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A $Nd^{III}Cu^{II}$ Molecular Material with a Honeycomb-like Structure

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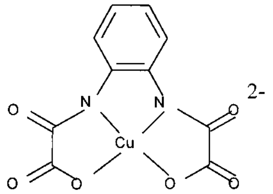
Introduction

One of the challenges in the field of molecular and supramolecular magnetism is to design materials exhibiting expected magnetic properties.[1−11] A necessary, if not sufficient, condition for this is obviously to control the architecture of the materials. For several years, we have been involved in the design of materials with different dimensionalities and topologies from a common precursor (which we also call a brick). Such an approach has been particularly developed in the case of the precursor $[Cu(opba)]^{2-}$, with opba standing for *o*-phenylenebis(oxamato), whose structure is schematized below:



From this precursor, it was already possible to design linear and zigzag chains,[12,13] two-dimensional networks with a honeycomb-like structure,[13,14] three-dimensional networks with an interlocked structure,[15−17] and ladder compounds.[18] The compounds with parallel ladder motifs were obtained through the reaction of $[Cu(opba)]^{2-}$ with a trivalent lanthanide ion, Ln^{III}. Their formula is $Ln_2[Cu(opba)]_3{\cdot}S$ with S standing for solvent molecules. The Ln_2Cu_3 stoichiometry is in principle also compatible with a two-dimensional honeycomb-like structure. The compounds of formula $cat_2M^{II}[Cu(opba)]_3{\cdot}S$, where M^{II} is a divalent 3d ion, have such a honeycomb-like structure, with cat^+ cations located between $M^{II}[Cu(opba)]$ layers.[13,14] For quite some time, we have been wondering whether a honeycomb-like structure of formula $Ln_2[Cu(opba)]_3{\cdot}S$ could be obtained. We report here on our results along this line.

Table 1. Crystallographic Data for $\{Nd_2[Cu(opba)_{0.5}(ox)_1]_3{\cdot}9DMF\}{\cdot}4.5DMF$

molecular formula: $Nd_{12}Cu_{18}N_{99}O_{184}C_{356}H_{522}$
a: 16.3144(12) Å
c: 52.470(2) Å
V: 12094(4) Å^3
Z: 9
R:[a] 7.90%
R_w:[b] 17.76%
fw: 11998
space group: *R*3 (No. 146h)
temp: 298 K
radiation: Mo Kα
D_{calc}: 1.648 g cm^{-3}
μ: 0.910 cm^{-1}

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$. $w = 1/[\sigma^2(F_o^2) + (0.0975P)^2 + 0.00P]$ where $P = ((F_o^2,0) + 2F_c^2)/3$.

Table 2. Selected Bond Distances

atom 1	atom 2	distance (Å)	atom 1	atom 2	distance (Å)
Nd1	O101	2.319(5)	Cu1	O13	1.892(10)
Nd1	O102	2.554(4)	Cu1	O14	1.861(13)
Nd1	O103	2.499(5)	Cu1B	N11B	1.880(11)
Nd2	O201	2.661(5)	Cu1B	O12B	1.829(12)
Nd2	O202	2.458(5)	Cu1B	O13B	2.275(2)
Nd2	O203	2.387(5)	Cu1B	N14B	1.937(8)
Nd3	O301	2.451(9)	Cu2	O21	2.06(3)
Nd3	O302	2.565(5)	Cu2	O22	1.883(6)
Nd3	O303	2.551(6)	Cu2	O23	2.011(9)
Nd4	O401	2.582(8)	Cu2	O24	2.349(7)
Nd4	O402	2.452(4)	Cu2B	O21B	1.761(8)
Nd4	O403	2.483(5)	Cu2B	N22B	1.888(9)
Cu1	O11	1.897(7)	Cu2B	N23B	1.896(8)
Cu1	O12	2.434(5)	Cu2B	O24B	1.891(2)

Experimental Section

Synthesis. Reaction in a sealed tube of two 10^{-4} M DMF = dimethylformamide solutions of hexahydrated Nd^{III} chloride and $Na_2[Cu(opba)]$ at 70 °C within ca. 3 days affords tiny but well-shaped crystals of a compound of formula $\{Nd_2[Cu(opba)_{0.5}(ox)]_3{\cdot}9DMF\}{\cdot}4.5DMF$, with ox = oxalato. During the synthesis, a partial hydrolysis of the oxamido groups into oxalato groups occurred. The yield of this reaction is 70%.

X-ray Crystallography. A single crystal was sealed in a glass capillary and mounted on a STOE IPDS single *φ*-axis diffractometer with a 2D area detector based on imaging plate technology. X-ray data were collected at room temperature; 300 images were recorded by using the rotation method (0° ≤ *φ* ≤ 150°) with Δ*φ* = 0.5° increments, an exposure time of 5 min, and a crystal to plate distance of 60 mm (EXPOSE).[19] The images were processed with the set of programs from

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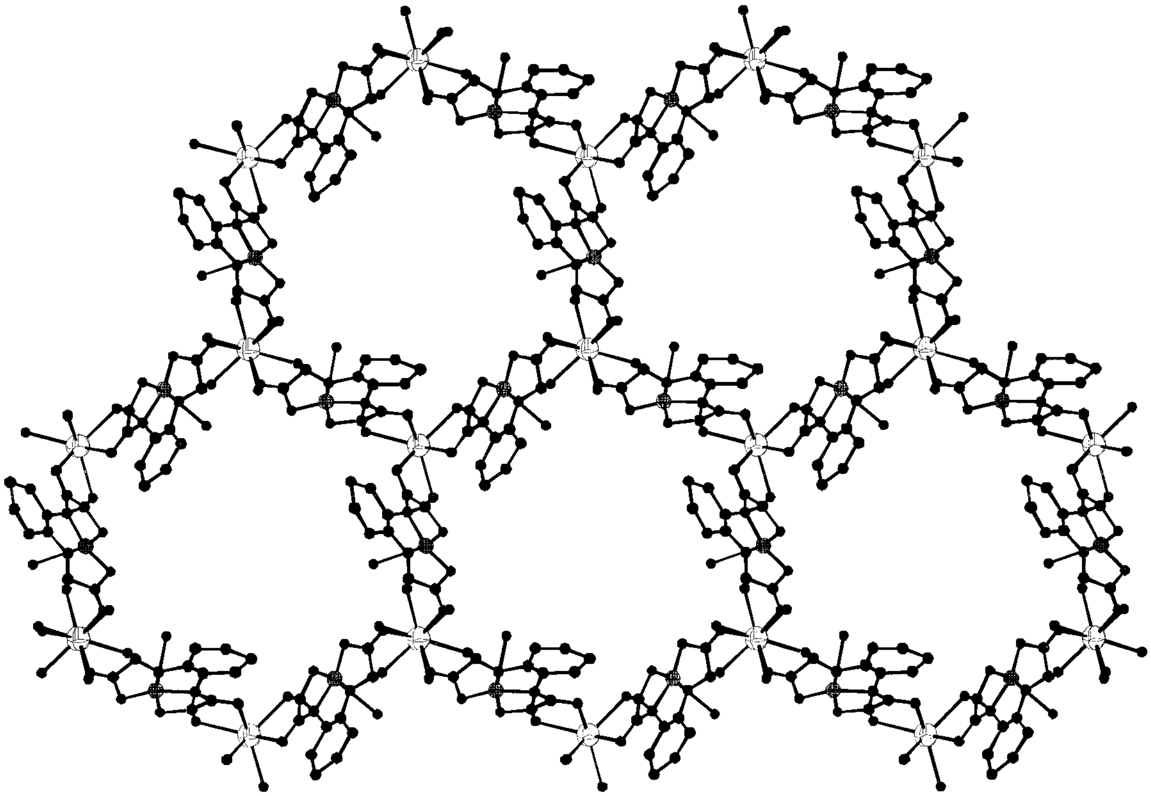

Figure 1. View of a layer for $\{Nd_2[Cu(opba)_{0.5}(ox)]_3 \cdot 9DMF\} \cdot 4.5DMF$ drawn at the 35% level.

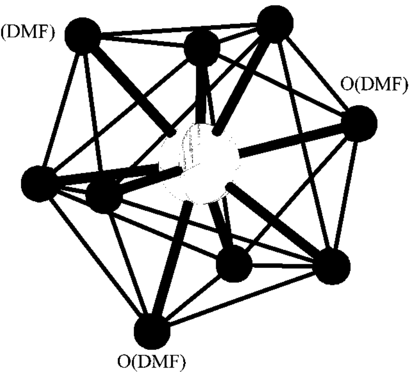

Figure 2. Coordination polyedron of the Nd^{III} ion.

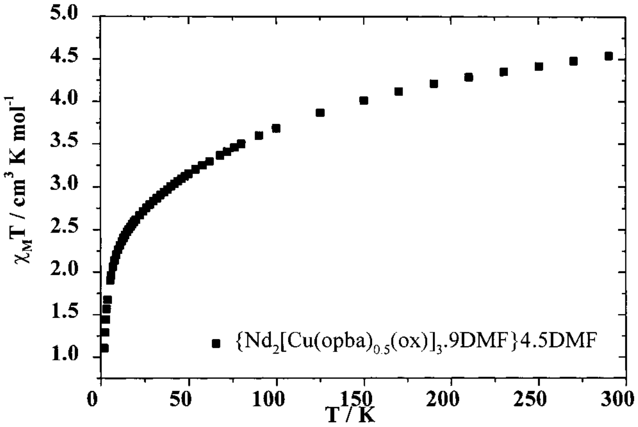

Figure 3. $\chi_M T$ versus T curve for $\{Nd_2[Cu(opba)_{0.5}(ox)]_3 \cdot 9DMF\} \cdot 4.5DMF$.

STOE (DISPLAY, INDEX, CELL, PROFILE, INTEGRATE).[19] Data were corrected by an empirical absorption correction (ABSCOR).[19] The structure was solved by direct methods with SHELXS-86[20] and refined by full-matrix least-squares calculations on F^2 with SHELXL-93.[21] The refinement was performed on F^2 for all reflections including those generally believed to be unobserved [$F < 4\sigma(F)$]. All non-hydrogen atoms were refined anisotropically. The crystallographic data are summarized in Table 1; selected bond distances are listed in Table 2.

Results and Discussion

The structure consists of corrugated honeycomb-like layers, as shown in Figure 1. The Nd^{III} ions occupy the corners of the edge-sharing hexagons, and the Cu^{II} ions occupy the middles of the edges. These edges are statistically made of Cu(opba) and $Cu(ox)_2$ groups, with a probability of 0.5 for each of them. The average values of the Nd−Cu and Nd−Nd separations along an edge are equal to 5.9 and 10.9 Å, respectively, and the average value of the diagonal of a hexagon is equal to 19.96 and 16.31 Å for Nd−Nd and Cu−Cu directions, respectively. Each Nd^{III} ion is located on a 3-fold axis and is surrounded by nine oxygen atoms, six of them arising from the bidentate oxamato or oxalato groups, and three of them arising from DMF molecules. The coordination polyhedron shown in Figure 2 may be described as a tricapped trigonal prism. Each Cu^{II} ion is in a square pyramidal environment, with two nitrogen and two oxygen atoms of two oxamato groups, or four oxygen atoms of two oxalato groups in the basal plane, and an oxygen atom of a DMF molecule occupying an apical position. The apical Cu−O bond length is equal to 2.4 Å. The corrugated layers are located with regard to each other in such a way that a Nd^{III} ion of a layer projects at the center of a hexagon belonging to adjacent layers. The interlayer separations are Nd−Nd = 9.6 Å, Cu−Cu = 9.9 Å, and Nd−Cu = 9.4 Å.

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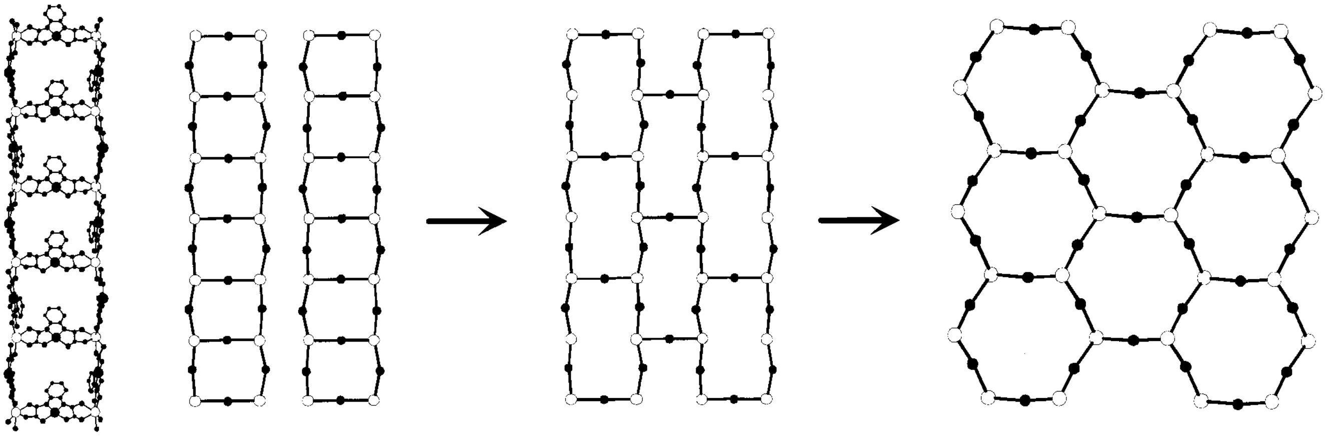

Figure 4. Transformation of the structure consisting of parallel ladderlike motifs into the honeycomb-like structure.

The variation of the magnetic susceptibility per Nd_2Cu_3 unit, χ_M, as a function of temperature, T, was measured. The results are shown in Figure 3 in the form of the $\chi_M T$ versus T plot. At room temperature, $\chi_M T$ is equal to 4.6 emu K mol^{-1}, which corresponds to what is expected for three Nd^{III} and two Cu^{II} ions. As the temperature is lowered, $\chi_M T$ decreases more and more rapidly; the $\chi_M T$ value at 2 K is 1.15 emu K mol^{-1}, and the value extrapolated for T approaching the absolute value is close to zero. The compound has a quasi nonmagnetic ground state. The same behavior was observed for other compounds with the Nd_2Cu_3 topology.[22] This behavior was attributed to an almost perfect but accidental compensation at low temperature between the two Nd^{III} and the three Cu^{II} magnetic moments. Such a compensation may append if the ratio $\rho = g'_{Nd}/g_{Cu}$ is equal or close to a critical value which has been calculated as 1.73; g'_{Nd} is the Zeeman factor associated with the ground Kramers doublet arising from the $^4I_{9/2}$ ground state of Nd^{III}, and g_{Cu} is the Zeeman factor for the Cu^{II} Kramers doublet. If the Nd^{III} and Cu^{II} magnetic moments were coupled antiferromagnetically, but without accidental compensation, the behavior would be ferrimagnetic, and $\chi_M T$ would not tend to zero as T approaches the absolute zero.

Conclusion

Our efforts to synthesize a honeycomb-like compound of formula $Ln_2[Cu(opba)]_3$ were partly successful. The expected topology was obtained, but half of the oxamato groups were lost and replaced by oxalato groups. All our synthetic attempts strongly suggest that the target topology could not be reached without this partial hydrolysis. The reason why the partial hydrolysis favors the honeycomb topology is not clear to us, especially as we failed to synthesize compounds with the $Ln_2[Cu(ox)_2]_3$ formula containing only oxalato bridges. Actually, the two structures, one consisting of parallel ladder motifs, the other consisting of a honeycomb network, are very close to each other. One can pass from the former to the latter by the displacement of one of every two rungs of the ladders in such a way as to link the ladders to each other, as emphasized in Figure 4.

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Supporting Information Available: Detailed crystallographic data, atomic position parameters, and bond lengths and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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