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New 3-D La(III)–Cu(II)-Containing Coordination Polymer with a High Potential Porosity

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A new 3-D coordination polymer containing both 3d and 4f ions has been designed. Its chemical formula is $La_2[Cu(pba)]_3(H_2O)_8\cdot 8H_2O$. It crystallizes in the quadratic system, space group $I41/a$ with $a = 42.4947(9)$ Å, $c = 16.3378(3)$ Å, and $Z = 16$. Its crystal structure can be described as a 3-D molecular framework exhibiting a complex network of interconnected zigzaglike channels. Once crystallization water molecules are removed, this compound presents a high potential porosity and a low density. The porosity has been evaluated using Connolly's algorithm.

For the past several years, the lanthanide-based coordination polymers have received special attention because of their ability to combine specific physical properties and original crystal structures. There is currently a renewed interest in that field partly because of the emergence of nanotechnology. Actually, the design of nanoporous open frameworks is a factor of this revival[1−4] because these compounds are anticipated to exhibit good efficiency as far as size-selective separation, catalysis, and gas storage are concerned.[5,6]

One of the major challenges in that field is to maintain the host framework integrity in the absence of guest molecules in order to allow reversible access to the cavities within the host. A synthetic strategy lies in the design of 3-D metal−organic frameworks that do not decompose or collapse upon removal of the guest molecules. Organic-binding ligands presenting rodlike topology with low steric hindrance along with a good affinity toward lanthanide ions are good promoters to 3-D coordination polymers.[7,8] Actually, many lanthanide-containing coordination polymers with benzenepolycarboxylates as binding ligands have been reported. However, when the porosity of the compounds is increased, the length of the organic part increases, the solubility in water of the ligand decreases, and the soft-chemistry routes are no longer suitable. We have thus undertaken the synthesis of a lanthanide-based coordination polymer where the binding entity would no longer be an organic ligand but a 3-D complex. We report here our first attempt. The chosen 3-D complex was $[Cu(pba)]^{2-}$, where pba stands for propylenebis(oxamato) (see Chart 1), which was extensively studied in the field of molecular magnetism during the 1990's.[9−11]

Chart 1. Schematic Representation of the Dianionic Complex $[Cu(pba)]^{2-}$

The compound $La_2[Cu(pba)_3]_3(H_2O)_8\cdot 8H_2O$ has been obtained by slow diffusion of $LaCl_3\cdot 7H_2O$ and $Na_2[Cu(pba)]\cdot 2H_2O$[12] in an agarose gel medium. It crystallizes in the quadratic system, space group $I41/a$ with $a = 42.4947(9)$ Å, $c = 16.3378(3)$ Å, and $Z = 16$. [Single crystals have been obtained by slow diffusion of $LaCl_3\cdot 7H_2O$ and $Na_2[Cu(pba)]\cdot 6H_2O$ through agarose gel in a U-shaped tube. Crystal data: $La_2Cu_3C_{21}N_6O_{34}H_{50}$, $M = 1399.09$ g mol^{-1}, tetragonal, space group I_1/a (No. 88), $a = 42.4947(9)$ Å, $c = 16.3378(3)$ Å, $V = 29502.8(10)$ Å^3, $Z = 16$, $D_{calcd} = 1.231$ g cm^{-3}, $\mu = 2.051$ cm^{-1}, $F_{000} = 10\,544$, 17 417 data

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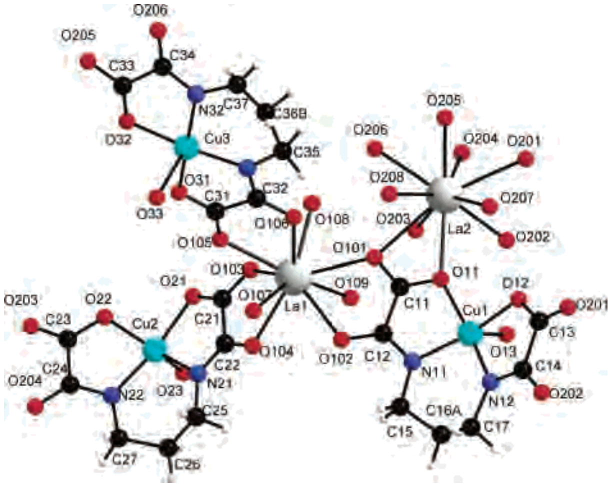

Figure 1. Extended asymmetric unit of $La_2[Cu(pba)]_3(H_2O)_8 \cdot 8H_2O$.

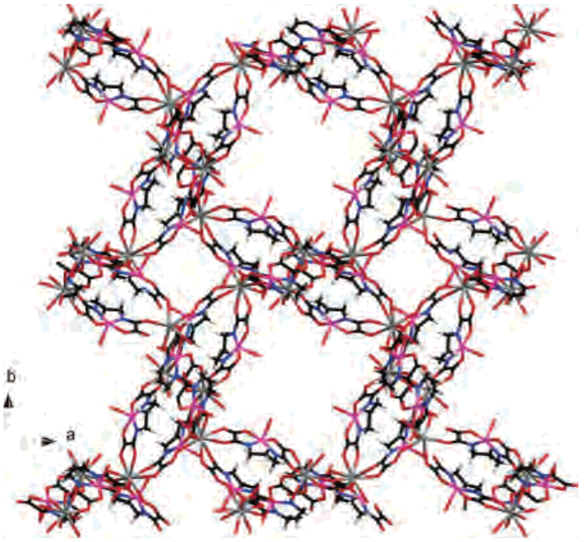

Figure 2. Projection view along the $\vec{c}$ axis showing large square section cavities. Crystallization water molecules have been omitted for clarity.

collected, 8892 observed data, 608 parameters refined, $R = 0.0736$, $R_w = 0.1952$, GOF $= 1.029$. CCDC 298861 contains the supplementary crytallographic 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 or CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., tel +44 1223 336408, fax +441223 336033]. The two independent La^{3+} ions are differently nine-coordinated. So, La1 is coordinated by six O atoms from the oxamato groups and three O atoms from the coordination water molecules, while La2 is coordinated by seven O atoms from the oxamato groups and two O atoms from the coordination water molecules (see Figure 1).

The three independent Cu^{2+} ions are five-coordinated by two O and two N atoms from the oxamato groups and by one O atom from a coordination water molecule in the apical position. As shown in Figure 1, all three independent $[Cu(pba)]^{2-}$ monomeric complexes are bonded to two La^{3+} ions in a bis-bidentate fashion. One out of the three is, in addition, bounded to a third La^{3+} ion thanks to a μ_2-O bridge. This leads to a 3-D molecular framework that shows a complex network of interconnected zigzaglike channels (Figure 2). A total of 8 out of the 16 water molecules present in the chemical formula are crystallization water molecules localized inside the channels and linked to the molecular skeleton by H bonds.

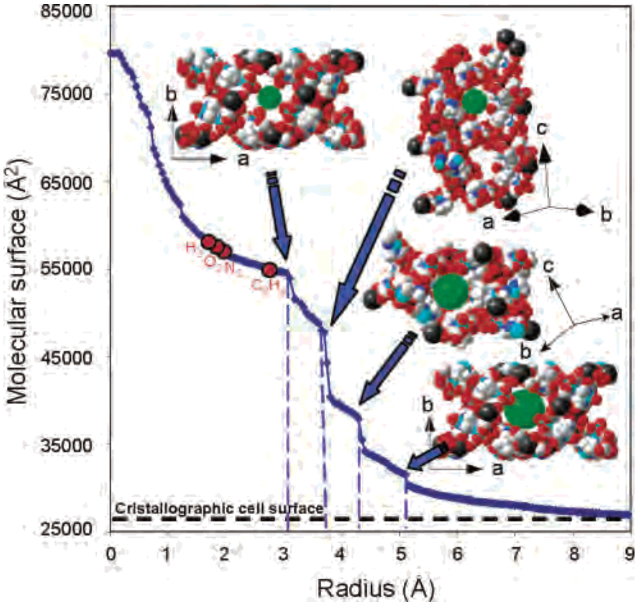

Figure 3. Porosity profile for $La_2[Cu(pba)]_3(H_2O)_8$. Red circles are symbolizing kinetic radii for selected usual molecules.

Table 1. Solvent-Accessible Surface Calculated According to Connolly's Algorithm for Various Kinetic Radii

	gas		
	H_2	O_2	N_2
kinetic radius (Å)	1.45	1.7	1.8
solvent-accessible surface ($m^2\ g^{-1}$)	1738	1596	1528

Unfortunately, this compound presents a low thermal stability, and the compound collapses during the heating required before Brunauer–Emmett–Teller measurements so it has not been possible to experimentally evaluate its porosity. However, crystallization water molecules are removable by cold drying at low temperature without destroying the molecular network. We have so formally removed them from the crystal structure and calculated the potential porosity of this partially dehydrated compound according to procedures already described elsewhere.[13,14] The results of these calculations are summarized in Table 1. These values are, to the best of our knowledge, the highest ones reported so far for lanthanide-containing coordination polymers.[15] The density of the partially dehydrated compound is 1.116 g cm^{-3}.

Thanks to Connolly's algorithm, it is also possible to obtain the molecular surface versus the probe sphere radius, that is, the kinetic radius (the kinetic diameter is the intermolecular distance of the closest approach for two molecules colliding with zero initial kinetic energy),[16−18] of

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the adsorbed molecules. This curve is represented in Figure 3. It is noticeable that this compound shows intricate zigzag channels with large sections.

In conclusion, we have presented here the first 3-D coordination polymer containing both a lanthanide ion and a transition-metal ion and exhibiting a very high potential porosity. This result confirms that the use of monomeric complexes as binding ligands is a good synthetic strategy for obtaining highly porous molecular frameworks. Furthermore, it confirms, once more, the good efficiency of gel media for obtaining original molecular topologies that cannot be obtained by other synthetic routes. At last, this result is also interesting because very few 3-D 4f−3d molecular materials have been reported so far.[19,20]

We are presently working toward achieving experimental measurements of the porosity and replacing La(III) ions by Gd(III) ions in order to study the magnetic properties of the Gd(III)-containing compound.

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