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Toward constructing nanoscale hydroxo–lanthanide clusters: syntheses and characterizations of novel tetradecanuclear hydroxo–lanthanide clusters

Ruiyao Wang, Datong Song and Suning Wang*
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada.
E-mail: wangs@chem.queensu.ca

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Two novel tetradecanuclear hydroxo–lanthanide complexes, formulated as $Ln_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}$, Ln = Tb, 1; Eu, 2; acac = acetylacetonato, were synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and phosphorescence spectroscopy.

Nanoscale-materials enjoy great popularity due to their rich electronic, optical, magnetic, and catalytic properties associated with their quantum size effects and large surface areas.[1,2] Of particular interest are lanthanide-based systems that have potential applications in electroluminescent displays, phosphors for fluorescent lighting, X-ray imaging, scintillators, fiber-optic amplifiers, solid state lasers as well as fluorescent tags of biological molecules.[1–3] However, the high expectations of using these particles have been compromised by the large crystalline sizes, agglomerative nature of the particles and the broad size distributions.[4] With the ultimate goal of solving the problem by constructing nanoscale molecules, which are thermodynamically stable and of monodisperse size distribution, our initial efforts focus on assembling large clusters *via* ligand-controlled hydrolysis of lanthanides.

Many polynuclear hydroxo–lanthanide clusters have been reported in the past two decades and, among them, two basic structural motifs of high symmetry are found, which are cubane-like clusters (*e.g.* $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$) and square pyramids (*e.g.* $[Ln_5(\mu_3\text{-}OR)_4]^{11+}$, R = H or alkyl). Zheng, Gao and co-workers' work on hydroxo–lanthanide complexes containing $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ established that 4 or 5 $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units can be assembled to form 'cubane-wheels' with Cl^-, Br^- or I^- as the anion-templates, and 3-dimensional infinite structures can be constructed by using aspartic acid or glutamic acid as the bridging ligands.[5,6] On the other hand, reports by Hubert-Pfalzgraf and co-workers and several other research groups on[7,8] $Ln_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu_2\text{-}OR)_4(OR)_5$ (square pyramid, Ln = La, Pr, Sm, Yb, Y; R = isopropyl, *tert*-butyl), $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu\text{-}\eta^2\text{-}R)_8(\eta^2\text{-}R)_8]^-$ (two apex-shared square pyramids, R = MeC(O)CHC(O)OEt),[9] $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ (octahedron, Ln = Nd, Sm, Gd, Dy, Er, Yb, Y)[6] and $Eu_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}DBM)_4(DBM)_6$ (square pyramid, DBM = 1,3-diphenylpropanedionato)[10] demonstrated the possibility of assembling large hydroxo–lanthanide clusters with either the square pyramid unit $[Ln_5(\mu_3\text{-}OR)_4]^{11+}$ or the octahedral unit $[Ln_6(\mu_4\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ as building blocks. By hydrolyzing $Ln(acac)_3{\cdot}4H_2O$ (Ln = Tb, Eu) in CH_2Cl_2–hexane with 2,2′-dipyridylsufide as the base,† we synthesized the first tetradecanuclear complexes $Ln_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}$ (Ln = Tb, **1**, Eu, **2**) that contain an octahedral Ln_6 unit sharing two opposing apexes with two square pyramidal Ln_5 units.

Both complexes have been fully characterized by elemental analysis, phosphorescent spectroscopy as well as single-crystal X-ray diffraction analysis,‡ which indicate that complexes **1** and **2** are iso-structural with comparable cell parameters and the same space group *I*4/*mmm*.

The molecular structure of $[Ln_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}]$ (Fig. 1 and 2, where Ln = Tb) has a crystallographically imposed D_{4h} symmetry. Due to the similarity of **1** and **2**, only the structure of **1** is presented herein. All Tb(III) ions in the molecule have a coordination number 8. The central portion of **1** is an octahedral Tb_6 unit with 8 hydroxo ligands capping all triangular faces. Within the Tb_6 unit, the Tb–Tb distances are 3.9304(10) Å [Tb(1)–Tb(3)] and 3.9697(13) Å [Tb(1)–Tb(1′)]. All previously known octahedral Ln_6 units in molecular compounds have a μ_6-oxo ligand in the center of the

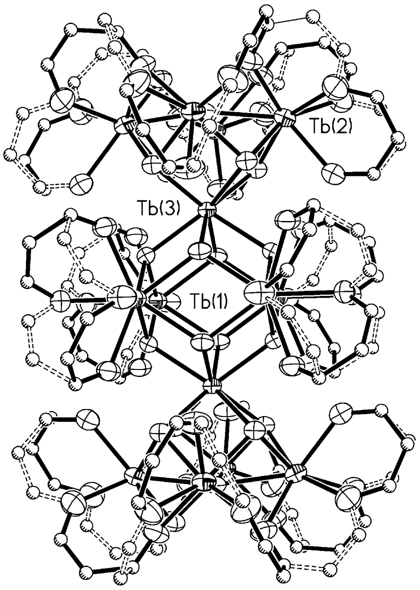

Fig. 1 A diagram showing the molecular structure of **1**. The carbon atoms on acac ligands are all disordered. One set of the disordered carbon atoms is shown by hollow bonds.

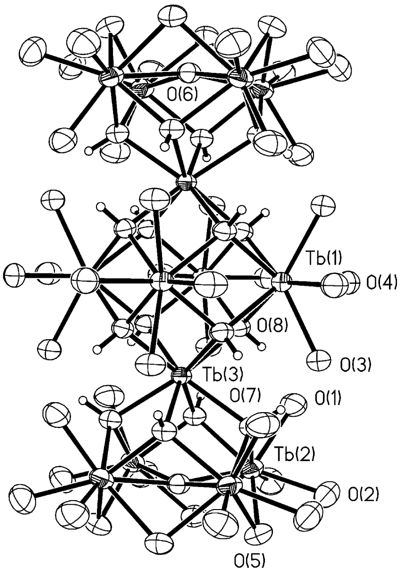

Fig. 2 A diagram showing the core structure of **1** with all carbon atoms omitted.

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octahedron, which is believed to play a key role in stabilizing the Ln$_6$ unit. To our best knowledge, compound **1** is the first example of a hydroxo–lanthanide complex that has a 'hollow' octahedral Ln$_6$ unit without the support of a μ_6-oxo ligand. Each of the four Tb(III) ions in the basal plane of the Tb$_6$ unit is chelated by two acac ligands. The carbon atoms of all acac ligands are disordered over two sites with 50% occupancy for each site. Similar site disordering, displayed by hexafluoroacetylacetonato ligands of lanthanide complexes, has been observed previously.[11] There are two square pyramidal Tb$_5$ units that are connected to the Tb$_6$ unit by sharing two opposite vertices of the Tb$_6$ unit. Within the Tb$_5$ unit, all triangular faces are occupied by μ_3-hydroxo ligands. The square face of the Tb$_5$ unit is occupied by a μ_4-hydroxo ligand that is at 0.303 Å above the Tb$_4$ basal plane. Each edge of the basal plane in the Tb$_5$ unit is bridged by one μ-η^2-acac ligand in a similar fashion as observed in $Eu_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}DBM)_4(DBM)_6$.[10] In fact the Tb$_5$ portion of compound **1** has a striking resemblance to those of $Eu_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}DBM)_4(DBM)_6$ and $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu\text{-}\eta^2\text{-}R)_8(\eta^2\text{-}R)_8]^-$.[9] As a consequence of the μ_4-hydroxo and acac bridges, the Tb–Tb distances [Tb(2)–Tb(2′) = 3.5867(11), Tb(2)–Tb(3) = 3.7664(11) Å] within the Tb$_5$ unit are much shorter than those of the hollow Tb$_6$ unit. The Tb$_4$ square plane in the Tb$_5$ unit is rotated by 45° with respect to the Tb$_4$ square plane in the central Tb$_6$ unit. The dimensions of compound **1** are approximately 19 × 13 × 13 Å.

Complex **1** yields bright green luminescence in both the solid state and solution. The UV–Vis, excitation and emission spectra of complex **1** in CH_2Cl_2 are shown in Fig. 3, which are similar to those of $Tb(acac)_3\cdot 4H_2O$. The UV–Vis spectrum of **1** resembles that of $Y(acac)_3\cdot nH_2O$ and the excitation spectrum of **1**, indicating that the excitation is mostly acac ligand-based. The emission spectrum of complex **1** is typical of Tb(III) emission with a decay lifetime of 797(8) μs and 931(5) μs in the solid state and CH_2Cl_2 solution, respectively, at 298 K. The absence of typical Tb(III) excitation bands in the excitation spectrum of **1** leads us to believe that indirect excitation (ligand assisted excitation) is operative in compound **1**. In the solid state, compound **1** is visibly much brighter than $Tb(acac)_3\cdot 4H_2O$, perhaps due to the increased rigidity of **1**. In CH_2Cl_2 solution, the brightness of **1** and $Tb(acac)_3\cdot 4H_2O$ is comparable. (The relative quantum-yield of complex **1** *vs.* that of $Tb(acac)_3\cdot 4H_2O$ in CH_2Cl_2 was determined to be ~0.53 at 298 K). Compound **2** is only weakly red-luminescent in solution and the solid state with a typical Eu(III) emission spectrum (decay lifetime = 345(2) μs in the solid state, 323(1) μs in CH_2Cl_2 at 298 K). The excitation spectrum of **2** in solution resembles that of **1**. However, in the solid state, the excitation spectrum of **2** is mostly characteristic of Eu(III). Hence, ligand-assisted or indirect excitation appears not to be effective in **2**, which is likely accountable for its low emission intensity.

Compounds **1** and **2** are soluble in polar organic solvents such as THF and CH_2Cl_2. However, mass spectroscopic studies by electron-spray methods did not reveal the molecular ions. The most intense peak observed in the ES mass spectra of **1** and **2** corresponds to the formula of $[Ln_9(OH)_{10}(acac)_{16}]^+$, which is an analogue of $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu\text{-}\eta^2\text{-}R)_8(\eta^2\text{-}R)_8]^-$ reported by Hubert-Pfalzgraf and co-workers.[9] The mass data appear to indicate that compounds **1** and **2** dissociate to a Ln$_9$ and a Ln$_5$ (observed in ES mass spectra) species in solution. Further study on the solution behavior of **1** and **2** and their potential applications in nano-scaled inorganic–organic composite materials and photonic devices are currently being explored in our laboratory.

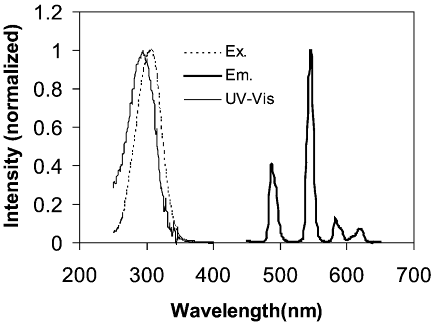

Fig. 3 The UV–Vis, excitation and emission spectra of **1**.

In summary we have accomplished the syntheses and characterization of two new members of the hydroxo–lanthanide cluster family that have an unprecedented 'hollow' Ln$_6$ octahedron with two apex-attached Ln$_5$ square pyramids. These two compounds demonstrate that large hydroxo–lanthanide clusters based on both square pyramid and octahedron building blocks can be assembled by controlled hydrolysis of $Ln(acac)_3\cdot 4H_2O$ in the presence of 2,2′-dipyridylsulfide. Modification of the reaction conditions could lead to the formation of even larger hydroxo–lanthanide clusters, something which is being investigated by our group.

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Notes and references

† *Experimental procedure*: In a typical synthesis, 0.50 mmol of $Ln(acac)_3\cdot 4H_2O$ was dissolved in 5 mL of CH_2Cl_2 and 0.50 mmol of 2,2′-dipyridylsulfide in 2 mL of CH_2Cl_2 was added dropwise. The mixture was allowed to stand at room temperature overnight and the solution was concentrated. About 30 mL of hexane was added to the residue thereafter and the solution was refluxed for about 3 h. The resulting clear solution was kept at ambient temperature and cubic block crystals were obtained in 2–3 weeks. **1**, analysis for vacuum dried samples, calc. for $C_{120}H_{186}O_{66}Tb_{14}$: C, 29.34; H, 3.79. Found: C, 29.67; H, 4.05%. **2**, calc. for $C_{120}H_{186}O_{66}Eu_{14}$: C, 29.95; H, 3.87. Found: C, 30.52; H, 3.96%.

‡ *Crystal data*: **1**, $C_{120}H_{186}O_{66}Tb_{14}\cdot 0.33C_6H_{14}$, M_r = 4937.6, tetragonal, space group *I*4/*mmm*, a = 21.090(4), b = 21.090(4), c = 21.213(5) Å, V = 9436(3) Å^3, Z = 2, D_c = 1.738 g cm^{-3}, μ(Mo-Kα) = 5.244 mm^{-1}, $F(000)$ = 4721, T = 296(2) K. The crystal of **1** was sealed in a glass capillary along with the solution. The data were collected on a Bruker CCD 1000 X-ray diffractometer at ambient temperature. Of the 34150 reflections collected, 3210 unique reflections with R_{int} = 0.0438 were used in all calculations. R_1 = 0.0731, wR_2 = 0.1480 for all 3210 data; **2** is isostructural to **1** with similar unit cell parameters. The remaining hydrogen atoms were neither calculated nor located.

CCDC reference number 167051.

See http://www.rsc.org/suppdata/cc/b105969f/ for crystallographic data in CIF or other electronic format.

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