Letter

The formation of Gd_4O_4 cubane cluster controlled by L-valine

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

[a] *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. E-mail: gaosong@chemms.chem.pku.edu.cn*

[b] *Changde Normal College, Changde 415000, P.R. China*

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Hydrolysis of $Gd(ClO_4)_3$ controlled by L-valine yields a novel tetranuclear cubane cluster $[Gd_4(\mu_3\text{-}OH)_4(Hval)_3(val)_3(H_2O)_8](ClO_4)_5\cdot 8\,H_2O$.

Lanthanide complexes were extensively studied in the past due to their significance in biological and materials chemistry. As luminescence materials, they find commercial applications in television picture tubes and light bulb filaments.[1] A $[Gd(DTPA)]^{2-}$ (H_5DTPA = diethylenetriaminepentaacetic acid) complex has been used in magnetic resonance imaging (MRI) as a contrast-enhancing agent for making tumor diagnostics.[2] Recently, with the development of rare earth additives to fertilizers in agriculture, rare earth ions may start to enter into the food chain of mankind.[3] Although the consequent metabolic effects are not clear at present, detailed structural information of lanthanide complexes with amino acid ligands will be relevant to the investigation of the interactions between rare earth ions and proteins.

We have previously made a systematic study of rare earth complexes with amino acids at low pH values.[4] Below pH 4, the amino acids are in zwitterionic form and commonly yield chain-like compounds with lanthanide ions. When the pH value is increased to between 5.5 and 6.5, the ligands may be partially or completely deprotonated. It is possible for the nitrogen and carboxylate oxygen atoms to participate in coordination simultaneously, yielding a fascinating pentadecanuclear lanthanide cluster $[Ln_{15}(Cl)(\mu_3\text{-}Tyr)_{10}(\mu_3\text{-}OH)_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2\cdot 56\ H_2O$ with tyrosine that consists of five corner-sharing Ln_4O_4 cubane units.[5] This is the largest known homonuclear lanthanide cluster.[6] Consequently, the related reaction with L-valine was attempted at higher pH values, giving rise to a tetranuclear structural motif. In the present work, the synthesis and structure of the tetranuclear cluster $[Gd_4(\mu_3\text{-}OH)_4(Hval)_3(val)_3(H_2O)_8](ClO_4)_5\cdot 8\ H_2O$, **1**, are reported.

Reaction of $Gd(ClO_4)_3$ and L-valine (Hval) in a 2 : 1 molar ratio at pH 6.3 under stirring and heating gave colorless prismatic crystals of **1**, which easily lose water in air.† X-Ray analysis revealed that the compound is composed of a discrete tetranuclear cation $[Gd_4(\mu_3\text{-}OH)_4(Hval)_3(val)_3(H_2O)_8]^{5+}$, perchlorate anions and lattice water molecules.‡ The tetrameric cation (Fig. 1) is based on a Gd_4 tetrahedron, in which the Gd···Gd separations are in the range 3.7676(6)–3.9017(6) Å. Each triangular metal face is capped by a triply bridging hydroxyl ligand with Gd–O bond lengths ranging from 2.361(6)–2.440(7) Å. These may be compared to 2.363(7)–2.412(7) Å in $[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}H_2O)_2(H_2O)_4(hfpd)_8]$ (Hhfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione),[7] which has a tetrahedral geometry with face-capping hydroxides. Meanwhile, each pair of adjacent Gd ions is also connected by one carboxyl group of a valine ligand in the *syn-syn* mode (mean $Gd\text{–}O_{carboxyl}$ bond length, 2.367 Å). Alternatively, the structure may be regarded as a distorted cubane, when considering the four bridging OH^- groups as vertices of the polyhedron. Each Gd ion is 8-fold coordinated by three OH^- groups, three carboxyl oxygen atoms and two aqua ligands (average $Gd\text{–}O_{aqua}$ bond length, 2.473 Å), leading to a distorted square antiprism. The neighboring clusters are linked through hydrogen bonds into a 3D network (Fig. 2).

The structure is something like that of $[Tb_4(OH)_4(pybet)_6(H_2O)_8]$,[8] in which pyridino acetate, analogous to an amino acid, was employed. They have similar cluster core motifs. Generally speaking, the cubane arrangement for tetranuclear lanthanoid complexes is relatively rare, compared with transition metal clusters,[9] and known examples are the alkoxide-bridged $[Eu(\mu_3\text{-}OCH_2CH_2OMe)_2\text{-}(OC_6H_3R_2\text{-}2,6)]_4{}^{4-}$, Se-bridged $[(py)_8Yb_4Se_4(SePh)_4]$ and $[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}H_2O)_2(H_2O)_4(hfpd)_8]$ mentioned above.[7,10]

The design and synthesis of high-nuclearity metal clusters is one of the most stimulating research fields and also a challenging subject. A commonly employed strategy is to control the hydrolysis or alcoholysis of metal ions with the help of auxiliary ligands. The assembly principle is that the hydrophilic groups lie within the cluster core to hold the metal ions together and the hydrophobic organic groups take up posi-

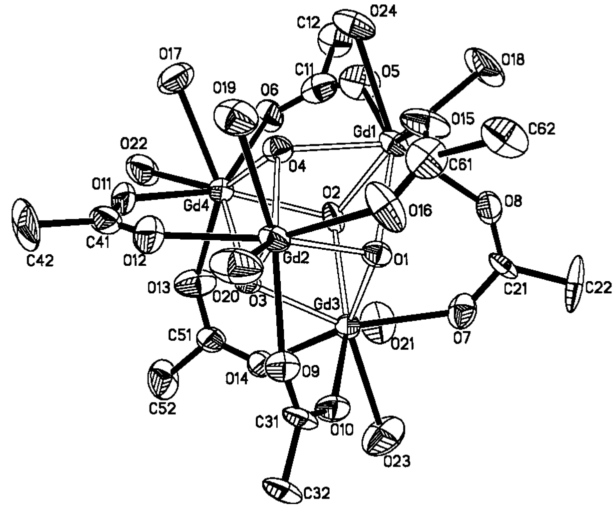

Fig. 1 Molecular structure of complex **1** with 30% probability ellipsoids (the isopropanyl and amino ligands are omitted for clarity). Selected bond lengths (Å): Gd1–O15 = 2.280(8), Gd1–O5 = 2.333(9), Gd1–O4 = 2.370(6), Gd1–O8 = 2.392(5), Gd1–O1 = 2.401(6), Gd1–O18 = 2.399(8), Gd1–O2 = 2.442(7), Gd1–O24 = 2.507(7), Gd2–O12 = 2.346(8), Gd2–O9 = 2.376(7), Gd2–O1 = 2.397(5), Gd2–O4 = 2.401(7), Gd2–O3 = 2.429(7), Gd2–O20 = 2.437(10), Gd2–O16 = 2.482(9), Gd2–O19 = 2.527(7), Gd3–O10 = 2.310(8), Gd3–O7 = 2.345(7), Gd3–O2 = 2.363(6), Gd3–O14 = 2.377(7), Gd3–O1 = 2.387(6), Gd3–O3 = 2.403(5), Gd3–O23 = 2.476(9), Gd3–O21 = 2.520(10), Gd4–O11 = 2.348(7), Gd4–O13 = 2.370(8), Gd4–O4 = 2.374(7), Gd4–O3 = 2.393(6), Gd4–O2 = 2.394(5), Gd4–O6 = 2.440(8), Gd4–O22 = 2.445(10), Gd4–O17 = 2.477(8).

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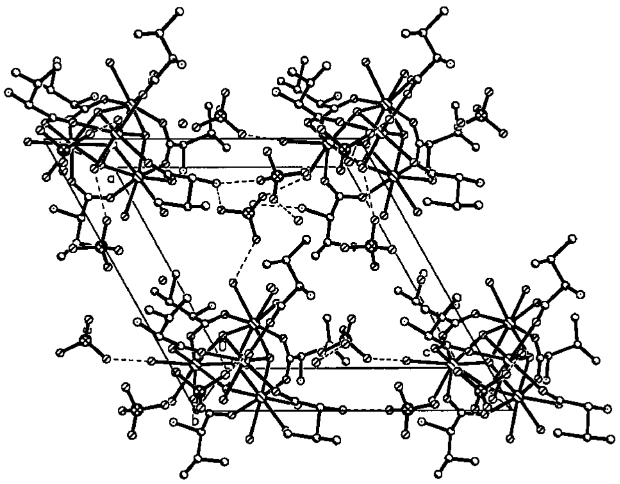

Fig. 2 The packing diagram of complex **1** along the *b* direction.

tions on the periphery, preventing the core from further aggregation. The selection of the supporting ligands is critical to cluster formation. Many interesting structures have been obtained mainly based on carboxylate,[11] polyketonates,[12] alkoxides,[13] and pyridionate.[14] After the initial success in synthesizing pentadecanuclear lanthanide–tyrosine complexes, the potential capability of amino acids in generating high-nuclearity complexes begins to emerge. This capability is further confirmed in the present context. Thus, an effective and promising family of ligands in the synthesis of lanthanide clusters is recognized. In view of the variety of amino acid members in this family, the occurrence of many other wonderful high-nuclearity clusters can be expected.

Interestingly, the compound crystallizes in a chiral space group, since a chiral amino acid ligand was employed. In addition, the cubane Ln_4O_4 core appears as a common structure type in lanthanide clusters and can function as a building block to construct multi-dimensional networks connected through bridging ligands[15] or other higher-nuclearity clusters, such as Ln_{15}.[5] Indeed, this work is currently in progress.

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Notes and references

† $Gd(ClO_4)_3$ (2.0 mmol) and L-valine (Hval) (1 mmol) were mixed in water (*ca.* 15 ml). The mixed solution was carefully adjusted to pH 6.3 with 0.5 M aqueous NaOH under heating and stirring for *ca.* 1 h until a precipitate formed due to hydrolyzation of Gd^{3+} ion. The mixture was then filtered and the filtrate was evaporated slowly at room temperature, yielding colorless prismatic crystals in 10 days (42% yield based on valine). Anal. found: N, 3.65; C, 16.49; H, 3.91. Calcd. for $C_{30}H_{99}Cl_5Gd_4N_6O_{52}$: N, 3.85; C, 16.50; H, 4.54%.

‡ The intensity data were collected on a Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 294 K. The crystal was covered with vaseline and sealed in a thin-walled capillary. For compound $[Gd_4(\mu_3\text{-}OH)_4(Hval)_3(val)_3(H_2O)_8](ClO_4)_5 \cdot 8H_2O$, $M = 2182.40$, monoclinic, $P2_1$ (no. 4), $a = 13.3492(7)$, $b = 25.9398(13)$, $c = 13.5326(8)$ Å, $\beta = 118.9664(15)°$, $U = 4099.8(4)$ Å^3, $Z = 2$, $\mu = 3.454$ mm^{-1}, GoF = 1.065, $F(000) = 2156$. Some terminal C atoms of L-valine were seriously disordered and refined isotropically with the same temperature factor. The crystal water molecules and ClO_4^- anions were also refined isotropically with the same free variable. The hydrogen atoms of the main complex molecule were added in calculated positions and other hydrogen atoms, including water molecules, were not found from the difference electron density map. The final R_1 and wR_2 are 0.0769 and 0.1873, respectively, for 754 parameters and 7020 reflections $[I > 2\sigma(I)]$

CCDC reference number 440/165. See http://www.rsc.org/suppdata/nj/a9/a910181k/for crystallographic files in .cif format.

1 R. C. Ropp, *Luminescence and the Solid State*, Elsevier, New York, 1991; J. R. McColl and F. C. Palilla, in *Industrial Applications of Rare Earth Elements*, ed. K. A. Gschneidner, Jr., ACS Symposium Series, American Chemical Society, Washington, DC, 1981, 164.

2 (*a*) R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901; (*b*) M. F. Tweedle, *Invest. Radiol.*, 1992, **27**, S2.

3 G. X. Xu, *Rare Earth*, Metallurgical Industry Inc., Beijing, 2nd edn., 1995.

4 R. Y. Wang, F. Gao and T. Z. Jin, *Chem. Bull.*, 1996, **10**, 14 (in Chinese) and references therein.

5 R. Y. Wang, Z. P. Zheng, T. Z. Jin and R. J. Staples, *Angew. Chem., Int. Ed.*, 1999, **38**, 1813.

6 R. Anwander, *Angew. Chem., Int. Ed.*, 1998, **37**, 599.

7 J. C. Plakatours, I. Baxter, M. B. Hursthouse, K. M. A. Malik, J. McAleese and S. R. Drake, *J. Chem. Soc., Chem. Commun.*, 1994, 2455.

8 X. M. Chen, Y. L. Wu, Y. X. Tong, Z. Sun and D. N. Hendrickson, *Polyhedron*, 1997, **16**, 4265.

9 (*a*) R. H. Holm, J. Huang and C. Goh, *Inorg. Chem.*, 1997, **36**, 356; (*b*) H. Kawaguchi, K. Yamada and K. Tatsumi, *J. Am. Chem. Soc.*, 1997, **119**, 10871.

10 (*a*) W. J. Evans, M. A. Greci and J. W. Ziller, *Inorg. Chem.*, 1998, **37**, 5221; (*b*) D. Freedman, J. H. Melman, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 1998, **37**, 4162.

11 (*a*) S. P. Watton, P. Fuhrmann, L. Pence, A. Caneschi, A. Cornia, G. L. Abbati and S. J. Lippard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2774; (*b*) R. C. Squire, S. M. J. Aubin, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1995, **34**, 6463.

12 (*a*) A. Caneschi, A. Cornia, A. C. Fabretti and D. Gatteschi, *Angew. Chem., Int. Ed.*, 1999, **36**, 1295; (*b*) J. C. A. Boeyens and J. P. R. De Villiers, *J. Cryst. Mol. Struct.*, 1972, **2**, 197; (*c*) G. L. Abbati, A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, W. Malavasi and L. Schenetti, *Inorg. Chem.*, 1997, **36**, 6443.

13 (*a*) R. C. Mehrotra, A. Singh and S. Sogani, *Chem. Soc. Rev.*, 1994, **23**, 215; (*b*) K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.

14 S. Parsons and R. E. P. Winnpeny, *Acc. Chem. Res.*, 1997, **30**, 89.

15 T. Z. Jin, S. Gao, B. Q. Ma, D. S. Zhang and G. X. Xu, *Angew. Chem., Int. Ed.*, submitted for publication.