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M_4L_4 cerium cages assembled from ligands with lower symmetry as a molecular flask



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A R T I C L E I N F O

ABSTRACT

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Keywords: Cages Molecular flask Cyanosilylation Cerium-based tetranuclear polyhedra Ce-**YB**₁ and Ce-**YB**₂ assembled from lower symmetrical ligands without three fold axle, can work as molecular flasks to catalyze cyanosilylation reactions of aldehyde molecules with suitable sizes. The size-selectively catalytic behavior of the cages was investigated by using large aldehydes as the substrate, based on which the corresponding cyanosilylation reactions could not be carried out on the same condition.

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Supramolecular assembly of predesigned organic and inorganic building blocks has been recognized as an excellent tool in constructing well-defined molecular hollows [1-3]. Similar to the pockets of enzymes [4–6], cavities of these synthetic hosts can encapsulate and stabilize guest substrates and fix them into orientations, favoring specific reaction paths that exhibit excellent size discrimination properties [7–9]. These hollow molecular structures could encapsulate guest molecules as molecular flask which could provide an environment for some reactions [10–13]. They can enable one to realize the unique properties to promote entropically unfavorable reactions and catalyze chemical transformations within the cage-like structures [14–16]. Certainly, the first step to construct a molecular flask is to obtain cage-like structures with enough inner space. Recently, substantial developments have been made in the creation of Werner-type capsules having larger inner volume that can be used for recognizing special guests [17,18] and worked as a catalyst to catalyze the relevant reactions of the special guests [19–21].

We have well established the strategy for assembling a series of well-defined Ce-based molecular polyhedra through incorporating NOO tridentate chelators into the rationally designed ligands with predesigned higher symmetries [22–24]. For example, by combining three phenol–imine groups as metal-bonding sites within one C_3 symmetrical central benzene ring, a Ce-based M₄L₄ tetrahedron with ideal *T* symmetry was obtained [25]. However, the tetrahedron just has a very small cavity with its inner volume being estimated as 220 Å³, which is difficult to encapsulate any substrates. To further apply such constructing strategy on molecular flask, we reported here the preparation of new cerium molecular polyhedra by incorporating three such NOO chelating groups into related bigger ligands without C_3 symmetry. The resulting M₄L₄ polyhedra have larger cavity for recognizing

aldehyde molecules and prompting the corresponding cyanosilylation reaction in a homogeneous phase (Scheme 1).

Ligand H₆YB₁ was easily obtained by a Schiff base reaction of salicylaldehyde with 5-(4-(hydrazinecarbonyl)phenoxy)-isophthalohydrazide dimethyl in methanol and identified by the relatively broadened and shifted resonance signals in ¹H NMR spectra. Compared to ligand NATB [25], the bigger ligand H₆YB₁ has the same three tridentate chelating units but lose the three-fold axial symmetry. H₆YB₁ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in DMF to give a black solution. The black crystal was isolated with 50% yield. Single crystal X-ray structural analysis reveals that compound Ce-YB1 is comprised of four cerium ions and four ligands, keeping the M₄L₄ structural feature as the reported Cebased tetrahedron Ce-NATB constructed from ligand NATB. But the molecular structure of compound Ce-YB₁ is a warping tetrahedron because of the flexibility of ligand H₆YB₁. Each cerium ion is chelated by three tridentate chelating groups from three different ligands to form a ternate coronary trigonal prism coordination geometry having a pseudo- C_3 symmetry. As shown in Fig. 1, four Ce centers site at the four corners of the warping tetrahedron and the Ce–O (phenol) and Ce–O (amide) distances of 2.209 Å and 2.444 Å and the Ce-N distance of 2.626 Å are consistent with the related Ce compounds. Every flexible ligand site on four corners is a face of warping tetrahedron. The three rigidly tridentate chelating groups in one deprotonated flexible ligand coordinate to three different metal centers with the Ce-Ce separation bridged ca. 13.276 Å and 9.731 Å. The inner volume of the cube is about 345 Å³ and the opening of the cube is a rectangle having the size of 5.6×7.2 Å², potentially allowing small molecules' ingress and egress [26]. The absence of any anions in the crystal structure suggests that the cube Ce-YB₁ is neutral and these phenol protons and only one third of the amide groups were deprotonated during coordination. The middle benzene groups of each ligand are parallel to each other and are likely work as π - π accumulation sites.

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Scheme 1. Schematic of the constitutive/constructional fragments and the structures of the Ce₄L₄ cubes Ce-YB₁ and Ce-YB₂

To expand ligand H_6YB_1 to H_6YB_2 which has one more methylene group, ligand H_6YB_2 was synthesized by the reaction of 5-(4(methoxycarbonyl)-benzyloxy)isophthalohydrazide with salicylaldehyde in methanol solution and characterized by ¹H NMR spectroscopic methods. The size of ligand H_6YB_2 is larger than ligand H_6YB_1 . Evaporating a DMF solution of H_6YB_2 with Ce(NO₃)₃·6H₂O in air led



Fig. 1. Crystal structure of Ce-**YB**₁ and its constitutive/constructional fragments. Hydrogen atoms were omitted for clarity, the Ce, O and N atoms were drawn in green, red and blue. Ce(1)–O(1) 2.194(6), Ce(1)–O((A) 2.203(5), Ce(1)–O(5) 2.211(5), Ce(1)–O(3A) 2.344(5), Ce(1)–O(6) 2.477(5), Ce(1)–O(2) 2.519(6), Ce(1)–N(5A) 2.604(6), Ce(1)–N(1) 2.626(7), Ce(1)–N(3) 2.645(7), Ce(2)–O(13) 2.203(6), Ce(2)–O(10) 2.217(6), Ce(2)–O(11A) 2.223(6), Ce(2)–O(12A) 2.568(6), Ce(2)–N(8) 2.598(7), Ce(2)–N(10A) 2.628(7), and Ce(2)–N(11A) 2.654(6). Symmetry code A: –x, y, –z + 1/2.

to the formation of compound Ce-YB₂, yield of 60%. The coordination of H₆YB₂ to the cerium metal ions is also identified by electrospray ionization mass spectrometry. Compounds Ce-YB₁ and Ce-YB₂ are soluble in acetonitrile and several organic solvents. Electrospray ionization mass spectrometry (ESI-MS) demonstrates substantial stability of Ce-YB₁ and Ce-YB₂ cages in solution. As shown in Fig. 2, Ce-YB₁ exhibits intense peaks at m/z = 1055.60 and m/z = 1584.53, assignable to the negative charged species $[Ce_4(YB_1)_4-16H]^{3-}$ and $[Ce_4(\mathbf{YB}_1)_4-16H]^{2-}$, based on the simulation of natural isotopic abundances. And Ce-**YB**₂ exhibits an intense peak at m/z = 1074.56 and m/z = 1612.52, assignable to the negative charged species $[Ce_4(\mathbf{YB_2})_4\text{-}16H]^{3-}$ and $[Ce_4(\mathbf{YB_2})_4\text{-}16H]^{2-}$, based on the simulation of natural isotopic abundances. In the case of a solution of Ce-YB₂ in the presence of 4-nitrobenzaldehyde, an exact comparison of the most interesting experimental peak which is observed at m/z = 1137.31and m/z = 1706.74 with the simulation results on the basis of natural isotopic abundances reveals that the -3 and -2 charged species can be reasonably assigned to $[Ce_4(\mathbf{YB_2})_4-16H \supset (\mathbf{2}) \cdot Na]^{3-}$ and $[Ce_4(\mathbf{YB_2})_4-16H \supset (\mathbf{2}) \cdot Na]^2^-$, thus providing evidence of a 1:1 stoichiometric host-guest behavior (Fig. 3).

As the polyhedron could encapsulate the aldehyde molecules, we focused on cyanosilylation reactions of aldehyde molecules which are important reactions that could provide a convenient route to cyanohydrins and the key derivatives in the synthesis of fine chemicals and pharmaceuticals. As shown in Fig. 4, the loading of 4 mol‰ Ce-YB₁ on the cyanosilylation reaction of 4-nitrobenzaldehyde led to a more than 99% conversion in 2 hours. When change the 4-nitrobenzaldehyde to other aldehyde molecules, the conversion of 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-hydroxybenzaldehyde is about 76%, 61% and 83% at the same condition. But the cyanosilylation reaction of 2naphthalaldehyde and 9-anthraldehyde hardly occur in the presence of Ce-YB₁, it is postulated that when the size of large aldehyde molecules is big, it could not be encapsulated in the cage Ce-**YB**₁. We also carried out the cyanosilylation reactions of aldehyde molecules with Ce-YB₂ worked as molecules flasks. As shown in Fig. 4, while the cyanosilylation reaction of 4-nitrobenzaldehyde, 2-nitrobenzaldehyde 3-nitrobenzaldehyde and 4-hydroxybenzaldehyde hardly take place in the absence of Ce-YB₂, but the loading of 4 mol‰ Ce-YB₂ led to a more than 99%, 78% ,67% and 98% conversion in 2 hours, respectively. When change the 4-nitrobenzaldehyde to larger aldehyde molecules 2-naphthalaldehyde and 9-anthraldehyde, the cyanosilylation reaction hardly occur in the presence of Ce-YB₂. Because the reaction of large aldehyde molecules hardly occur in the presence of Ce-YB₁ and Ce-YB₂, it



Fig. 2. ESI-TOF spectra of compound Ce- YB_1 (top) and compound Ce- YB_2 (bottom) in CH_3CN solution.



Fig. 4. Conversion for the cyanosilylation reactions of different aldehyde molecules in the presence of Ce- YB_1 (top), and conversion for the cyanosilylation reactions of different aldehyde molecules in the presence of Ce- YB_2 (bottom).

is suggested that the complexes Ce-**YB**₁ and Ce-**YB**₂ were worked as a molecular flask for cyanosilylation reactions of certain size.

To further investigate the process of cyanosilylation reaction, we use ¹H NMR spectra to track the reaction. As shown in Fig. 5, when the cyanosilylation reaction of 4-nitrobenzaldehyde took place in the presence of Ce-**YB**₁, the rate constant is 0.16 $M \cdot h^{-1}$. And when the cyanosilylation reaction took place in presence of Ce-**YB**₂, the reaction was slower and the rate constant is 0.045 $M \cdot h^{-1}$. The product



Fig. 3. ESI-TOF spectra of compound Ce-YB₂ upon addition of 4-nitrobenzaldehyde in CH₃CN solution.



Reaction conditions: $(CH_3)_3$ SiCN (0.8 mmol), aldehyde (0.16 mmol), Ce-**YB₁**/Ce-**YB₂** (0.64 µmol) room temperature under N₂ for 2 h in 2 ml DMF/CDCl₃ ($\nu/\nu = 1/99$) solution.

formation was pseudo-zeroth-order during the first 30 min and 2 h respectively, and the kinetics behavior suggested that the catalytic process was enzymatic-like catalysis. Because substrate binding is a first equilibrium prior to the rate-limiting step of the reaction, the catalysis behavior is analogous to the Michaelis–Menten mechanism.

In conclusion, we have synthesized two new molecular cages assembled from related bigger ligands without three fold axle and the resulting molecular structure of the compound remained the M_4L_4 structural feature and could be looked as a warping tetrahedron. Their host–guest complexation behavior was investigated by ESI-MS spectrum. The molecular polyhedron could encapsulate aldehyde molecules and acted as a molecular flask to catalyze the cyanosilylation reactions of aldehyde molecules, showing obvious size selectivity.



Fig. 5. The conversion of the reaction with 4-nitrobenzaldehyde took place in the presence of Ce- YB_1 (black line) and Ce- YB_2 (red line) respectively.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2013.09.071.

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