Layered Compounds

DOI: 10.1002/ange.200602502

Layered Rare-Earth Hydroxides: A Class of Pillared Crystalline Compounds for Intercalation Chemistry**

Felipe Gándara, Josefina Perles, Natalia Snejko,
Marta Iglesias, Berta Gómez-Lor,
Enrique Gutiérrez-Puebla, and M. Ángeles Monge**

The well-known layered double hydroxides (LDHs) and their thermal-treatment products, which are used as adsorbents, drug-delivery vehicles, polymer stabilizers, and catalysts,[1–7] are generally based on brucite-like materials doped with d-block elements, although studies on a Li^+–Al^{3+} LDH[8] and on ionic europium and gadolinium complexes intercalated in pillared LDHs have recently been reported.[9] Compounds of the type presented herein, which are formed by pure cationic rare-earth hydroxide layers, have not yet been reported; they represent a new generation of pillared materials, in which the properties of intercalation materials are combined with those of rare-earth elements. $[R_4(OH)_{10}(H_2O)_4]_nA_n$ (R = rare-earth ions, A = intercalated organic anions, 2,6-naphthalenedisulfonate (NDS^{2-}) and 2,6-anthraquinonedisulfonate ($AQDS^{2-}$)) is the first family of layered rare-earth hydroxides (LRHs). In these LRHs, the positive charge of the inorganic layer is created only by trivalent rare-earth hydroxocations, which arises from the high and variable coordinative capability of the rare-earth centers and to the tendency of the hydroxide ion to form μ_n connections in structures that contain these rare-earth centers. Rigid organic anions are intercalated to neutralize the positive charge. Apart from their potential as ion exchangers, these new materials contain a great number of active metal centers with the capability of varying the coordination number in catalytic processes, which confers to them great possibilities in the field of green chemistry. In fact, the performed tests in hydrodesulfurization (HDS), sulfide oxidation, and redox reactions reveal these new LRHs to be high-quality heterogeneous catalysts. Other interesting physical properties emerging from both the f–f interactions and those of intercalated organic anions are also to be expected.

---

[*] F. Gándara, J. Perles, Dr. N. Snejko, Dr. M. Iglesias,
Dr. B. Gómez-Lor, Prof. Dr. E. Gutiérrez-Puebla,
Prof. Dr. M. A. Monge
Instituto de Ciencia de Materiales de Madrid
Cantoblanco, 20849-Madrid (Spain)
Fax: (+34) 91-3720623
E-mail: amonge@icmm.csic.es

[**] F.G. and J.P. acknowledge their FPI fellowship from Spanish Ministry for Education and Science (MEC) co-funded by Fondo Social Europeo. This work was supported by the Spanish MCYT projects MAT 2004-02001, CTQ2004-02865/BQU, and CAM-CSIC 200580M133).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

The compounds were synthesized under hydrothermal conditions. Single crystals suitable for X-ray diffraction studies were obtained only for the YbAQDS and YNDS compounds. Powder diffraction patterns show that the DyAQDS, HoAQDS, and YbAQDS compounds have the same structure (Figure 1), whereas in the diffraction pattern of YNDS, a shift of the first peak (020) shows that the corresponding structure has a shorter basal spacing.

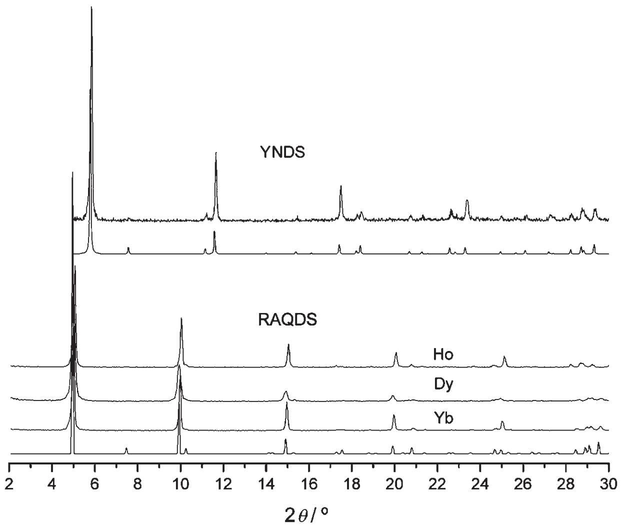

Figure 1. Experimental (upper) and calculated (lower) powder X-ray diffraction patterns. Top: YNDS; bottom: HoAQDS, DyAQDS, and YbAQDS. The first peak is (020).

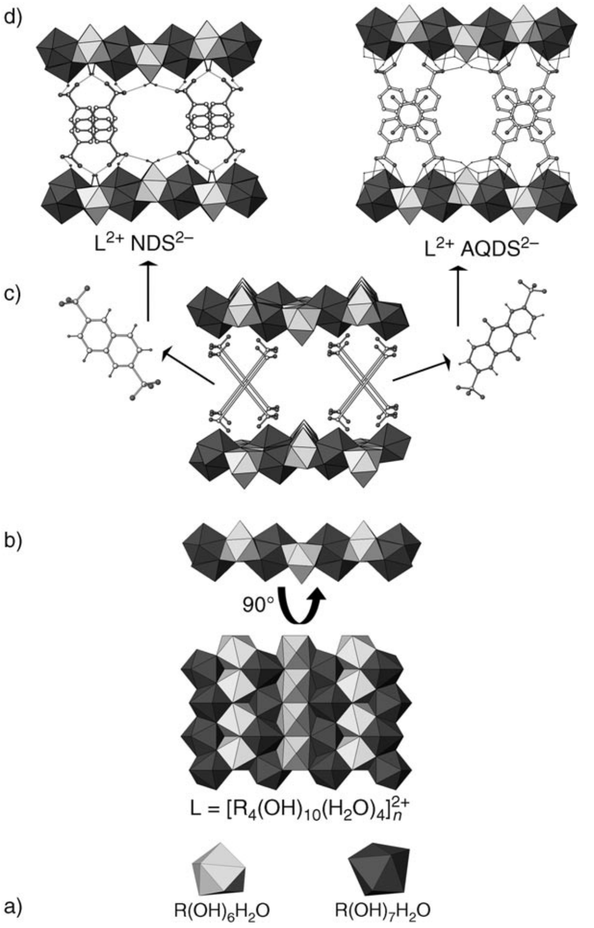

Figure 2. a) Rare-earth polyhedra; b) a layer of polyhedra (top and side view); c) organic ions (sticks represent the S–S axes) intercalated between two layers; d) structures of $[R_4(OH)_{10}(H_2O)_4]^{2+}{}_n$ with NDS^{2-} (left) and $AQDS^{2-}$ (right).

YbAQDS and YNDS crystallize in the orthorhombic system (see Experimental Section). The structures consist of $[R_4(OH)_{10}(H_2O)_4]^{2+}{}_n$ cationic layers formed by eight- and nine-coordinated rare-earth atoms, which are linked through μ_3-hydroxy groups. In addition to the coordination from the OH groups, each rare-earth atom is coordinated by one water molecule to give two different coordination polyhedra: one is a dodecahedron, the other is a monocapped square antiprism. Polyhedra of the same type are placed in alternating rows parallel to the [001] direction to form the layers parallel to the *ac* plane. These hydroxide layers are separated by *b*/2 (17.826 Å for YbAQDS and 15.263 Å for YNDS), and their positive charge is compensated by organic anions, which are localized between the layers with the sulfonate groups directed toward the cationic layers. In previous work, values of the basal spacing in LDHs with intercalated $AQDS^{2-}$[10] and NDS^{2-}[11] were reported on the basis of powder X-ray diffraction measurements, which predicted a tilted orientation of the organic molecules into the interlayer space. In these new LRH compounds, the titling angles formed between the S–S axes of the organic anions and the normal of the respective hydroxide layers are 30.86° and 37.80° for the $AQDS^{2-}$ and NDS^{2-} compounds. These anions are situated parallel to the *ab* plane in an alternating configuration, and separated by 3.5 Å (*c*/2) and 12.5 Å (*a*) along the [001] and [100] directions, respectively (Figure 2). This arrangement gives rise to π–π stacking interactions among the $AQDS^{2-}$ central rings, and O–π stacking interactions among one oxygen atom from each quinone moiety and lateral aromatic rings. In the YNDS compound only C–π stacking interactions are possible. In the 3D lanthanide polymeric framework (LnPF) reported previously Ln(1,5)NDS,[12] the NDS^{2-} ligands are $\eta^2\mu^2,\eta^2\mu^2$ and $\eta^3\mu^3,\eta^3\mu^3$ coordinatively bonded to the metal atoms. In contrast, in the LRHs the organic anions are hydrogen-bonded to the rare-earth hydroxide cationic layers (Table 1). Apart from the more convenient configuration of the (2,6)NDS^{2-} isomer, the LRH structure seems to be kinetically favored by small rare-earth ions. However, ongoing screenings of the synthesis conditions do not rule out the possibility of obtaining LRH materials for the first half of the rare-earth series. A proper choice of synthesis conditions—molar composition, temperature, and dilution—seems to be decisive in obtaining either an LRH or an LnPF metal-oxide framework (MOF) as a pure phase. Zigzag channels of approximately 10 × 10 Å or 8 × 8 Å in the $AQDS^{2-}$ and NDS^{2-} compounds, respectively, run along the *a* direction. In the LDH materials, the interlayer region is substantially disordered.[13] However, the interlayer galleries of the LRHs are well-ordered, thus supplying a high control of the basal spacing from the as-synthesized products, which has a value of

Table 1: Bond lengths [Å] and angles [°] of hydrogen bonds in YNDS and YbAQDS (in italics).[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢(D-H-A)
O_{W1}–H···O (×2)	0.82	2.04	2.81	156
	0.85	*1.94*	*2.77*	*167*
O_{W2}–H···O (×2)				
	0.85	*2.12*	*2.85*	*144*
O_H–H···O (×2)	0.98	2.00	2.939	163
	1.12	*2.32*	*3.023*	*119*
O_H–H···O	0.98	2.14	3.032	151
	0.92	*2.60*	*3.097*	*115*

[a] The hydrogen bonds are between oxygen atoms from the ligand sulfonate ions and water molecules (O_W) or hydroxy groups (O_H) around the rare-earth ions in the inorganic layers. D = donor, A = acceptor.

b/2. From a crystallographic point of view, a direct relation exists between the brucite-derived hexagonal lattice of the LDHs and that of the new LRHs. Given that in the latter there are two independent well-ordered R atoms because of their asymmetric coordination environments, the ideal hexagonal superlattice would have an a' parameter twice that of the mineral (that is, $a' = 2a$). As the interatomic distances among R atoms are not uniform, this hexagonal superlattice has a distortion that gives rise to a larger orthorhombic cell. The lattice vectors of the LRH unit cell can be deduced from those of the LDH cell by applying the transformation matrix (2 −2 0, 0 0 −1, 2 2 0), as shown in Figure 3.

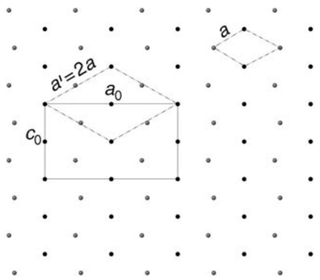

Figure 3. Crystallographic transformation from the ideal brucite-type structure to the new orthorhombic LRH structure. See text for details.

Thermogravimetric analysis and simultaneous differential thermal analysis (TGA–DTA) in an N_2 atmosphere (50 mL min^{-1}) and thermodiffraction X-ray experiments (vacuum) show that the NDS^{2-} compounds are stable up to 600 °C and the AQDS^{2-} compounds up to 500 °C. The IR spectra of these compounds show a broad band near 3500 cm^{-1}, with several maxima corresponding to the ν(M–OH) frequencies of the coordinated hydroxy groups and water molecules. The broadening of this band is due to the hydrogen bonding between these coordinated oxygen atoms and the sulfonate groups. The uncoordinated SO_3 group gives rise to unsplit bands in the region 1000–1100 cm^{-1}, which are consistent with the retention of C_{3v} symmetry.

Rare-earth metals are increasingly being used as catalysts in various organic transformations. These new materials offer the possibility of combining the catalytic properties of rare-earth atoms with the advantages of a solid catalyst. The capability of the new LRH materials as heterogeneous catalysts has been tested on key processes in green chemistry. 1) In the hydrodesulfurization (HDS) of thiophene, YbAQDS shows a conversion of 50 % in 26 h to yield hydrogen sulfide and butane (both components are easily separable) under 7 bar of H_2 at only 70 °C. It is worth pointing out that these results are obtained under much milder conditions than those usually used (high H_2 pressure (30–60 bar) at 350–400 °C[14,15]). 2) As an alternative to hydrodesulfurization reactions, the removal of refractory sulfur-containing compounds can be accomplished by oxidation. This catalyst effects the oxidation of various alkyl phenyl sulfides. Sulfides were selectively mono-oxygenated to the corresponding sulfoxides (100 %) in 30 min by using H_2O_2 as oxidant. The YbAQDS catalyst has a remarkably high turnover frequency (TOF) of 2000 h^{-1},[12] which is due to the small quantity of catalyst (0.1 %) needed and the fast conversion of the substrate. The results here are better, both in activity and in selectivity, than those previously obtained with a rare-earth succinate polymeric framework.[16] 3) The catalytic activity for the competitive epoxidation of 3,7-dimethylocta-1,6-dien-3-ol (linalool) using an excess of hydrogen peroxide was also tested. Linalool was oxidized to pyranoid and furanoid ethers (ratio 1:1) with > 80 % conversion over 24 h by using YNDS as a bifunctional redox–acid catalyst. The catalyst activity is comparable with that of both LnPF-1[12] and microporous bifunctional titanium aluminosilicate.[17] The sulfoxidation reaction proceeds through the corresponding peroxo species, as happens in the hydrolysis of phosphodiesters[18] and RNA[19] when these are catalyzed by peroxide rare-earth complexes formed in rare-earth/H_2O_2 mixtures.

To verify that the observed process is a heterogeneous catalysis, the reactions were carried out under standard conditions. After about 30 % conversion, the solid was removed by filtration whereupon the reactions stopped completely. The solid was then used again without any loss of performance. A powder X-ray diffraction pattern of the recovered catalysts showed no change in the structure of the catalyst.

In conclusion, LRHs have an ordered and tunable porous structure and combine advantages of LDH catalysts with the chemical and physical properties of rare-earth compounds. Although the full range of properties of these compounds have yet to be elucidated,[20–23] their discovery should be of general interest.

Experimental Section

Synthesis and characterization: All reagents were purchased at high purity (AR) grade from Aldrich and used without further purification. $R(NO_3)_3 \cdot 6H_2O$ (R = Yb, Dy, Ho, Y) was used as the source of rare-earth cations; the sulfonic acids were used in their disodium salt forms. In a typical synthesis procedure, the initial mixture with molar composition $R^{3+}/A^{2-}/H_2O = 4:1:4400$ was adjusted to pH 6.5 with Et_3N ($Et_3N/R^{3+} = 2.5$). The mixture was stirred for about 20 min and sealed in a 46 mL teflon-lined stainless-steel bomb. The bomb was kept at 180 °C under autogenous pressure for 18 h. After the reaction mixture was cooled to room temperature, the product was removed by filtration and washed with deionized water and acetone. A grayish white (Dy and Yb) or pink (Ho) powder was obtained for the $AQDS^{2-}$ compounds, and a pale yellow powder for YNDS.

The IR spectra from KBr pellets were recorded in the range $4000–400\,cm^{-1}$ on a Perkin–Elmer spectrometer. TGA–DTA were performed with a SEIKO TG/DTA 320 apparatus between 25 and 700 °C in N_2 (flow rate of $50\,mL\,min^{-1}$) at a heating rate of $5\,K\,min^{-1}$.

X-ray structural analyses: Data for single crystals of the YbAQDS and YNDS compounds were collected on a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source ($Mo_{K\alpha}$ radiation = 0.71073 Å). Data were collected over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in ω. Unit-cell dimensions were determined by a least-squares fit of 60 reflections with $I > 2\sigma(I)$. The compounds crystallize in the orthorhombic system, space group *Ibam*, with $a = 12.5401(6)$, $b = 35.652(2)$, and $c = 7.0347(4)$ Å for YbAQDS, and $a = 12.639(1)$, $b = 30.525(2)$, and $c = 7.1348(6)$ Å for YNDS. The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the hydroxy groups and water molecules were located in difference Fourier maps. Calculations were carried out by using the SMART program for data collection and data reduction, and SHELXTL. CCDC-604276 (YNDS) and CCDC-604277 (YbAQDS) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The compounds reported herein are covered under the patent: F. Gándara, J. Perles, N. Snejko, M. Iglesias, B. Gómez-Lor, E. Gutiérrez-Puebla, M. A. Monge (ICMM, CSIC), ES200601422, **2006**.

Received: June 21, 2006
Revised: September 11, 2006

Keywords: heterogeneous catalysis · hydrogen bonds · intercalations · layered compounds · rare earths

---

[1] a) G. R. Williams, T. G. Dunbar, A. J. Beer, A. M. Fogg, D. O'Hare, *J. Mater. Chem.* **2006**, *16*, 1222; b) G. R. Williams, T. G. Dunbar, A. J. Beer, A. M. Fogg, D. O'Hare, *J. Mater. Chem.* **2006**, *16*, 123.

[2] H. Cai, A. C. Hillier, K. R. Franklin, C. C. Nunn, M. D. Ward, *Science* **1994**, *266*, 1551.

[3] B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P. Jacobs, *Nature* **1999**, *400*, 855.

[4] B. F. Sels, D. E. De Vos, P. A. Jacobs, *Catal. Rev.* **2001**, *43*, 443.

[5] *Handbook of layered Materials*, Dekker, New York, **2004**.

[6] V. Rives, *Layered Double Hydroxides: Present and Future*, Nova Science Publishers, New York, **2001**.

[7] M. J. Climent, A. Corma, S. Iborra, J. Primo, *J. Catal.* **1995**, *151*, 60.

[8] M. B. J. Roeffaers, B. F. Sels, H. Uji-i, F. C. De Schryver, P. A. Jacobs, D. E. De Vos, J. Hofkens, *Nature* **2006**, *439*, 572.

[9] S. Gago, M. Pillinger, R. A. S. Ferreira, L. D. Carlos, T. M. Santos, I. S. Goncalves, *Chem. Mater.* **2005**, *17*, 5803.

[10] a) E. Kanezaki, S. Sugiyama, Y. Ishikawa, *J. Mater. Chem.* **1995**, *5*, 1969; b) W. K. Kuk, Y. D. Huh, *J. Mater. Chem.* **1997**, *7*, 1933.

[11] L. Raki, J. J. Beaudoin, L. Mitchell, *Cem. Concr. Res.* **2004**, *34*, 1717.

[12] N. Snejko, C. Cascales, B. Gomez-Lor, E. Gutiérrez-Puebla, M. Iglesias, C. Ruiz-Valero, M. A. Monge, *Chem. Commun.* **2002**, 1366.

[13] G. S. Thomas, P. V. Kamath, *J. Chem. Sci.* **2006**, *118*, 127.

[14] K. R. Sharma, E. S. Olson in *Processing and Utilization of High-Sulfur Coals IV* (P. R. Dugan, D. R. Quigley, Y. A. Attia), Elsevier Science, Amsterdam, **1991**, p. 377.

[15] T. Chapus, F. Morel (Institut Français du Pétrol), US 2002195375, **2002**.

[16] J. Perles, M. Iglesias, C. Ruiz-Valero, N. Snejko, *J. Mater. Chem.* **2004**, *14*, 2683.

[17] A. Corma, M. Iglesias, F. Sánchez, *J. Chem. Soc. Chem. Commun.* **1995**, 1635.

[18] Y. Mejia-Radillo, A. K. Yatsimirsky, *Inorg. Chim. Acta* **2002**, *328*, 241, and references therein.

[19] J. Kamitani, J. Sumaoka, H. Asanuma, M. Komiyama, *J. Chem. Soc. Perkin Trans. 2* **1998**, 523.

[20] R. M. Jones, T. S. Bergstedt, D. W. McBranch, D. G. Whitten, *J. Am. Chem. Soc.* **2001**, *123*, 6726.

[21] N. D. Hutson, S. A. Speakman, E. A. Payzant, *Chem. Mater.* **2004**, *16*, 4135.

[22] A. I. Khan, D. O'Hare, *J. Mater. Chem.* **2002**, *12*, 3191.

[23] A. I. Khan, L. X. Lei, A. J. Norquist, D. O'Hare, *Chem. Commun.* **2001**, 2342.