A symmetry-controlled and face-driven approach for the assembly of cerium-based molecular polyhedra†

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A well-defined Ce-based molecular tetrahedron and a cube-like architecture were achieved via self-assembly by incorporating NOO tridentate chelators into the rationally designed ligands with $C_1$ or $C_3$ symmetries, respectively.

The coordination driven self-assembly of Plato polyhedra containing internal cavities with well-defined shape and size has achieved increasing prominence, owing to their promising functionalities as artificial metalated host platforms to mimic protein receptors or enzymes in their abilities to effectively bind substrates, stabilize reactive intermediates, and catalyze chemical transformations.1,2 These highly symmetrical structures could be particularly susceptible to rational design by careful matching of the symmetry properties of metal ions and rigid ligands.3 While the predictable nature of the coordination chemistry has been used to successfully generate a variety of high order oligonuclear cages containing highly directionally coordinated transition metal ions, the lanthanide ions are seldom used to construct the molecular capsules,4,5 despite the fact that such molecular cages have the potential to exhibit interesting physical and chemical properties.6 In most cases, the low stereochemical preferences of the lanthanide ions require more precise control of the chelator predisposing and spatial restricting of the ligands to construct high order structures. Nevertheless, the high coordination number of the lanthanide ions, in some cases, might be an important criterion in the assembly of special polyhedra.7

Tridentate coordinated units sharing two five- (or six-) membered chelating rings are one kind of efficient building blocks. They have been widely used to construct stable and functional discrete architectures with regular structure and high symmetry.8 Such kinds of polydentate chelating site can also limit the number and orientation of the ligands coordinating to the lanthanide centers, so that the better control of the lanthanide ions assembling into highly ordered architecture can be achieved.9 On the other hand, the cerium ion which has the specific electronic structure with the directional $5d$ orbits participating in the coordination modes was found to be able to allow the better control of the assembly of highly ordered architecture.10,11 Herein, we report a strategy to create a well-defined Ce-based molecular tetrahedron and a cube-like architecture by incorporating NOO tridentate chelators into the rationally designed ligands with $C_1$ or $C_3$ symmetries, respectively. The possibility of the lanthanide ions coordinating to three of these tridentate chelators in a pseudo $C_1$ symmetrical configuration is the key factor to establish the face-driven strategy based on four-connected ligands and three-connected Ce ions.

Ligand NATB was obtained from the reaction of 2-hydroxy-1-naphthaldehyde and 1,3,5-tricarbohydrazine benzene in an ethanol solution. Layering a methanol solution of Ce(NO$_3$)$_3$·6H$_2$O on a chloroform/methanol (1 : 1) solution of NATB containing KOH led to the formation of Ce$_4$(NATB)$_4$. The ESI-MS spectrum of Ce$_4$(NATB)$_4$ in the presence of KOH exhibited two intense peaks at $m/z = 1133.00$ and 1700.11 with the isotopic distribution patterns separated by 0.33 and 0.50 Daltons, respectively (Fig. 1). An exact comparison of these experimental peaks with the simulation results obtained on the basis of the natural isotopic abundances suggested that the negatively charged species were assigned to [Ce$_4$(NATB)$_4$-19H]$^-$ and [Ce$_4$(NATB)$_4$-18H]$^-$, respectively, indicating the stability of the tetranuclear complex in solution.

Single crystal structure analysis revealed that Ce$_4$(NATB)$_4$ crystallized in a cubic space group $Fd\bar{3}$. The cage had the ideal $T$ symmetry with one twelfth of the tetrahedral cage: one third of the metal centre and one third of the ligand appearing in an unsymmetrical unit. The four identical planar ligands position on the four triangle faces of the tetrahedron were defined by four metal ions, keeping their crystallographic $C_1$ symmetry with the three identical rigidly tridentate chelating groups coordinating to three identical metal centers (Fig. 2). Each vertical metal center sits in a crystallographic $C_1$ axis and coordinates to three tridentate chelating groups in a ternate coronary trigonal prism geometry, thus six oxygen atoms form a triangular prism with three nitrogen atoms extending outside each rectangle face (Scheme 1). Such that the four Ce centers are axial-symmetric related and thus have the same absolute coordination configuration, like the face-driven $M_4L_4$ tetrahedra previously reported.11 The Ce–O (phenol) and Ce–O(amide) distances are 2.337(3) and 2.447(3) Å, and the Ce–N distance is 2.570(4) Å, respectively. The Ce···Ce separation is about 9.92 Å with the inner volume being estimated as 220 Å$^3$. The (NH)$_2$C=O bond distances at about 1.25 Å coupled with (O)C–N(H) bond distances at about 1.32 Å suggests the existence of an acyllediazone form in the tridentate chelator that bonds to the cerium center.12

Such a rational strategy was further extended to the preparation of a cubic cage, by incorporating four tridentate chelating sites into a $C_3v$ symmetric facial ligand, TBMS, which was also obtained by the simple Schiff-base reaction of 2-hydroxy-1-naphthaldehyde with 3,3’,5,5’-tetracarbohydrazidediphenylmethane. Evaporating DMF solution of Ce(NO$_3$)$_3$·6H$_2$O and ligand TBMS containing KOH in air for several weeks led to the formation of compound Ce$_4$(TBMS)$_4$. The ESI-MS spectrum of Ce$_4$(TBMS)$_4$ exhibited only one peak at $m/z = 2397.85$ assignable to a [Ce$_4$(TBMS)$_4$-15H]$^-$ species, supporting the successful assembly of an octanuclear complex.
Fig. 1  ESI-MS spectra of Ce₄(NATB)₄ in methanol–DMF solution upon addition of KOH. The inserts exhibit the simulated and the measured isotopic patterns at about 1133.0 and 1700.1, respectively.

Fig. 2  Structure of the tetrahedral cage Ce₄(NATB)₄. Hydrogen atoms and solvent molecules are omitted for clarity. The metal, oxygen, nitrogen and carbon atoms are drawn in green, red, blue and yellow, respectively.

Single-crystal structure analysis revealed that the Ce₄(TBMS)₆ molecule comprised eight cerium ions and six TBMS ligands in a cubic-like cage (Fig. 3). Eight cerium centres sat at the eight corners of the cube-like cage, and each was also nine-coordinated by three tridentate chelating groups from different ligands. The coordination geometry was ternary coronary trigonal prism also, with the average Ce–O (phenol), Ce–O(amide) and Ce–N distances being 2.19, 2.41 and 2.59 Å, respectively. The average ($NH$)$C=O$ and ($O$)C–N($H$) bond distances of 1.19 and 1.34 Å, respectively, also suggested the existence of an acylhydrazone form. The TBMS molecule adopted a “shrinking” configuration with the dihedral angle between two phenyl rings and the connected methylene ranging from 55° to 60°. Four of the six ligands were parallel to each other with the methylene group bend inside the cage, and the other two of the six ligands which bend outside the cube were positioned in the direction perpendicular to that of the four ligands. Accordingly, the cube-like cage exhibited pseudo-$S_4$ symmetry. The Ce···Ce separations of the chelating rings in the meta site within one benzene ring (11.07 Å) is larger than that of the chelating rings attached in different benzene rings (9.71 or 10.34 Å), and the cage should be described as a tetragonal prism.

These cerium-based architectures were functionalized by twelve and twenty-four amide groups, the well-known guest-accessible sites, around the cavities of the tetrahedron and tetragonal.

Scheme 1  A schematic representation of the generation of the polyhedra from the robust synthon approach by well-positioned cerium centres and the ligands having tridentate NOO chelators.
protonated tetrahedral cage. No additional cations were found in the structure. The chloride anion attached to one of the six edges of the tetrahedral cage forms two-fold Cl⋯···H–N hydrogen bonds with the Cl⋯···N separations of 3.12 Å and 3.16 Å, respectively, and the Cl⋯···H–N angles of 127° in an average. Moreover, the C⋯···Cl separation (3.75 Å for the carbon atoms in the benzene rings) with the C⋯···Cl angles of 157° indicates the potential C⋯···Cl hydrogen bonds. Despite the fact that the quality of the crystals of compound Ce$_4$(NATB)$_4$-Cl was quite poor, the preliminary results suggested that the cooperation of these hydrogen bonds and the spatial constraints thus made these spaces unsuitable for other halide anions with bigger or smaller sizes, except the chloride anion.

In a summary, by incorporating NOO tridentate chelators into the rationally designed ligands with C$_3$ or C$_5$ symmetries, respectively, the face-driven strategy for the preparation of molecular tetrahedron and a cube-like architecture were achieved. Through limiting the number and orientation of the ligands coordinating to the lanthanide centers, such an approach is validated to be powerful in assembling highly ordered lanthanide architectures.

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**Notes and references**


