From Cubane to Supercubane: The Design, Synthesis, and Structure of a Three-Dimensional Open Framework Based on a Ln_4O_4 Cluster[**]

Bao-Qing Ma, Da-Shun Zhang, Song Gao,[*]
Tian-Zhu Jin, Chun-Hua Yan, and Guang-Xian Xu

High-nuclearity clusters are of great interest due to their fascinating structures and potential magnetic, optical, electronic, and catalytic applications, which may ultimately lead to new materials.[1] Additionally, high-nuclearity clusters represent a mesoscopic state between the macro- and microphase in terms of dimension.[2] As nanoparticles, they may exhibit unusual physical and chemical properties as exemplified by the well-known Mn_{12} cluster which displayed a quantum tunnel effect.[3] On the other hand, the nanoparticles prepared by the cluster complex method have advantages such as being grain-homogeneous and the ability to control the size through modifying the dimension of the cluster core. The synthesis of the high-nuclearity clusters is still a great challenge. The commonly employed strategy is to control the hydrolysis or alcoholysis of metal ions with the aid of supporting ligands.[4] In general, hydrophilic groups such as hydroxy, oxo, and carboxylate, lie within the core and induce the core aggregation, while hydrophobic groups form the periphery preventing the core from infinite aggregation. The choice of auxiliary ligands is critical to the cluster formation. Very recently, we have shown that amino acids, such as proline, valine, tyrosine, leucine, methionine, alanine, isoleucine, are an effective and promising family of ligands for the formation of lanthanide clusters at higher pH (6–6.5). Most of the clusters obtained display a Ln_4O_4 cubane structural motif. Even a pentadecanuclear lanthanide cluster with tyrosine comprises five corner-sharing Ln_4O_4 units.[5] Thus, the cubane Ln_4O_4 core appears to be a common type[6] and can serve as a building block for condensed clusters. The next logical step for us was to investigate whether the cubane units could be connected through bridging ligands to give multidimensional networks. In principle, the aqua position can be replaced by ligands capable of strong coordination such as 4,4′-bipyridine, and the partial monocarboxylate can be substituted by a dicarboxylate such as 1,4-benzenedicarboxylic acid. Among the natural amino acids there are two dicarboxylates, namely L-aspartic acid (asp) and L-glutamic acid (glu); these not only retain the nature of amino acids but also possess bridging capability. Thus it should be feasible to link discrete Ln_4O_4 cubane units into an extended network and this assumption has been confirmed by the reaction of $Dy(ClO_4)_3$ and asp to give a three-dimensional supercubane open framework. Although metal–organic open frameworks have been extensively exploited because of their gas sorption, guest inclusion, and ion-exchange properties,[7] the microporous networks containing lanthanide ions are still limited in spite of their special luminescence properties and catalytic activity.[8] Herein we describe a lanthanide microporous framework, to the best of our knowledge, the first assembly of a discrete lanthanide cluster into a three-dimensional (3D) network.

As typical examples, we report the tetranuclear cluster **1** and the three-dimensional network **2** , which were prepared by mixing $Ln(ClO_4)_3$ ($Ln = Gd$, Dy) and L-proline or L-aspartic acid, respectively, in aqueous solution, and subsequently adjusting pH values to about 6.5 using aqueous NaOH solution.

$[Gd_4(Hpro)_4(pro)_2(\mu_3\text{-}OH)_4(H_2O)_7](ClO_4)_6 \cdot 6\,H_2O$ **1**

$\{[Dy_4(\mu_3\text{-}OH)_4(asp)_3(H_2O)_8](ClO_4)_2 \cdot 10\,H_2O\}_n$ **2**

X-ray structure analysis reveals that the compound **1** is composed of a discrete tetranuclear cation $[Gd_4(Hpro)_4(pro)_2(\mu_3\text{-}OH)_4(H_2O)_7]^{6+}$, perchlorate, and lattice water.[9] The tetrameric cation (Figure 1) is based on a Gd_4 trigonal pyramid, in which Gd1 is located on a threefold axis, and occupies the apical position, while the other three Gd2 ions lie in the basal plane. The Gd1⋯Gd2 and Gd2⋯Gd2A separations are 3.8542(11) and 3.8629(8) Å, respectively; thus the Gd_4 unit is very close to a regular tetrahedron. Each triangular Gd_3 face is capped by a triply bridging hydroxy ligand with Gd–O bond lengths in the range between 2.367(3) and 2.482(3) Å. These may be compared to the Gd–O distances of 2.363(7)–2.412(7) Å in $[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}H_2O)_2(H_2O)_4(hfpd)_8]$ (hfpd-H = 1,1,1,5,5,5-hexafluoropentane-2,4-dione),[6b] which has a tetrahedral geometry with

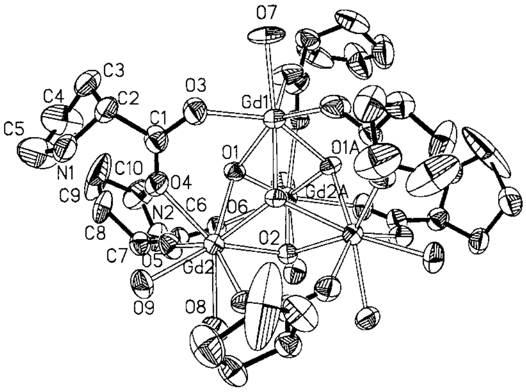

Figure 1. A perspective view of partial structure in compound **1**.

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[*] Prof. Dr. S. Gao, Dr. B.-Q. Ma, Prof. T.-Z. Jin, Prof. Dr C.-H. Yan, Prof. Dr. G.-X. Xu
State Key Laboratory of Rare Earth Materials Chemistry and Applications
PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry
Peking University
Beijing 100871 (P. R. China)
Fax: (+86) 10-6275-1708
E-mail: gaosong@chemms.chem.pku.edu.cn
Prof. D.-S. Zhang
Changde Normal College, Changde 415000 (P. R. China)

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face-capping hydroxy groups. Each pair of adjacent Gd ions are also bridged by one carboxy group of a proline ligand in the *syn–syn* mode (mean Gd–$O_{carboxyl}$ bond length, 2.367 Å). Alternatively, the structure may be regarded as a distorted cubane, in which the four bridging OH^- groups are also considered as vertices of the polyhedron. The Gd1 ion is seven-coordinate, surrounded by three OH^- groups, three carboxy oxygen atoms, and an aqua ligand O7 lying in the C_3 axis, yielding a monocapped trigonal antiprism. The Gd2 ion is eight-coordinate, surrounded by three OH^- groups, three carboxy oxygen atoms, and two aqua ligands in a square antiprism, in which the top and bottom planes are defined by O1, O2, O5, O8 and O4, O9, O1B, O6B, respectively.

Compound **2** forms a three-dimensional network based on a Dy_4O_4 cubane core connected by bridging asp ligands.[9] The Ln_4O_4 cubane core is similar to that observed in **1** (Figure 2). The Ln_4 tetrahedron is embedded in the Dy_4O_4 cubane core; the Dy···Dy separation ranges between 3.7211(5) and 3.8526(6) Å. Each triangular face is capped by a triply bridging hydroxy ligand (av Dy–O 2.357 Å, Dy-O-Dy 106.62°). Each Dy ion is eight-coordinate, surrounded by three OH^- groups, three carboxy oxygen atoms (av Dy–O 2.342 Å), and two aqua ligands (av Dy–O 2.441 Å), yielding a distorted square antiprism.

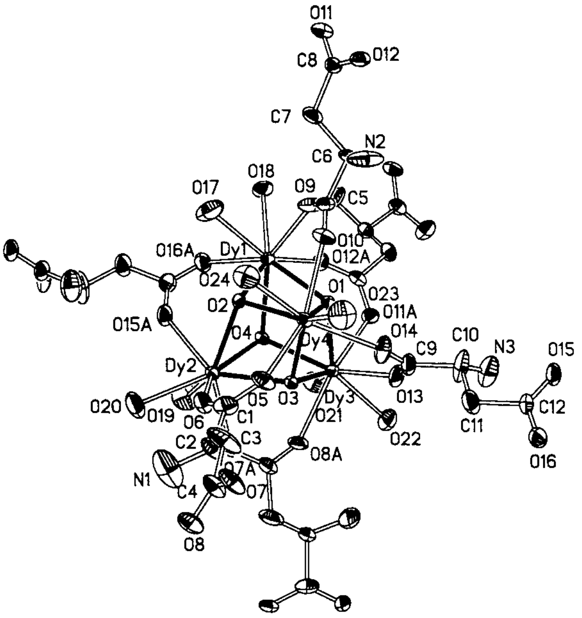

Figure 2. Structure of one of the units that forms the extended network of compound **2**.

Each edge of each Dy_4 tetragon is connected by dicarboxylate ligands to give a $\{Ln_4(OH)_4(COO)_6\}$ cluster as a basic unit. These are then further extended to form a three-dimensional network with an intersecting parallelepiped-shaped pore (11.78 Å), which houses water molecules and ClO_4^- ions. Allowing for the van der Waals radii, the free pore volume of the structure is 33.1 %, based on the calculation approach adopted by Yaghi et al.;[10] this value is large among the known microporous networks (Figure 3). When the bound water molecules are removed, the volume increases up to 50.1 %, close to that observed in $[Zn_4O(bdc)_3(DMF)_8(C_6H_5Cl)]$ (bdc = benzenedicarboxylate), which is regarded as the prototype for a third generation of open framework,[7] in which a regular Zn_4O tetrahedron is linked by O_2-C-C_6H_4-C-O_2 struts to give an extended network with a three-dimensional intersecting channel with a spacing between the centers of adjacent clusters of 12.94 Å.

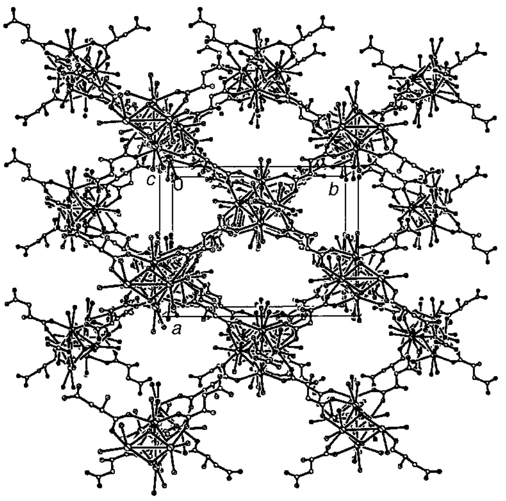

Figure 3. 3D network of compound **2** along [001] direction, exhibiting large channels.

The variable-temperature magnetic susceptibility of both compounds was measured and $\chi_M T$ values for the $[Ln]_4$ unit at room temperature are 31.40 and 55.84 $cm^3 K mol^{-1}$ for **1** and **2**, respectively, very close to the expected values of 31.5 and 56.5 $cm^3 K mol^{-1}$ for four noninteracting Ln^{3+} free ions. The $\chi_M T$ value of **1** remains almost constant from room temperature to about 20 K, and then decreases rapidly on further cooling, reaching a minimum value of 25.82 $cm^3 K mol^{-1}$ at 5 K. The data in the range between 5 and 300 K can be well fitted to the Curie–Weiss law with $C = 31.37$ $cm^3 K mol^{-1}$, and $\theta = -1.01$ K, indicating weak antiferromagnetic interactions between the Gd^{3+} ions. Compound **2** has a $\chi_M T$ versus T curve similar to that of **1**. However, the rapid drop of $\chi_M T$ at low temperature probably results primarily from the splitting of ligand field of the Dy^{3+} ion together with some contribution from the weak antiferromagnetic coupling between Dy^{3+} ions, as for the Gd_4O_4 unit.

In summary, a rational synthesis route from discrete cubane to supercubane has been designed and established. A three-dimensional framework has been obtained with intersecting channels of 11.78 Å. The large size of the cavities and access channels in **2** offer appreciable potential for guest molecule occupation and investigations in this direction are in progress.

Experimental Section

1: $Gd(ClO_4)_3$ and L-proline (pro) were mixed in a 2:1 molar ratio in water. The mixed solution was adjusted to pH 6.3 with 0.1 M aqueous NaOH under heating and stirring. The lanthanide ions were partially hydrolyzed to form a precipitate. The precipitate was filtered off and the filtrate was evaporated slowly at room temperature to afford colorless prismatic crystals. Yield: 45 %. Elemental analysis calcd for $C_{30}H_{82}C_{16}Gd_4N_6O_{53}$ (%): N 3.79, C 16.25, H 3.73; found: N 3.12, C 13.81, H 3.69.

2: L-Aspartic acid (asp) (1 mmol) was added to an aqueous solution of $Dy(ClO_4)_3$ under stirring and heating at 80 °C, then 0.1 M aqueous NaOH was added to adjust the pH to 6.5. The precipitate formed due to the partial hydrolysis of Ln^{3+} ions was filtered off and the filtrate was allowed to stand at room temperature. Colorless block-shaped crystals were obtained after one month. Yield: 34 % based on the aspartic acid. Elemental analysis calcd for $C_{12}H_{54}Cl_2Dy_4N_3O_{42}$ (%): N 2.57, C 8.82, H 3.31; found: N 2.16, C 7.49, H 3.22.

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[9] Crystal structure analysis data: compound **1**: $[Gd_4(Hpro)_4(pro)_2(\mu_3\text{-}OH)_4(H_2O)_7](ClO_4)_6 \cdot 6H_2O$, $M_r = 2216.72$, rhombohedral, $R3$, $a = b = c = 12.8953(15)$ Å, $\alpha = \beta = \gamma = 100.663(17)°$, $V = 2016.8(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.825$ Mg m^{-3}, $\mu = 3.545$ mm^{-1}, $GOF = 1.083$, $F(000) = 1086$, $R1 = 0.0683$, $wR2 = 0.1876$, 317 parameters, 4130 reflections $[I > 2\sigma(I)]$. The intensity data was collected at 294 K on a Rigaku RAXIS IIc imaging-plate diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min} = 3°$, $2\theta_{max} = 55°$, 34 oscillation frames in the range of 0–180°, exposure 8 min per frame). A self-consistent semiempirical absorption correction based on Fourier coefficient fitting was applied using ABSCOR. Compound **2**: $C_{12}H_{54}Cl_2Dy_4N_3O_{42}$, $M_r = 1633.48$, orthohombic, $P2_12_12_1$, $a = 14.011(3)$, $b = 18.822(4)$, $c = 23.421(5)$ Å, $V = 6176(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.757$ Mg m^{-3}, $\mu = 4.958$ mm^{-1}, $F(000) = 3124$, $GOF = 1.013$. The data were collected on a Nonius Kappa CCD with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXL 97 program. $R1 = 0.0497$, $wR2 = 0.1354$, 483 parameters, 12942 reflections $[I > 2\sigma(I)]$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-141086 (**1**) and CCDC-141085 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Remarkable Anionic Axial Ligand Effects of Iron(III) Porphyrin Complexes on the Catalytic Oxygenations of Hydrocarbons by H_2O_2 and the Formation of Oxoiron(IV) Porphyrin Intermediates by *m*-Chloroperoxybenzoic Acid[**]

Wonwoo Nam,[*] Mi H. Lim, So-Young Oh, Jung H. Lee, Ha J. Lee, Seung K. Woo, Cheal Kim, and Woonsup Shin

The reactions of iron(III) porphyrin complexes with various oxidants such as peroxy acids and hydroperoxides have been extensively studied for the past two decades, with the intention of elucidating the mechanisms of O–O bond activation and developing biomimetic oxygenation reactions.[1] Since hydrogen peroxide (H_2O_2) is a biologically important and environmentally clean oxidant, use of the oxidant in catalytic oxygenation of hydrocarbons by iron porphyrin complexes has attracted much attention in the communities of bioinorganic and oxidation chemistry.[1] Traylor et al. reported for the first time that the reactions of iron porphyrins with H_2O_2 in a protic solvent such as CH_3OH generate oxoiron(IV) porphyrin cation radical complexes $[Fe^{IV}(porp)^{+\bullet}(O)]$ that epoxidize olefins to give the corresponding oxide products.[2] We and Mansuy et al. also showed recently that highly electron-deficient iron porphyrin complexes react with H_2O_2 to form intermediates that are capable of oxygenating olefins and unactivated alkanes in aprotic solvent.[3, 4]

Another oxidant that has been widely used in the mechanistic studies of O–O bond activation by iron(III) porphyrin complexes is peroxy acids such as *m*-chloroperoxybenzoic acid (*m*-CPBA).[1] It is generally believed that iron porphyrins react with peroxy acids to form $[Fe^{IV}(porp)^{+\bullet}(O)]$ by O–O bond heterolysis in polar solvents such as CH_2Cl_2.[5] As far as we have been able to discern, there is no report that shows that both heterolysis and homolysis can occur concurrently in the *m*-CPBA reactions in polar solvent. Herein, we report two novel results that were obtained using an electron-deficient iron(III) porphyrin complex containing different anionic axial ligands: the remarkable anionic axial ligand effects on 1) the catalytic epoxidation and hydroxylation of hydrocarbons by

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[*] Prof. Dr. W. Nam, M. H. Lim, S.-Y. Oh, J. H. Lee, H. J. Lee
Department of Chemistry and Division of Molecular Life Sciences
Ewha Womans University, Seoul 120-750 (Korea)
Fax: (+82) 2-3277-2384
E-mail: wwnam@mm.ewha.ac.kr

Prof. Dr. C. Kim
Department of Fine Chemistry
Seoul National Polytechnic University
Seoul 139-743 (Korea)

S. K. Woo, Prof. Dr. W. Shin
Department of Chemistry
Sogang University
Seoul 121-742 (Korea)

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