Insertion of Magnetic Bimetallic Oxalate Complexes into Layered Double Hydroxides

Eugenio Coronado, José R. Galán-Mascarós,*
Carlos Martí-Gastaldo, and Antonio Ribera

*Instituto de Ciencia Molecular Universidad de Valencia
Polígono de la Coma, s/n 46980 Paterna, Spain*

The field of molecule-based materials has shown a significant growth in recent years. They can compete with classic solid-state inorganic solids in magnetic, optical, or transport properties, and their intrinsic characteristics can be an extraordinary added value for current technological development.[1] In particular, the hybrid approach to molecular materials in which two or more molecular building blocks are assembled has been incredibly successful in the preparation of multifunctional materials.

Regarding magnetic hybrid materials, the family of bimetallic oxalate-based 2D magnets has been shown to be very versatile. They are formed by an anionic layer and cations that occupy the interlayer space and define the interlayer separation.[2] This type of networks has been formed with many different types of cations, including electroactive ones, in a general approach to multifunctional multilayers. The use of decamethylmetallocenium cations, or paramagnetic nitronyl nitroxide radicals, shows a chemical approach to magnetic multilayers.[3,4] Organic cations with nonlinear optical (NLO) activity showed a hybrid approach to NLO active ferromagnets.[5] Organic radicals of the TTF type were used in the discovery of the first family of molecular ferromagnetic metals,[6−8] which is an example that shows the real power of the hybrid approach. While maintaining the overall structure, and by selecting or chemically designing the right building block, one can tune the magnetic and transport properties of these materials from ferromagnetic to paramagnetic, and from metallic to semiconducting and to insulator.

All these examples of hybrid materials are formed from the combination and assembling of molecular building blocks. A much more unusual combination is that of molecular materials with solid-state structures. Some mesoporous frameworks have been used to organize and confine at the nanoscale functional molecules, with particular interest in optical and magnetic properties.[9] This strategy could also in principle be explored using the much more flexible layered double hydroxides (LDHs), also known as hidrotalcite-like compounds or anionic clays, as the host structure. These laminate compounds are represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{m-}]_{x/m} \cdot nH_2O$ where M^{II} and M^{III} represent metallic cations and A^{m-} the interlayer anion. The layered structure of the LDH is built by the periodical stacking of positively charged $(M^{II},M^{III})(OH)_2$ octahedral layers related to brucite, balanced by interlayer anions and water molecules that bind the sheets together. The highly tunable LDH intralayer composition coupled with the wide possible choice of anionic organic moieties affords a large variety of LDH hybrid materials, and several review articles and book chapters are devoted to the intercalation chemistry of LDHs and their applications.[10] To achieve the incorporation of organic molecules within the interlayer gallery of LDH materials, one may consider several strategies: (i) anion exchange reaction, (ii) direct synthesis, (iii) reconstitution, and (iv) restacking.[10] Since 1970, when the first patent based on a compound with LDH structure appeared as a precursor for the preparation of hydrogenation catalysts, hydrotalcite-like compounds have found practical applications in catalysis, chemical industry, medicine, etc., because of their interesting properties, with one of the main properties being its anionic exchange capacity (AEC). In this communication, we report our first successful results in the construction via an ion-exchange reaction of hybrid layered materials built from a solid-state insoluble structure (LDH MgAl) and a bimetallic molecule-based polymeric network (Mn−Cr oxalate complexes).

The hydrotalcite-like $[Mg_{1-x}Al_x(OH)_2](NO_3)_x$ material was prepared according to the method proposed by Miyata.[11] In this case, we used nitrate instead of carbonate as the interlayer anion in order to facilitate the anion-exchange reaction. The exchange was done by suspension of the LDH MgAl−NO₃ into a solution of the building blocks required for the formation of bimetallic oxalate-based magnetic complexes: $[Cr(ox)_3]^{3-}$ anions, inert toward ligand substitution, that act as a ligand for the Mn^{II} cation. Two different solutions were used: a 50% (v/v %) mixture of water and ethylene glycol with $Mn_3[Cr(ox)_3]_2$ prepared in situ with excess $MnCl_2$ to yield sample **1** (Procedure A), and a water solution of the

(1) Miller, J. S. *Adv. Mater.* **1990,** *2,* 98−99.
(2) (a) Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwan, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992,** *114,* 6974−6979. (b) Mathonière, C.; Nuttall, C. J.; Carling, S. G.; Day, P. *Inorg. Chem.* **1996,** *35,* 1201−1206.
(3) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Ensling, J.; Gütlich, P. *Chem.—Eur. J.* **2000,** *6,* 552−563.
(4) Alberola, A.; Coronado, E.; Giménez-Saiz, C.; Gómez-García, C. J.; Romero, F. M.; Tarazón, A. *Eur. J. Inorg. Chem.* **2005,** 389−400.
(5) (a) Bénard, S.; Yu, P.; Audiére, J. P.; Riviére, E.; Clément, R.; Ghilhem, J.; Tchertanov, L.; Nakatani, K. *J. Am. Chem. Soc.* **2000,** *122,* 9444−9454. (b) Bénard, S.; Riviére, E.; Yu, P.; Nakatani, K.; Delouis, J. F. *Chem. Mater.* **2001,** *13,* 159−162.
(6) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000,** *408,* 447−449.
(7) Alberola, A.; Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J. *J. Am. Chem. Soc.* **2003,** *125,* 10774−10775.
(8) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Martínez-Ferrero, E.; van Smaalen, S. *Inorg. Chem.* **2004,** *43,* 4808−4810.
(9) Clemente-León, M.; Coronado, E.; Forment-Aliaga, A.; Amorós, P.; Ramírez-Castellanos, J.; González-Calbet, J. M. *J. Mater. Chem.* **2003,** *13,* 3089−3095.
(10) (a) *Layered Double Hydroxides: Present and Future*; Rives, V., Ed.; Nova Science Publishers: New York, 2001 and refs therein. (b) Leroux, F.; Besse, J. P. In *Clay Surfaces: Fundamentals and Applications*; Wypych, F., Satyanarayana, K. G., Eds.; Elsevier: London, 2004; pp 459−495.
(11) (a) Miyata, S. *Clays Clay Miner.* **1980,** *28,* 50−56. (b) Miyata, S. *Clay Miner.* **1980,** *19,* 591−596. (c) Miyata, S.; Okada, A. *Clays Clay Miner.* **1977,** *25,* 14−18.

soluble [K(18-crown-6)]$_3$[Mn$_3$(H$_2$O)$_4$\{Cr(C$_2$O$_4$)$_3$\}$_3$] magnet[12] to yield sample **2** (Procedure B).[13]

X-ray powder patterns were collected on a Siemens D-500 X-ray powder diffractometer (CuK$_\alpha$ radiation $\lambda = 1.5418$ Å) with step scans over a 2.16 h period in the 5° < 2θ < 70° range with a step size of 0.05° (see the Supporting Information). The data indicate that the crystallinity of the starting material is well-maintained in all cases. The indexation of these peaks as (00l), by assuming the rhombohedral symmetry previously assigned by Miyata[11] to a similar material, allowed us to calculate the basal spacing for each material. A small shift in the peaks at lower angles is observed that corresponds to an increase in the interlayer separation from 8.90 to 9.83 Å. No other phase was observed in these diffraction patterns, indicating that only LDH materials are present. The complete absence of the peaks corresponding to the original LDH MgAl−NO$_3$ also confirms that oxalate complexes are present in all interlayer spaces. Because the van der Waals thickness of the brucite sheets is ca. 4.71 Å,[11] the calculated basal spacing is indicative of a gallery height of ca. 5.12 Å for the bimetallic oxalate-based complexes. This interlayer separation is identical for both samples, beyond the experimental error, and is in good agreement with that found for the insertion of the isolated [Cr(ox)$_3$]$^{3-}$ trianions.[14] This corresponds to the size of these complexes along their 3-fold axis, indicating that the oxalate complexes are indeed inserted with their 3-fold axis perpendicular to hydroxide layers.

Despite the use of Cr/Mn equimolar ratios or those lower than 1 for the exchange procedures, the Cr/Mn values consistently obtained in our samples were 3.5 and 2 for procedures A and B, respectively. From the metal analysis (Table 1) we can estimate a [Mg$_2$Al(OH)$_6$][NO$_3$]$_{1+2y-3z}$-\{Mn$_y$[Cr(ox)$_3$]$_z$\} stoichiometry, with $y = 0.05$ and $z = 0.17$ for **1** (A) and $y = 0.16$ and $z = 0.32$ for **2** (B). The large value of the Cr/Mn ratio observed may be due to the stronger tendency of the anionic building blocks to enter the overall

(12) Coronado, E.; Galán-Mascarós, J. R.; Martí-Gastaldo, C. *Inorg. Chem.* **2006**, *45*, 1882−1884.

(13) All manipulations were carried out under an inert atmosphere. Ag$_3$Cr-(C$_2$O$_4$)$_3$·xH$_2$O was prepared by methatesis, adding an excess of AgNO$_3$ (7.65 g, 45 mmol) to a water (100 mL) solution of K$_3$Cr(C$_2$O$_4$)$_3$·xH$_2$O (4.87 g, 10 mmol). The immediate precipitate obtained of the product is filtered, washed with water and acetone, and dried at room temperature. Procedure A: Ag$_3$Cr(C$_2$O$_4$)$_3$ (1.280 g, 2 mmol) and MnCl$_2$·4H$_2$O (2.156 g, 11 mmol) are mixed in 20 mL of a 50% v/v solution of water and ethylene glycol. After filtration of the AgCl precipitate, the LDH MgAl−NO$_3$ (170 mg) is suspended and stirred for 90 hours at room temperature; it was later filtered, washed with water until the elimination of nitrate, and finally washed with methanol and dried in air. [Mg$_2$Al(OH)$_6$][NO$_3$]$_{0.59}$\{Mn$_{0.05}$[Cr(ox)$_3$]$_{0.17}$\}·0.72H$_2$O, Mn$_{0.05}$N$_{0.59}$O$_{10.53}$AlCr$_{0.17}$Mg$_2$C$_{1.02}$H$_{7.44}$, M_w = 283.67. Calcd: N, 2.91; C, 4.32; H, 2.64. Found: N, 3.03; C, 4.59; H, 2.62. Procedure B:The LDH MgAl−NO$_3$ (170 mg) was suspended in a solution of [K(18-crown-6)]$_3$\{Mn$_3$(H$_2$O)$_4$[Cr(C$_2$O$_4$)$_3$]$_3$\} (0.410 g, 0.2 mmol) in 20 mL of water and stirred for 90 hours at room temperature; it was later filtered, washed with water until the elimination of nitrate, and finally washed with methanol and dried in air. [Mg$_2$Al(OH)$_6$][NO$_3$]$_{0.36}$\{Mn$_{0.16}$-[Cr(ox)$_3$]$_{0.32}$\}·0.52H$_2$O, Mn$_{0.16}$N$_{0.36}$O$_{11.44}$AlCr$_{0.32}$Mg$_2$C$_{1.92}$H$_{7.04}$, M_w = 319.25. Calcd: N, 1.57; C, 7.22; H, 2.22. Found: N, 1.63; C, 7.45; H, 2.26.

(14) (a) Prevot, V.; Forano, C.; Besse, J. P. *J. Solid State Chem.* **2000**, *153*, 301−309. (b) del Arco, M.; Gutiérrez, S.; Martín, C.; Rives, V. *Inorg. Chem.* **2003**, *42*, 4232−4240.

(15) EDAX analysis was performed on a PHILIP XL 30 ESEM with a PV 9760 EDAX analyzer.

Table 1. Metal Content for Samples 1 and 2[15]

	R^a	Al/Cr	Cr/Mn
Procedure A	0.38	6.02	3.48
Procedure B	0.37	3.12	2.00

^{a} R = Al/(Al + Mg). It remains constant and identical to that of the starting material, indicating that no changes occur in the hydroxide layers during the intercalation process.
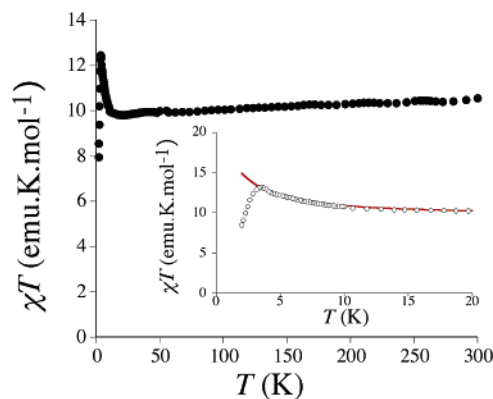

Figure 1. Thermal behavior of the χT product for compound **1** at 100 G represented per mol of Mn^{II} ions. The red line in the inset shows the best fitting. Diamagnetism has been corrected according to the Pascal constants.

cationic framework compared to that of the cationic ones. Thus, the Mn^{II} cations probably enter the framework as part of small anionic oligomers built with the anions in solution. A higher excess of the divalent cation (for Procedure A) did not allow us to decrease the Cr/Mn ratio. Better results, from the point of view of elemental analysis, are obtained through Procedure B for both Cr/Mn and Al/Cr ratios, maybe because the presence of the [K(18-crown-6)]$^+$ cation stabilizes the formation of bigger oligomeric structures in water. Of course, these procedures should end up with the interlayer space occupied by some remaining nitrate anions and different bimetallic anionic species of variable nuclearity. Some valuable information about these species can be obtained by looking at the magnetic data.
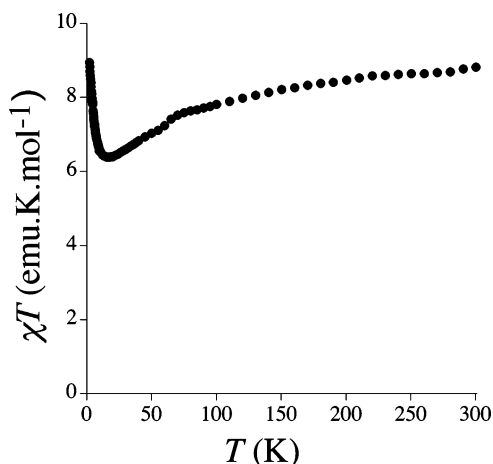
Magnetic susceptibility measurements were carried out with an applied magnetic field of 10 mT in the 2−300 K range. The χT product for compound **1** (Figure 1) gives a room-temperature value of 10.60 emu K mol^{-1} per mol of Mn. This value is in good agreement with that expected for a sample containing one Mn^{II} and three and a half Cr^{III}, which would reach a spin-only value of 10.93 emu K mol^{-1}, in good agreement with the metal ratio found. From this temperature, the χT product remains essentially constant when the temperature is decreased. Below 10 K, χT starts to increase and reaches a maximum of 12.4 emu K mol^{-1} at 3.6 K. The increase in the χT product is a signature of the presence of ferromagnetic interactions; for this system, these interactions can be originated only from bis(chelating) Mn−Cr oxalate bridges, as this is the only bridging mode that allows for ferromagnetic exchange for any possible combination of the oxalate ligand and these two metal ions.[2] Given the metal ratio, the most abundant species should be the tetrameric cluster \{[Mn[Cr(ox)$_3$]$_3$\}$^{7-}$, with a central Mn surrounded by three Cr atoms. Indeed, the data can be modeled to such a tetramer[16] with an isotropic Hamiltonian: $H = -2J[S_{Mn}S_{Cr1}+S_{Mn}S_{Cr2}+S_{Mn}S_{Cr3}]$ with the addition of one-half of an isotropic Cr^{III} center ($S = 3/2$, $g = 2$) to account

Figure 2. Thermal behavior of the χT product for compound **2** at 100 G represented per mol of M^{II} ions. Diamagnetism has been corrected according to the Pascal constants.

for the excess Cr^{III} ions. The parameters that yield the best fitting (without taking into account the very low temperature regime) are $g = 1.86$ and $J = +0.2$ K (Figure 1, inset), with the addition of a mean-field constant to account for intermolecular interactions ($\theta = -0.4$ K). These parameters are comparable with those found for other discrete Mn–Cr oxalate-bridged molecules.[17]

The room-temperature value (8.83 emu K mol^{-1}) of the χT product for compound **2** (Figure 2) per mol of Mn^{II} is also in good agreement with the metal ratio found, (very close to the spin only value of 8.125 emu K mol^{-1}). In this case, when the temperature is decreased, χT decreases, suggesting the presence of antiferromagnetic interactions. χT reaches a minimum at 17 K (6.4 emu K mol^{-1}) and then increases continuously to 8.91 emu K mol^{-1} at 2 K. This behavior suggests the coexistence of ferro- and antiferromagnetic interactions in this material. This indicates that in addition to the bis-chelating bridging mode already discussed,

chelating-monodentate oxalate bridges (favoring antiferromagnetic interactions)[18] must be also present. In general, this suggests that a higher diversity of oligomeric species, in which the Mn cations are not fully coordinated by the trivalent anions, is formed in this case.

In conclusion, we have shown how it is possible to insert into layered double hydroxides not only simple anions but also more complex coordination structures from their building blocks. In this case, we have used the well-known Mg–Al hydrotalcite-like LDH to insert oxalate-bridged bimetallic complexes in the interlayer space by a simple ion-exchange procedure. Magnetic data confirm that several bimetallic oxalate-bridge oligomers with different bridging modes are present in the interlamellar region, with predominance of the bis(chelating) Mn–ox–Cr bridge for compound **1** and a mixture of this and other bridging modes for compound **2**. This is the first example of such a hybrid material formed by a lamellar solid-state framework. A more detailed structural characterization would be very valuable for establishing further magneto-structural correlations, and this could be provided by the use of EXAFS.[19] On the other hand, optimization of this strategy could lead, in the near future, to the preparation of molecule-based magnets inserted into solid-state materials, if the synthetic conditions are optimized for these oligomers to grow to extended structures inside these lamellar hosts.

Supporting Information Available: X-ray diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

CM062054Z

(16) (a) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Inorg. Chem.* **1999**, *38*, 6081−6088. (b) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985−991.

(17) (a) Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Ruiz-Pérez, C. *Eur. J. Inorg. Chem.* **2003**, 2290−2298. (b) Ohba, M.; Tamaki, H.; Matsumoto, N.; Okawa, H. *Inorg. Chem.* **1993**, *32*, 5385−5390.

(18) Ballester, G.; Coronado, E.; Giménez-Saiz, C.; Romero, F. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 792−795.

(19) Beaudot, P.; De Roy, M. E.; Besse, J. P. *Chem. Mater.* **2004**, *16*, 935−945.