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Unusual Incorporation of Neutral and Low Water-Soluble Guest Molecules into Layered Double Hydroxides: The Case of Cucurbit[6 and 7]uril Inclusion Hosts

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Supporting Information

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Layered double hydroxides (LDH) of general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot yH_2O$ (abbreviated notation M^{II}_{R}-M^{III}-A^{n-}) are well-known intercalation compounds, also referred to as anionic clays, made of positively charged brucite-like layers where M^{II} and M^{III} are the metallic cations within the hydroxide layers, interleaved with A^{n-} negatively charged species. Owing to their anion-exchange properties, a large variety of anionic molecules may be sandwiched between LDH layers, in particular organic molecules giving rise to hybrid organic inorganic O/I assembly.[1] The identities and ratio ($R = (1 - x)/x$) of the divalent and trivalent cations can also be varied over a wide range[2] resulting in a huge diversity of LDH intercalation compounds spreading from simple anions such as surfactants to more cumbersome molecules with specific properties like organic chromophores,[3] DNA,[4] and other related bionanohybrids.[5] Up to now, the intercalated guest species mainly focus on anionic molecules, because of the positive charge of LDH host layers. To the best of our knowledge, C_{60} intercalated LDH is the only known example so far of intercalation of neutral entities in LDH.[6] These authors have shown that upon simple dissolution in appropriate solvents (toluene, hexane), fullerene molecules can penetrate into the hydrophobic interlayer space of dodecyl sulfate modified LDH. Inspired by this pioneering work, we aimed in the present study to investigate the intercalation of relevant neutral macrocyclic molecules and are focused on cucurbituril (CB[*n*]) molecules. They are thoroidal-shaped molecules consisting of *n* glycoluril units bonded by methylene bridges between the nitrogen atoms of the monomers (Figures S1 and S2 in Supporting Information). These structures form D_{nh} symmetric macrocycles in which a hydrophobic cavity is delimited by two equivalent distal portals formed by the oxygen atoms from the carbonyl groups of the monomers and resulting in high electron densities at the cavity entrances. As the number of glycoluril units increases, both the portal's and the cavity's diameters increase, but the associated height remains similar (0.91 nm from XRD data;[7] theoretical calculations in vacuum lead to a lower value of ca. 0.62 nm). The CB[*n*] structure and size make them very good inclusion matrices, able to entrap numerous chemical species such as alkanes, amines alcohols, aromatics, and even gases.[7]

We report here, for the first time, the intercalation of CB[*n*] (*n* = 6,7) into Zn_2Al-LDH material. CB[6, 7] molecules (internal diameters ø: 0.58 and 0.73 nm, respectively), which are the most studied representatives of the cucurbituril family and the most easily produced, bear no charge and are very slightly soluble in water and most solvents. Thus, at first glance, it may seem that the intercalation of CB[*n*] within LDH galleries is rather challenging. The charge problem was overcome by neutralizing the positive charge of LDH host layers with co-intercalating entities, namely, dodecyl sulfate anions (DS), reminiscent of the C_{60} incorporation procedure,[6] but also with nitrate or chloride anions.

Experimentally, CB[6, 7] were prepared and purified according to a procedure described elsewhere.[8] On the other hand, Zn_2Al LDH host was prepared using the coprecipitation method.[9] Guest species such as dodecyl sulfate (DS) and CB[6 or 7] were added to the reaction medium prior to the addition of the mixed-metal salt solution as described in the synthesis paragraph of the Supporting Information. $Zn_2Al/(Cl^-)$/CB[6 or 7] samples were obtained by using the double-phase anion exchange method,[10] in which Zn_2Al/DS was first reacted with *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide (CTAB) and then exchanged with chloride anions. Extractions of intercalated CB[*n*] were carried out by stirring CB[*n*] containing LDH in 1,6-hexanediamine (Aldrich) aqueous solutions (2.5×10^{-2} mol·dm^{-3}) for 72 h, filtering off the supernatant, and washing the solid with deionized water. The notation used for DS intercalate is: $\mathbf{Zn_2Al/DS}$ ($Zn_{0.67}Al_{0.33}(OH)_2(DS)_{0.33}\cdot 1.5H_2O$); DS and CB[6 or 7] intercalates: $\mathbf{Zn_2Al/DS/CB7}$ ($CB[7]_{0.03}@Zn_{0.69}Al_{0.31}(OH)_2(DS)_{0.31}\cdot 2.3H_2O$) and $\mathbf{Zn_2Al/DS/CB6}$ ($CB[6]_{0.03}@Zn_{0.67}Al_{0.33}(OH)_2(DS)_{0.33}\cdot 2.9H_2O$); double phase anion-exchanged samples: $\mathbf{Zn_2Al/exc(DS)/CB7}$ ($CB[7]_{0.03}@Zn_{0.67}Al_{0.33}(OH)_2(Cl)_{0.33}\cdot 0.6H_2O$) and $\mathbf{Zn_2Al/exc(DS)/CB6}$($CB[6]_{0.03}@Zn_{0.67}Al_{0.33}(OH)_2(Cl)_{0.33}\cdot 0.5H_2O$). Nitrate intercalate: $\mathbf{Zn_2Al/NO_3^-}$ ($Zn_{0.67}Al_{0.33}(OH)_2(NO_3)_{0.33}\cdot 0.5H_2O$); co-intercalated nitrate and CB[6 or 7] samples: $\mathbf{Zn_2Al/NO_3^-/CB6}$ ($CB[6]_{0.03}@Zn_{0.69}Al_{0.31}(OH)_2$

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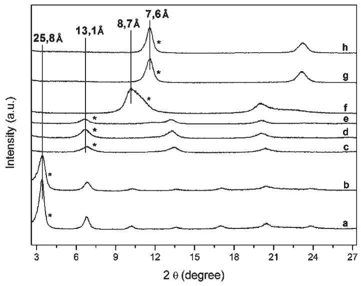

Figure 1. PXRD patterns of (a) Zn_2Al/DS, (b) $Zn_2Al/DS/CB7$, (c) $Zn_2Al/exc(DS)/CB7$, (d) $Zn_2Al/NO_3^-/CB7$, (e) $Zn_2Al/NO_3^-/CB6$, (f) Zn_2Al/NO_3^-, (g) $Zn_2Al/NO_3^-/ext(CB6)$, and (h) $Zn_2Al/NO_3^-/ext(CB7)$. Asterisk indicates d_{003}. Measurement conditions are given in the Supporting Information.

$(NO_3)_{0.31}\cdot 0.5H_2O)$ and **$Zn_2Al/NO_3^-/CB7$** $(CB[7]_{0.03}@Zn_{0.69}Al_{0.31}(OH)_2(NO_3)_{0.31}\cdot 0.6H_2O)$. Samples extracted with 1,6-hexanediamine: **$Zn_2Al/NO_3^-/ext(CB6)$** $(Zn_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.16}\cdot 0.5H_2O)$ and **$Zn_2Al/NO_3^-/ext(CB7)$** $(Zn_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.16}\cdot 0.4H_2O)$. CB[*n*]@ notation is used to indicate that CB[*n*] molecules are intercalated into LDH interlayer space. The amounts of zinc and aluminum within LDH hydroxide layers were determined by means of atomic absorption spectroscopy while the number of water and organic molecules was estimated from thermogravimetric analysis (Table 1 and Figure S3 in Supporting Information).

IR vibrational spectra of CB[*n*] display intense peaks around 1734, 1480, 968, and 806 cm^{-1} corresponding to C=O, N—C—N, CH_2, and C—N—C modes, respectively (Figure S4 in Supporting Information). The carbonyl band (1734 and 1721 cm^{-1} for CB[6] and CB[7], respectively) corresponds to the sum of both symmetric and asymmetric stretching modes. Highly sensitive to coordination with metals through degeneracy, this vibration band did not exhibit any splitting for the hybrids $Zn_2Al/DS/CB6$ and $Zn_2Al/DS/CB7$, indicating rather weak interaction between the intercalated macrocycles and LDH layers. In a similar way, the interaction between the DS and CB[7] resulted in a small shift of the carbonyl band from 1721 to 1731 cm^{-1}. This agrees with theoretical calculations showing DS molecules partially included into CB[*n*] from their nonpolar moieties (Figure S2 in Supporting Information), thus forming a labile anionic caviplex which may be subsequently inserted into LDH galleries as shown below. The other vibration bands for DS-organo-modified LDH were of common occurrence.[11]

Co-intercalated $Zn_2Al/DS/CB$(6 or 7) phases display an interlayer distance of ca. 25.8 Å as determined from powder X-ray diffraction data, a value identical to that of Zn_2Al/DS, thus suggesting that the gallery height in such co-intercalated systems is actually governed by DS anions (Figure 1a,b). Using the double-phase exchange method,[10] DS molecules were removed from the interlayer space and then exchanged for chloride ions. In the resulting material $Zn_2Al/exc(DS)/CB7$, the IR bands at 2919 and 2849 cm^{-1} characteristic of DS $-(CH_2)-$ vibration disappear while the macrocycle bands remain. Besides, the LDH basal distance is reduced to 13.1 Å (Figure 1b,c) leading to a gallery height of 5.6 Å by subtracting LDH layer thickness (~2.1 Å) and the guest—host hydrogen bond distance (2 × 2.7 Å). Similar results were obtained for $Zn_2Al/exc(DS)/CB6$ as well as with $Zn_2Al/NO_3^-/CB$(6 or 7) samples (Figure 1d,e). This observed gallery height, that is, 5.6 Å, is close to the macrocycle height calculated in vacuum (0.62 nm) which is in favor of a vertical position of both cucurbituril molecules with the cylinder axis oriented perpendicular with respect to the hydroxide layers. Indeed, a parallel position would have led to different interlayer distances, the diameter of the cylindrical cavities being different depending on the number of glycoluril units.

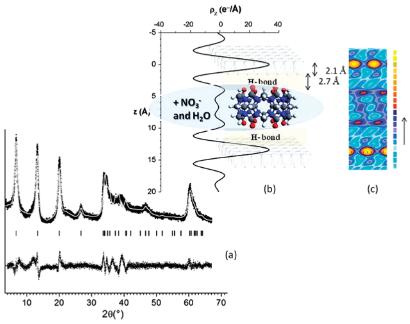

Figure 2. (a) Profile analysis of the XRD pattern of $Zn_2Al/NO_3^-/CB7$: experimental X-ray diffraction (black dots), calculated (gray line), Bragg reflections (ticks), and difference profiles (bottom). (b) One-dimension electron density projected along the *c*-stacking axis; (c) contoured Patterson map of the (*x*0*z*) plane (summed from 0 to 1 along the *b*-axis); the electron density scale is given on the right in arbitrary units.

In contrast to C_{60} incorporation,[6] neither prior intercalation of DS nor the use of any solvent is needed for CB[*n*] intercalation as evidenced with $Zn_2Al/NO_3^-/CB$(6 or 7) samples where CB molecules are co-intercalated with nitrate anions, acting as charge compensating species. A more detailed structural study was attempted in the case of $Zn_2Al/NO_3^-/CB7$ based on X-ray diffraction data. First, the cell parameters ($a = 3.0725(4)$ Å and $c = 40.11(1)$ Å) were refined from peak profile analysis[12] considering the rhombohedral space group $R\bar{3}m$ generally reported for LDH (Figure 2a). Using the relationship between the cell parameter *a* and the molar ratios *R* of metal ions established for Zn_RAl LDH series,[13] a Zn^{2+}/Al^{3+} molar ratio of 2 was obtained, in good agreement with the chemical analysis. Moreover, the cell parameter *c* gives an interlayer distance d_{003} of 13.37 Å. Figure 2b,c displays respectively the one-dimensional (1-D) electron density map along the *c*/*z* stacking axis calculated from the intensity of 003*n* diffraction lines (four harmonics; phases and structure factors computed from the known configuration of the hydroxide layer part of the structure) and the Patterson map on the (*x*0*z*) plane presented in the form of contour plot and plotted with the GFourier program.[14] Note that the differences in the electron density between spots in the interlayer space were quite small, preventing us from making the distinction between interlayer species, that is, CB[7], NO_3^-, and water molecules. Nevertheless, the high density peaks observed at the outer parts of the interlayer space, at ~4 Å from the center of the hydroxide layers, can be reasonably assigned to the carbonyl-laced portals of the CB[7] molecule. This distance is consistent with hydrogen bonding interactions between these carbonyl groups and OH groups of LDH host layers. Upon comparison with the dimensions of the CB[7] molecule (cylinder height 0.62 nm), a perpendicular arrangement of CB[7] (cylinder axis) against the hydroxide layer can be proposed.

To get further evidence for CB[*n*] intercalation into LDH, in situ high temperature XRD experiments were performed on $Zn_2Al/NO_3^-/CB7$ (Figure 3). Although the thermogravimetric analysis of $Zn_2Al/NO_3^-/CB7$ indicates a continuous weight loss in the temperature range between 25 and 300 °C (total weight loss of ~30%) attributed to the dehydration processes (Figure S3

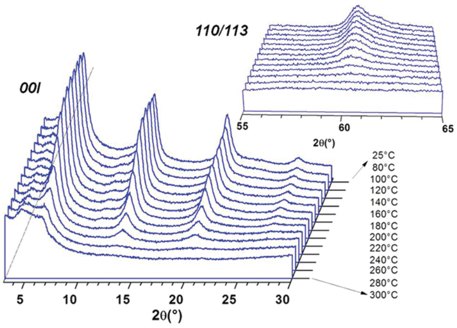

Figure 3. In situ HTXRD measurements for $Zn_2Al/NO_3^-/CB7$ carried out in air, in the temperature range 25−300 °C (heating ramp of 5 °C/min) showing the thermal evolution of the 00*l* and 110/113 diffraction lines on the left and on the right, respectively. Measurement conditions are given in the Supporting Information).

in Supporting Information), the interlayer distance as determined by XRD from the position of the 00*l* diffraction lines is practically not affected by heat treatment up to 260 °C. Besides, the observation of the 110/113 lines indicates that the hydroxide layer structure is also preserved up to 260 °C. Similar measurements done on Zn_2Al/NO_3^- show a completely different thermal behavior with a gradual decrease of the interlayer distance as soon as we applied the temperature and a collapse of the hydroxide layer structure above 200 °C (Figure S4 in Supporting Information). These observations support the formation of a pillared structure as the result of a uniform distribution of voluminous CB pillars in LDH interlayer space and minimizing the deformation of the hydroxide layers that could occur with temperature increase.

CB[*n*] intercalation into LDH is furthermore supported by extraction experiments using alkanediammonium ions. Both CB[6, 7] exhibit very high affinities for 1,6-hexanediammonium ions fitting perfectly the macrocycles cavity.[15] When $Zn_2Al/NO_3^-/CB(6\text{ or }7)$ were stirred in water in the presence of 1,6-hexanediammonium ions, the macrocycles were found to leave the interlayer space resulting in a decrease of the basal distances to 0.76 nm (Figure 1 g,h) and attributed to carbonate intercalate consistently to the appearance of the ν_3 characteristic IR band at 1360 cm^{-1}.[16] Even under N_2 flow, it was not possible to avoid the present carbonate contamination very common in LDH chemistry. Nevertheless, these results clearly demonstrate that CB[6,7] can be removed from LDH interlayer space under mild conditions and further confirm their presence in $Zn_2Al/NO_3^-/CB(6\text{ or }7)$.

It was demonstrated that cucurbit[6, 7]uril inclusion matrices, free of any charge, are able to crawl in between the LDH layers in the absence of interleaved surfactant molecules or solvent swelling. It is also noteworthy that this uptake is observed despite the low solubility of CB[*n*] in water. Moreover, it was shown that such guest caviplexes can be removed from the LDH interlayer space without breaking down the LDH stucture and host capacity. In order to get some answers for such a facile intercalation of neutral CB molecules at low concentration, microcalorimetric measurements are going to need to be realized, allowing a determination of the standard molar enthalpy of reaction and a comparison with similar data reported elsewhere for the intercalation of dicarboxylate anions in Zn_2Al-LDH.[17] Furthermore, we intend to investigate the porous structure developed by such a pillaring process, and this study will be realized in connection with the use of these materials as sorbents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis details, graphics showing chemical structures, TGA plots, FTIR spectra, XRD measurements, and table of LDH chemical formulas (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Forano, C.; Hibino, T.; Leroux, F.; Taviot-Guého, C. In *Handbook of Clay Science*; Bergaya, F., Theng, B., Lagaly, G., Eds.; Elsevier: Amsterdam, 2006; Vol. 1, cap. 13.1., pp 1021−1095. (b) Leroux, F.; Taviot-Guého, C. *J. Mater. Chem.* **2005**, *15*, 3628–3642.

(2) Evans, D. G.; Duan, X. *Chem. Commun.* **2006**, *5*, 485–496.

(3) (a) Kafunkova, E.; Lang, K.; Kubat, P.; Klementova, M.; Mosinger, J.; Miroslav Slouf, M.; Troutier-Thuilliez, A. L.; Leroux, F.; Verney, V.; Taviot-Gueho, C. *J. Mater. Chem* **2010**, *20*, 9423–9432. (b) Wypych, F.; Bail, A.; Halma, M.; Nakagaki, S. *J. Catal.* **2005**, *234*, 431–437. (c) Barbosa, C. A. S.; Ferreira, A. M. D. C.; Constantino, V. R. L. *Eur. J. Inorg. Chem.* **2005**, *8*, 1577–1584. (d) Wang, Z.-L.; Kang, Z.-H.; Wang, E.-B.; Su, Z.-M.; Xu, L. *Inorg. Chem.* **2006**, *45*, 4364–4371.

(4) (a) Choy, J.-H.; Oh, J.-M.; Park, M.; Sohn, K.-M.; Kim, J.-W. *Adv. Mater.* **2004**, *16*, 1181–1184. (b) Désigaux, L.; Bben Belkacem, M.; Cellier, J.; Léone, P.; Cario, L.; Leroux, F.; Taviot-Guého, C.; Pitard, B. *Nano Lett.* **2006**, *2*, 199–204. (c) Xu, Z. P.; Walker, T. L.; Liu, K.-l.; Cooper, H. M.; Lu, G. Q. M.; Bartlett, P. F. *Int. J. Nanomed.* **2007**, *2*, 163–174.

(5) Choy, J.-H.; Choi, S.-J.; Oh, J.-M.; Park, T. *Appl. Clay Sci.* **2007**, *36*, 122–132.

(6) Tseng, W.-Y.; Lin, J.-T.; Mou, C.-Y.; Cheng, S.; Liu, S.-B.; Chu, P. P.; Liu, H.-W. *J. Am. Chem. Soc.* **1996**, *118*, 4411–4418.

(7) (a) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870. (b) Demets, G. J. F. *Quim. Nova* **2007**, *30*, 1313–1322.

(8) Day, A.; Arnold, P. A.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094–8100.

(9) Miyata, S. *Clays Clay Miner.* **1980**, *28*, 50–56.

(10) Crepaldi, E. L.; Pavan, P. C.; Valim, J. B. *Chem Commun.* **1999**, *2*, 155–156.

(11) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173–301.

(12) Rodríguez-Carvajal, J. *Newsletter of the Powder Diffraction Commission of the International Union of Crystallography* **2001**, *26*, 12–19.

(13) Leroux, F.; Adachi-Pagano, M.; Intissar, M.; Chauviére, S.; Forano, C.; Besse, J. P. *J. Mater. Chem.* **2001**, *11*, 105–112.

(14) Roisnel, T.; Rodriguez-Carvajal, J. WinPLOTR: a Windows tool for powder diffraction patterns analysis, Materials Science Forum. In *Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)*; Delhez, R., Mittenmeijer, E. J., Eds.; 2000, pp 118−123.

(15) Mock, W. L.; Shih, N.-Y. *J. Org. Chem.* **1986**, *51*, 4440–4446.

(16) Sun, Z.; Jin, L.; Shi, W.; Wei, M.; Duan, X. *Chem. Eng. J.* **2010**, *162*, 293–300.

(17) Morel-Desrosiers, N.; Pisson, J.; Israeli, Y.; Taviot-Gueho, C.; Besse, J.-P.; Morel, J.-P. *J. Mater. Chem.* **2003**, *13*, 2582–2585.