. Typical examples of these solids are the phyllosilicate clays, the layered double hydroxides, the divalent metal thiophosphates, and the metal(IV) phosphates and phosphonates.[1,2] The subsequent host−guest chemistry of these intercalated solids is restricted to exchange of the interlamellar charged species for other ions and, to a limited extent, adsorption of polar molecules, e.g., crown ethers[3] and poly(ethylene oxide),[4,5] through ion−dipole interactions. The host−guest chemistry of these solids can, however, be extended to include nonpolar molecules by appropriate functionalization of the internal surface of the solid. It is well established that grafting of long-chain surfactant molecules to the walls of the galleries, to form intercalated bilayers, allows for the solubilization of a wide variety of neutral organic molecules in the hydrophobic interior of the bilayer.[6−9]

Host structures are, of course, not limited to inorganic solids; a variety of organic hosts are known, the most well-known of which are the crown ethers, cyclodextrins, calixarenes, and spherands.[10] In principle, if the two host structures, the layered inorganic solid and the organic host, can be integrated, a new family of host structures can be envisaged. Indeed, such structures have been realized; modified cyclodextrins have been successfully intercalated in montmorillonite clays,[11] zirconium phosphates,[12] and layered double hydroxides[13] to create a new generation of host structures. Cyclodextrins, herein abbreviated as CDs, are cyclic oligomers of D-glucopyranose ($C_6H_{10}O$) with cylindrical hydrophobic cavities into which a variety of small molecules may be introduced.

Layered double hydroxides (LDHs), the so-called anionic clays, consist of positively charged brucite-like layers and interlamellar exchangeable anions.[14] Hydrotalcites are layered double hydroxides with the chemical composition $[Mg_{1-x}Al_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$ (Mg−Al LDH) that consists of positively charged layers constructed from edge-sharing $Mg(OH)_6$ and $Al(OH)_6$ octahedra.[15−18] The positive

---

* Author to whom correspondence should be addressed. E-mail: svipc@ipc.iisc.ernet.in.

(1) *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.
(2) Alberti, G.; Costantino, U. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Wiley: Chichester, U.K., 1996; Vol. 7, p 1.
(3) Gluech, D. S.; Brough, A. R.; Mountford, P.; Green, M. L. H. *Inorg. Chem*. **1993**, *32*, 1893.
(4) Aranda, P.; Ruiz Hitzky. *Adv. Mater*. **1990**, *2*, 545.
(5) Jeevanandam, P.; Vasudevan, S. *Chem. Mater*. **1998**, *10*, 1276.
(6) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 2593.
(7) Venkataraman, N. V.; Mohanambe, L.; Vasudevan, S. *J. Mater. Chem.* **2003**, *13*,170.
(8) Venkataraman, N. V.; Vasudevan, S. *J. Phys. Chem. B* **2003**, *107*, 5371.
(9) Wouter, L.; Pinnavaia, T. J. *Green Chem.* **2001**, *3*, 10.
(10) (a)Vogtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 1991. (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
(11) Kijima, T.; Tanaka, J.; Goto, M.; Matsui, Y. *Nature* **1984**, *310*, 45.
(12) Kijima, T.; Matsui, Y. *Nature* **1986**, *322*, 533.
(13) Zhao, H.; Vance, G.F. *J. Chem. Soc., Dalton. Trans*. **1997**, *11*, 1961.
(14) Khan, I.K.; Hare, D.O. *J. Mater. Chem.* **2002**, *12*, 3191.
(15) Constantino, V. R. L.; Pinnavaia, T. J. *Inorg. Chem*. **1995**, *34*, 883.
(16) Miyata, S. *Clays Clay Miner*. **1977**, *25*, 14.

10.1021/ic0495721 CCC: $27.50

charge of the layers is compensated for by interlayer anions that are usually hydrated. The interlayer anion can be exchanged for other inorganic or organic anions, thus imparting new functionality to the LDH. For example, the NO_3^- ions in $[Mg_{1-x}Al_x(OH)_2][NO_3]_x$ may be exchanged for halide ions such as I^- to give $[Mg_{1-x}Al_x(OH)_2][I]_x$. It is this anion-exchange capability of the LDHs that has been investigated for many years. They have been used as catalysts and catalyst precursors, as sorbents and scavengers for halogens and weak acids,[19−23] and more recently for storing and delivering biologically active materials.[24,25] The guest species, however, have, out of necessity, to be anions for charge neutrality to be preserved, and as a consequence, the host−guest chemistry of the LDHs is limited to ion-exchange reactions. Insertion of neutral, nonpolar or poorly water soluble guest molecules is not possible. Here we show that, when the internal surface of a Mg−Al LDH is functionalized by grafting cyclodextrin cavities to the gallery walls, the LDH can adsorb iodine from vapor as well as from polar and nonpolar solutions. Insertion occurs by the complexation of iodine by the intercalated cyclodextrin cavities.

Experimental Section

Preparation and Characterization. $Mg_{1-x}Al_x(OH)_2(NO_3)_x$-[LDH-$NO_3$] was prepared by coprecipitation by dropwise addition of known volumes of aqueous $Mg(NO_3)_2$(0.04 M) and $Al(NO_3)_3$-(0.02M) into NaOH at a constant pH of 8, under a N_2 atmosphere, following the procedure reported by Meyn et al.[26] The resulting white precipitate was aged for 24 h prior to washing with decarbonated water. The grafting of β-cyclodextrin cavities within the Mg−Al LDH was achieved by ion-exchanging the NO_3^- ions in $Mg_{1-x}Al_x(OH)_2(NO_3)_x$ with methyl carboxylate-derivatized β-cyclodextrin ions. The sodium salt of (carboxymethyl)-β-cyclodextrin, $C_{42}H_{70-n}O_{35}(CH_3COONa)_n$ (CMCD), was obtained from Cerestar Co. (Hammond, IN). The average number of carboxylate groups per β-CMCD molecule, as established by pH titrations, is 3.8. The ion-exchange intercalation of β-CMCD in the LDH was effected following the procedure of ref 13. A 100 mg sample of LDH-NO_3 was added to 10 mL of a 10 mM aqueous β-CMCD solution at 65 °C, and the resulting solution was stirred for 24 h. Completion of the intercalation of the β-CMCD was confirmed by the absence of 00*l* reflections with a basal spacing of 8.9 Å in the powder X-ray diffraction (Shimadzu XD-D1, Cu Kα) and the appearance of a new set of 00*l* reflections with a basal spacing of 24.6 Å. The β-CMCD stoichiometry in the LDH was established from C, H, N elemental analysis (C, 18.9; H, 5.06) and also by estimation of the unexchanged β-CMCD in the reactant solution. Mg/Al ratios in the LDH were determined by inductively coupled plasma spectroscopy (Jobin Yvon JY24). The composition of the starting LDH-NO_3 was $Mg_{0.7}Al_{0.3}(OH)_2(NO_3)_{0.3}$, and that of LDH-CMCD was $Mg_{0.7}Al_{0.3}(OH)_2(CMCD)_{0.073}$.

Inclusion of iodine in LDH-CMCD was effected by three different routes: (i) exposure of the solid LDH-CMCD to iodine vapor, (ii) adsorption from a nonaqueous solution of iodine, e.g., iodine in CCl_4, and (iii) adsorption from an aqueous solution of iodine. The reaction, in all three cases, was carried out at room temperature and allowed to equilibrate for 24 h. In the first route iodine crystals and LDH-CMCD were placed in the two arms of a sealed glass U-tube and allowed to equilibrate at room temperature. The inclusion was rapid as could be judged from the change in color of the solid LDH-CMCD from white to yellow and finally brown within a period of 30 min. A similar experiment carried out with the starting Mg−Al LDH (NO_3) showed no change in color even after extended exposure (24 h) to iodine vapor. The adsorption isotherm for uptake of iodine from aqueous solutions was obtained by monitoring the absorbance at $\lambda \approx 460$ nm by UV−vis spectroscopy. The adsorption measurements were made after 2 mg of LDH-CMCD was allowed to equilibrate with 10 mL of iodine solution with a concentration varying from 2.36 to 0.786 mM for a period of 24 h. The maximum uptake was 2.45 I_2 molecules per grafted cyclodextrin cavity. This corresponds to a chemical composition of $[Mg_{0.7}Al_{0.3}(OH)_2][CMCD]_{0.073}(I_2)_{0.179}$ (LDH-CMCD−I_2).

Measurement Techniques. Absorbance spectra of the solid samples were recorded on a Hitachi U3000 UV−vis spectrophotometer. The powder X-ray diffraction pattern of LDH-NO_3, LDH-CMCD, and LDH-CMCD−iodine was recorded on a Shimadzu XD-D1 X-ray diffractometer using Cu Kα radiation of $\lambda = 1.54$ Å. The samples were mounted by pressing the powders on a glass plate, and the data were collected at a scan speed of $2\theta = 2°$/min. FT-IR spectra were recorded as KBr pellets on a Bruker IFS55 spectrometer operating at 4 cm^{-1} resolution. FT-Raman spectra were recorded on a Bruker IFS FT-Raman spectrometer using a Nd:YAG ($\lambda = 1064$ nm) laser for excitation. Spectra were recorded at a resolution of 4 cm^{-1} with an unpolarized beam using an Al sample holder. The laser power was kept at 150 mW. ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR was recorded on a Bruker DSX-300 solid-state spectrometer at a Larmor frequency of 75.46 MHz with a contact time of 1 ms. The spectra were externally referenced to tetramethylsilane (TMS). C, H, N analysis was performed on a CHNS (Carlo Erba) elemental analyzer.

Results and Discussion

The ion-exchange intercalation of β-CMCD, with an average degree of carboxymethyl substitutions of 3.8 per cyclodextrin molecule, in $Mg_{0.7}Al_{0.3}(OH)_2(NO_3)_{0.3}$ occurs with an increase in the interlayer lattice spacing from 8.9 to 24.6 Å (Figure 1a). The latter corresponds to a separation of the brucite layers by 19.8 Å. The ion exchange is complete; the stoichiometry as established by elemental analysis is $[Mg_{0.7}Al_{0.3}(OH)_2][CMCD]_{0.073.}$ Completion of the ion exchange was also verified by the absence of the bands due to the NO_3^- ion in the infrared and Raman spectra and the presence of bands due to the carboxylate (COO^-) anion of the intercalated β-CMCD (see the Supporting Information). The ^{13}C CP-MAS NMR spectrum of LDH-CMCD and that of the sodium salt of β-CMCD are shown in Figure 1b along with the assignments for the resonances. The positions of the resonances in the two compounds are identical, indicating that the integrity of the cyclodextrin cavity is preserved on intercalation. This was further confirmed by the fact that the

---

(17) Miyata, S. *Clays Clay Miner*. **1983**, *31*, 305.
(18) Miyata, S. *Clays Clay Miner*. **1975**, *23*, 369.
(19) De Roy, A.; Forano, C.; El Malki, K.; Bessi, J. P. *Expanded Clays and Other Microporous Solids*; Occelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 2, 108.
(20) Cavani, F.; Trifiró, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.
(21) Newman, S.; Jones, W. *New J. Chem*. **1998**, *22*, 105.
(22) Vaccari, A. *Appl. Clay Sci.* **1999**, *14*, 161.
(23) Rives, V.; Ulibarri, M. *Coord. Chem. Rev.* **1999**, *181*, 61.
(24) Choy, J. H.; Kwak, S.Y.; Park, J.S.; Jeong, Y.J.; Portier, J. *J. Am. Chem. Soc.***1999**, *121*, 1399.
(25) Choy, J. H.; Kwak, S. Y.; Jeong, Y. J.; Park, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4042.
(26) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201.

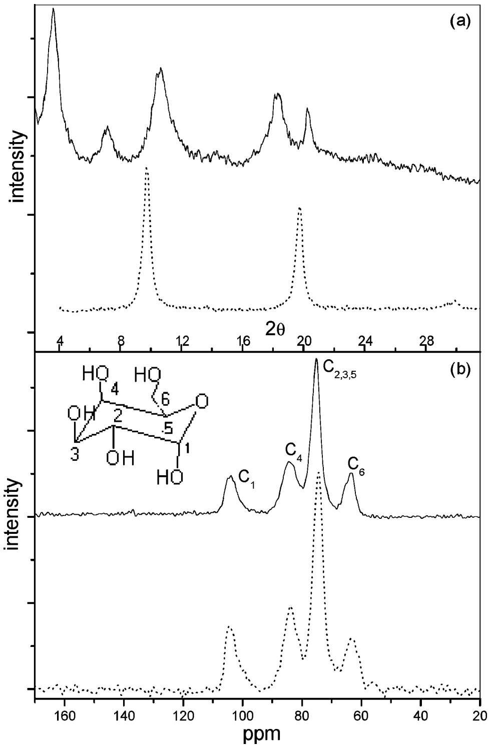

Figure 1. (a) X-ray diffraction pattern of LDH-NO_3 (dotted line) and LDH-CMCD. (b) ^{13}C CP-MAS NMR spectra of LDH-CMCD and the sodium salt of β-CMCD (dotted line).

positions of the infrared and Raman bands of the two compounds were identical (see the Supporting Information). The intercalated LDH-CMCD is stable on exposure to the atmosphere as well as moisture, and the grafted β-CMCDs are no longer exchangeable, e.g., with carbonate ions.

The observed lattice expansion and stoichiometry can be accounted for by a perpendicular bilayer arrangement of the cyclodextrin molecules in the galleries, with the axis of the cyclodextrin cavities parallel to the interlayer normal. The β-cyclodextrin molecule may be considered as a truncated cone with an approximate torus thickness of 7.8 Å.[10] The outer diameter of the wider end of the cone is 15.4 Å, while that of the narrower end is 7.8 Å. The carboxymethyl groups are attached by substitution of the primary hydroxyl groups located at the narrower end of the truncated cone.[10] Molecular modeling shows that the presence of the carboxymethyl groups increases the effective torus thickness by 1.46 Å.[27] The perpendicular bilayer arrangement would therefore result in an interlayer expansion of 18.52 Å, which is close to the experimental value of 19.8 Å. The stoichiometry of the functionalized LDH $[Mg_{0.7}Al_{0.3}(OH)_2][CMCD]_{0.073}$ too can support such an assignment. Assuming a hexagonal close packing of the β-CMCDs grafted to a layer, the effective area per molecule is $(\sqrt{3}/2)(15.4)^2$ or 205 Å^2. The area of the unit cell of the brucite layer is $(\sqrt{3}/2)(3.05)^2$ or 8.05 Å^2. Hence, the maximum value of "x" for a perpendicular bilayer arrangement is $x = (8.05 \times 2)/205 = 0.078$. The observed stoichiometry of $x = 0.073$ is well within the requirements of a close-packed bilayer arrangement while also satisfying charge neutrality. We propose a model shown in Figure 2 as the possible arrangement of grafted cyclodextrin cavities in the galleries of Mg−Al LDH. For this model, the average distance between the centers of the cyclodextrin cavities is ~17 Å and the volume fraction of the galleries occupied by the cyclodextrin cavities is ~50%.

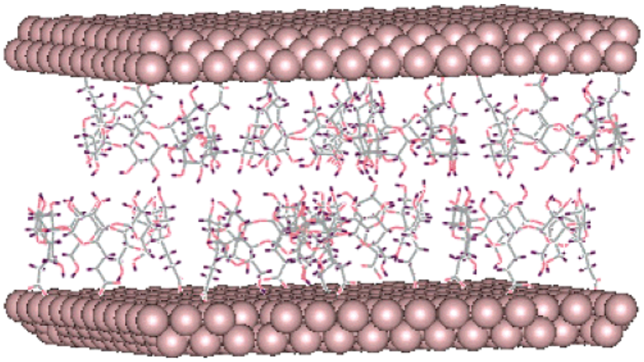

Figure 2. A model representing the arrangement of grafted CMCD molecules within the galleries of a Mg−Al LDH.

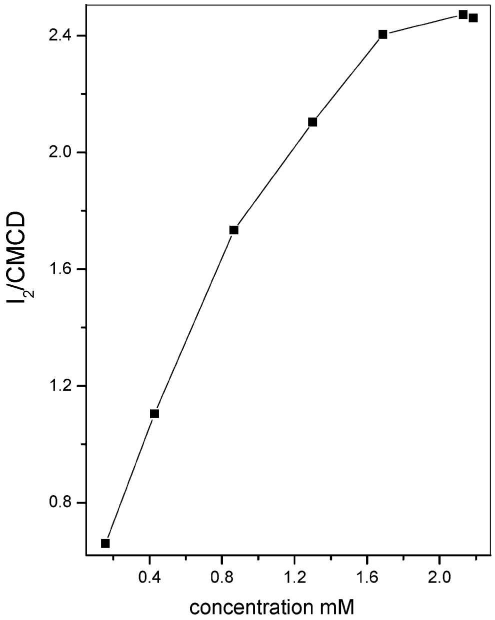

Figure 3. Adsorption isotherm for the inclusion of iodine in LDH-CMCD from an aqueous I_2 solution.

Adsorption Isotherm. Inclusion of iodine in LDH-CMCD was achieved by three different routes: (i) exposure of the solid LDH-CMCD to iodine vapor, (ii) adsorption from a nonaqueous solution of iodine, e.g., iodine in CCl_4, and (iii) adsorption from an aqueous solution of iodine. In all three cases the inclusion was rapid as could be judged from the change in color of the solid LDH-CMCD from white to yellow and finally brown. The starting LDH-NO_3 when exposed to I_2 vapor or when treated with I_2 solutions, under similar conditions, showed no change in color. The adsorption isotherm at 298 K for the uptake of iodine from aqueous solution by LDH-CMCD is shown in Figure 3. The amount of iodine adsorbed by the intercalated β-CMCD, expressed as the molar ratio of adsorbed iodine to grafted β-CMCD (henceforth referred to as the iodine/CMCD ratio), is plotted as a function of the concentration of iodine in the aqueous

---

(27) InsightII, v.4.0.0.P+, Molecular-modelling system, Molecular Simulations Inc., 1998.

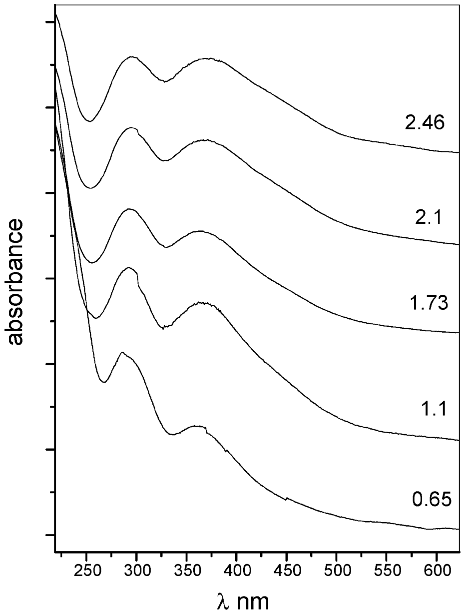

Figure 4. UV−vis spectra of LDH-CMCD−I_2 for different I_2/CMCD ratios as indicated in the figure.

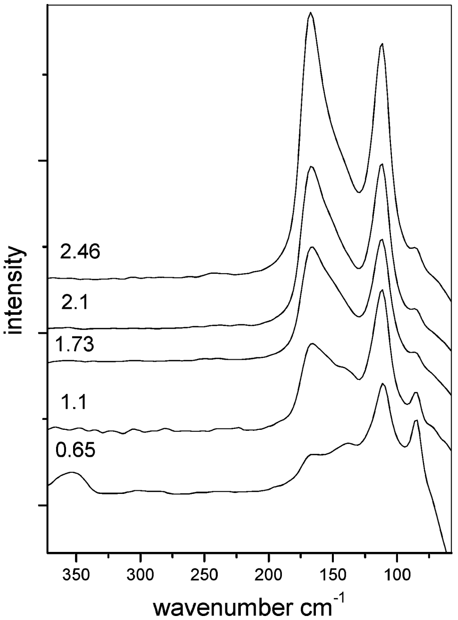

Figure 5. Raman spectra of LDH-CMCD−I_2 for different I_2/CMCD ratios.

solution. The maximum iodine uptake was 4.9 iodine atoms per intercalated cyclodextrin cavity. The X-ray diffraction pattern of LDH-β-CMCD showed no change on inclusion of iodine; the pattern was identical to that in Figure 1a. Insertion of iodine does not lead to any change in the composition of the host LDH-CMCD. Thermogravimetric measurements showed that the iodine inclusion compounds were thermally stable up to 550 K, at which temperature the parent LDH-CMCD decomposes. Thermal stability could also be ascertained by the fact that the yellow-brown color is retained even after heating to 500 K, which also rules out the possibility of iodine sticking to the outer surface of the LDH.

Electronic Spectra. The UV−vis spectra of the products of the three routes are identical. The UV−vis electronic spectra of LDH-CMCD−I_2 for different I_2/CMCD ratios are shown in Figure 4. Surprisingly, although the compounds were prepared by adsorption of neutral iodine, either from vapor or solution, bands due to I_2 (~460 nm) are not seen. The spectra of LDH-CMCD−I_2 with a I_2/CMCD ratio of 0.65 show two absorption maxima at 294 and 362 nm. These bands are characteristic of the triodide, I_3^-, species; the transitions correspond to the spin- and symmetry-allowed $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions of the linear, $D_{\infty h}$ or $C_{\infty v}$, I_3^- ion.[28] The analogous $\sigma_g \rightarrow \sigma_u^*$ and $\pi_g \rightarrow \sigma_u^*$ transitions of the I_2^- ion expected at 380 and 690 nm[29] are absent, and consequently, the presence of this species may be ruled out. The spin-forbidden singlet−triplet transitions of the I_3^- ion, expected at ~440 and ~560 nm, are not seen, indicating that the linear I_3^- ion is in a highly symmetric environment in the LDH-CMCD. These bands are known to show significant enhancement in intensity when the symmetry of the I_3^- ion is lowered, e.g., in the solid state.[28]

With increasing I_2/CMCD ratio the UV−vis spectra (Figure 4) of LDH-CMCD−I_2 show increasing intensity and broadening of the band at 362 nm. For the highest iodine content compound (I_2/CMCD = 2.45) the band is red-shifted to 375 nm and the broadening skewed toward higher wavelengths. These changes indicate the formation of polyiodide species.[30]

Vibrational Spectroscopy. Raman vibrational spectroscopy provided complimentary evidence for the existence of triodide and polyiodide species in LDH-CMCD−I_2. Attention is focused on the low-frequency Raman spectra since it is well established that features in this region are characteristic of the nature and symmetry of polyidide species.[31] The inclusion of iodine does not lead to any change in the position of the infrared and Raman vibrational modes of the intercalated cyclodextrin (see the Supporting Information). The Raman spectra of LDH-CMCD−I_2 for different I_2/CMCD ratios from 0.65 to 2.46 are shown in Figure 5. The low-frequency Raman spectrum of the I_2/CMCD = 0.65 compound shows an intense band at 110cm^{-1} and a weak band at 137 cm^{-1} (the low-frequency band at 85 cm^{-1} is due to the LDH). These features are the characteristic signature of the triodide ion.[32] The I_3^- ion has three vibrational modes—the symmetric, ν_1 (110 cm^{-1}), and antisymmetric, ν_2 (140 cm^{-1}), stretching modes and a bending, ν_3, mode (70 cm^{-1}) which is usually very weak (the figures in parentheses are typical band positions[33]).

For a linear symmetric I_3^- ion the antisymmetric, ν_2, mode is infrared allowed but Raman forbidden, whereas for the linear asymmetric ion both stretching modes are Raman allowed. The fact that in the Raman spectra of LDH-

---

[28] Gabes, W.; Stufkens, D. J. *Spectrochim. Acta: Part A: Mol. Biomol. Spectrosc.* **1974**, *30A*, 1835.

[29] Howard, W. F.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 6.

[30] Heyde, M. E.; Rimai, L.; Kilponen, R. G.; Gill, D. *J. Am. Chem. Soc.* **1972**, 5222.

[31] Nour, E. M.; Chen, L. H.; Laane, J. *J. Phys. Chem.* **1986**, *90*, 2841.

[32] Klaboe, P. *J. Am. Chem. Soc.***1967**, *89*, 3667.

[33] Maki, A. G.; Forneris, R. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.* **1967**, *23A, 867*.

CMCD−I_2 the ν_1 band (110 cm^{-1}) is intense while the ν_2 band (137 cm^{-1}) weak implies that the I_3^- ion in the grafted β-CMCD cavities is linear and symmetric. At higher I_2/CMCD ratios a new band at 167 cm^{-1} appears in the Raman spectra that grows in intensity with increasing iodine content (Figure 5). This band is assigned to the Raman-allowed ν_1 symmetric stretching (outer) mode of a linear symmetric I_5^- species.[31] The Raman-allowed ν_2 symmetric stretch (inner) of the linear I_5^-, expected below 70 cm^{-1}, is obscured by the LDH modes. The Raman spectra of the I_2/CMCD = 2.46 LDH-CMCD−I_2 compound shows the presence of both I_3^- and I_5^- species. The results of the Raman spectra are in agreement with the observations of the electronic spectra of LDH-CMCD−I_2.

Conclusions

The internal surface of Mg−Al LDH can be functionalized by ion-exchange intercalation of (carboxymethyl)-β-cyclodextrin cavities. The structural integrity of the cyclodextrin cavity is preserved even after grafting to the gallery walls. We have shown here that the functionalized LDH can adsorb neutral I_2 molecules from vapor as well as from polar and nonpolar solutions. Insertion occurs by the complexation of the iodine molecules by the grafted cyclodextrin cavities. UV−vis and Raman spectra provide conclusive evidence for the existence of linear, symmetric, triodide, I_3^-, ions when iodine is included within cyclodextrin cavities grafted in a Mg−Al LDH. At higher iodine content polyiodide species, such as the linear I_5^-, are formed.

The iodine inclusion chemistry of cyclodextrin confined in the galleries of the layered solid $Mg_{0.7}Al_{0.3}(OH)_2$ LDH is similar to that of cyclodextrin in solution where, too, the presence of triodide species has been reported,[34,35] following heterolytic disassociation of I_2. The inclusion reaction may, therefore, be represented, as in the case of cyclodextrin in solution,[36] as

$$\text{(LDH-cyclodextrin)} + 2I_2 \rightarrow \text{(LDH-cyclodextrin}-I^+)\cdots I_3^-$$

$$\text{(LDH-cyclodextrin}-I^+)\cdots I_3^- + I_2 \rightarrow \text{(LDH-cyclodextrin}-I^+)\cdots I_5^-$$

Similar reactions are known to occur between iodine and amylase[36] as well as oxygen- and nitrogen-containing macrocycles.[36] The polyiodide species I_3^- and I_5^- present in LDH-CMCD−I_2 are not ion-exchangeable with other anionic species, indicating that they are associated with the grafted cyclodextrin cavities. The absence of the blue color, typical of the iodine−amylase complexes,[37] implies that I_3^- and I_5^- are isolated from each other in LDH-CMCD−I_2.

As mentioned in the introductory paragraph the host−guest chemistry of the layered double hydroxides is generally restricted to ion-exchange reactions, e.g., the exchange of nitrate ions in $Mg_{1-x}Al_x(OH)_2(NO_3)_x$ for halide ions. Insertion of neutral halogens was hitherto not possible. We have shown that, by appropriate functionalization of the internal walls of the inorganic solid, in this case by intercalation of cyclodextrin cavities in a Mg−Al LDH, it is possible to adsorb iodine molecules within the galleries of the layered solid. Although the iodine molecules once adsorbed dissociate heterolytically to form polyiodide anionic species, such as I_3^- and I_5^-, the host−guest chemistry of the functionalized LDH is conceptually very different from the usual ion-exchange chemistry of the parent LDH. The polyiodide species I_3^- and I_5^- present in LDH-CMCD−I_2 have no part to play in maintaining charge neutrality of the LDH unlike, for example, the role of I^- ions in $[Mg_{1-x}Al_x(OH)_2][I]_x$. The iodine content in LDH-CMCD−I_2 has, therefore, no relation to the negative charge deficit (the Mg/Al ratio) of the LDH layers. The polyiodide anions formed by the heterolytic disassociation of neutral I_2 in the grafted cyclodextrin cavities are weakly bound to the cyclodextrin cavities and are not ion-exchangeable unlike the I^- ions, for example, in $[Mg_{1-x}Al_x(OH)_2][I]_x$. In subsequent work we show how a variety of neutral molecules ranging from aromatic hydrocarbons to neutral organometallics can be inserted in the galleries of the functionalized LDH. The method outlined in this work may easily be extended to other layered solids, by appropriate choice of the derivatized β-cyclodextrin for functionalization, thereby extending the range of their host−guest chemistry.

Acknowledgment. The (carboxymethyl)cyclodextrin was received as a gift from Cerestar Co. (Hammond, IN).

Supporting Information Available: X-ray *d* spacings for LDH-CMCD, infrared and Raman spectra of LDH-CMCD and LDH-CMCD−I_2, and a table of band positions and assignments for LDH-CMCD and LDH-CMCD−I_2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0495721

---

(34) Minns, J. W.; Khan, A. *J. Phys. Chem. A* **2002**, *106*, 6421.

(35) Diard, J. P.; Saint-Aman, E.; Serve, D. *J. Electroanal. Chem.* **1985**, *189*, 113.

(36) Semnani, A.; Shamsipur, M. *J. Chem. Soc., Dalton Trans*. **1996**, 2215.

(37) Nimz, O. K.; Gessler, I.; Usón, S.; Laettig, H.; Welfle, Sheldrick,G.; Saenger, M. W. *Carbohydr. Res*. **2003**, *338*, 977.