Synthesis and characterization of decanuclear Ln(III) cluster of mixed calix[8]arene-phosphonate ligands (Ln = Pr, Nd)

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ABSTRACT

Two novel decanuclear Ln(III) compounds (Ln = Pr for 1, Nd for 2) have been solvothermally obtained by using p-tert-butylcalix[8]arene (H8TBC8A) and phenylphosphonate (PhPO3H2) as ligands. Single crystal X-ray diffraction studies reveal that both compounds are stacked by dumbbell-like Ln10 clusters, which are capped by two TBC8A8− supports and linked by four complementary PhPO32− ligands as well as other bridging anions. In addition, the self-assembly behavior of both compounds is interesting: the cationic Ln10 cluster layers are separated by the layers of H8TBC8A2− ligands. Moreover, the luminescent and magnetic properties of both compounds were examined.

The design and construction of high-nuclearity lanthanide (Ln) clusters is one of the most active research frontiers in coordination chemistry, not only due to their aesthetically pleasing structures [1] but also their potential applications including luminescence [2], magnetism [3], catalyst [4] and so on [5]. In recent years, chemists have paid more attention on constructing polymerical complexes by using calixarenes [6]. A variety of alkali, transition (TM), or lanthanide metal coordination compounds supported by calixarenes have been obtained so far, especially for thiacalix[4]arenes [7]. However, the number of coordination compounds supported by p-tert-butylcalix[8]arene (H8TBC8A) is relatively less [8]. This might be in part ascribed to the reasons that the H8TBC8A molecule is limited solubility in most organic solvents, more flexible in comparison to those smaller membered calix[4]arenes and hard to control over stereoselective substitution reactions at the rims, which present many kinds of structural conformations and hence make the large calix[8]arene difficult to arrange in long-range order in the solid state [8d].

On the other hand, phosphate and phosphonate ligands, which possess different anionic forms and thus can adopt various coordination modes, have been confirmed to be excellent ligands for making polymeric compounds [9]. Very recently, by using these as co-ligands, we have isolated some (thia)calix[4]arene-based high-nuclearity complexes with interesting architectures and properties. For example, we have synthesized a series of thiacalix[4]arene-based high-nuclearity TM4n nanocages (TM = Co, Ni; n = 2–6) constructed by bridging TM4-calix[4]arene molecule building blocks (MBBs) with phosphate/phosphonate ligands [10], two calix[4]arene-based Co6 clusters with an obvious structural change in the metallic skeleton converting from regular tricapped trigonal prisms to distorted ones by employing auxiliary phosphonate ligands [11], and two alkali-metal templated Na2Co24 and KCo24 clusters based on thiacalix[4]arene and phosphate ligands [12].

As we know, several compounds with cluster motifs containing 1, 2 and 4–8 Ln centers based on H8TBC8A have been reported previously by the research groups of Dalgarno and Harrowfield [13]. Therefore, we have attempted to investigate whether it is possible to obtain high-nuclearity clusters by introducing phosphate ligand into the larger membered calix[8]arene system. Fortunately, we have successfully isolated two novel dumbbell-like decanuclear Ln10 clusters (Ln = Pr, Nd) constructed from the H8TBC8A and phenylphosphonate ligand under solvothermal conditions (Fig. 1). Herein we report their syntheses, structures, photoluminescent and magnetic properties.

The reaction of Ln(NO3)3·6H2O, H8TBC8A and PhPO3H2 in a basic DMF–CH3OH mixed solvent (1:1, v/v) at 130 °C produced colorless plate crystals, namely [Pr10(TBC8A)2(PhPO3)4(OH)2(HCO3)2(HCOO)2(DMF)14]·(H8TBC8A)·2DMF·2CH3OH (1) and [Nd10(TBC8A)2(PhPO3)34(OH)2(HCO3)2(HCOO)4(DMF)14]·(H8TBC8A)·8CH3OH (2). Single crystal X-ray diffraction experiments reveal that the dumbbell-like Ln10 cluster houses within two TBC8A8− supports and four complementary PhPO32− ligands as well as other bridging anions. Up to now, there...
have been few reported decanuclear lanthanide clusters in combinato-
rial configurations and their cores adopt Z-shaped or plate structures.
However, this dumbbell-like architecture here has not been reported
so far [14]. Notably, compounds 1 and 2 also represent the largest
pure lanthanide aggregates to be formed with H8TBC8A ligands.

Crystals of title compounds are in triclinic systems and structure so-
solutions are performed in the space group P-1. Except the co-crystallized
solvents, these two calix[8]arene based clusters are structurally similar,
and thus compound 1 is described in detail as representative hereafter.
Within the asymmetric unit, there are five crystallographically indepen-
dent PrIII sites and they can be divided into three types with Pr1, Pr2 and
Pr4 being in eight-coordinate O8 environment, Pr3 nine-coordinate O9
environment and Pr5 seven-coordinate O7 environment. Moreover,
four PrIII ions (Pr2–Pr5) coordinate to eight lower-rim phenolic oxygens
from one fully deprotonated TBC8A8− ligand and one central μ4-OH in
the basal plane to form a double-cone tetraneuclear praseodymium-
calixarene entity (Fig. 2). We note that the protonation levels of central
OH− were determined by bond valence sum (BVS) calculations (Table S1,
in the Supporting Information). Then, two of the abovementioned
double-cone entities are connected in a head-to-head style by one
HCOO− anion, one HCO3− anion, two PrIII ions and four PhPO3H2− ligands,
forming a dumbbell-like entity, which is larger than our previous reported
should be noted that one of the bridging anions is HCO3− rather than
CO32− in this structure because one of the distances between the carbon
and oxygen atom is much longer than the remaining two distances. The
formate anion comes from the decarbonylation of DMF solvent under
solvolothermal reaction conditions, and the bicarbonate anion originates
from the incorporation of atmospheric carbon dioxide. Charge balance
is maintained through the deprotonation of two phenolic hydroxyl
groups of a cocrystal H8TBC8A molecule. Moreover, the remaining six
underprotonated phenolic hydroxyl groups form six intramolecular hy-
drogen bonds with the O–O distances ranging from 2.449 to 2.632 Å,
which are in agreement with the reported examples [8b]. All auxiliary
phosphonate ligands bind to four metal ions in this structure with a
4.112 coordination mode according to Harris notation [16]. Moreover,
the distance between the two planes formed by four PrIII ions from the
upper and bottom of the dumbbell-like entity is about 5.05 Å. It should
be mentioned that the Pr5 metal site and some ligated DMF molecules
are disordered (see CIF file for details), and thus we avoid discussing
detailed bond lengths and angles of this structure. Due to the additional
H8TBC8A2− anions, the examination of the extended structure of com-
 pound 1 is unusual, which contains two different kinds of layers: the
Pr10 cluster layer and co-crystallized H8TBC8A2− layer, as can be seen
from Fig. 3. Interestingly, these two different layers are separated by
each other leading to sandwich-like arrays via weak interactions. More-
over, the co-crystallized H8TBC8A2− ligands in this structure adopt
pleated-loop conformations, which are different from those being in
double-cone conformations in Pr10 cluster.

In recent years, Dalgarno and co-workers have communicated four
interesting examples of calixarene-based manganese clusters by the
introduction of co-ligands. Specifically speaking, combination of phosphinate and 2-(hydroxymethyl)pyridine co-ligands results
in the formation of unusual [Mn7III2IV2] cages [18] supported by calix[4]arenes, respective-
ly. Very recently, they have obtained a calix[4]arene-based [Mn10III]3MnII]
cluster by employing 3,5-dichlorobenzoate as co-ligand [19]. Moreover,
by using phenyl salicylaldoxime as co-ligand, a novel [Mn11III4MnII]2 dimer
based on the larger membered calix[8]arene has also been prepared
However, there is no example of calixarene-based Ln clusters through the strategy of introducing co-ligands. The solid-state emission spectra of compounds 1 and 2 at room temperature are depicted in Fig. 4. When excited at 412 nm, compound 1 shows a broad emission band at visible region centered at 512 nm (Fig. 4a). This kind of emission can be ascribed to the n → π* electron transitions of coordinated ligand. Compound 2 exhibits the characteristic emissions of Nd3+ ion at the near-infrared region (Fig. 4b): 913, 1079, and 1351 nm, which are attributed to the 4F3/2 → 4I15/2, 4F3/2 → 4I11/2, and 4F3/2 → 4I13/2 transitions of Nd3+ ion, respectively [21].

The temperature dependence of magnetic susceptibilities is investigated on the polycrystalline sample of title compounds from 2 K to 300 K with an applied direct-current field of 1000 Oe (Fig. 5). The observed values of χT at 300 K are 15.21 and 16.04 cm3 K mol−1 for 1 and 2, respectively, which are close to the theoretical values of 16.00 and 16.40 cm3 K mol−1 for ten PrIII (3H4, S = 1, L = 5, g = 4/5) and NdIII (4I15/2, S = 3/2, L = 6, g = 8/11) in the free-ion approximation [22], respectively. Upon the temperature cooling, the χT curves decrease continuously until reaching 1.40 and 10.24 cm3 K mol−1 for 1 and 2 at 2 K, respectively. The decrease of χT for 1 is more rapidly than that of 2 in the low temperature region. For both compounds, the χT vs. T data in the temperature range 50–300 K can be fitted by Curie–Weiss law to give C = 16.56 cm3 K mol−1 and θ = −27.27 K for 1, and C = 17.37 cm3 K mol−1 and θ = −23.45 K for 2. The negative θ values together with the decrease of the χT curves upon cooling may be due to either antiferromagnetic interactions between spin centers or depopulation of the Stark sublevels of the PrIII and NdIII ions.

In conclusion, by employing phosphonate as co-ligand, we have obtained two new Ln10 clusters (Ln = Pr, Nd) with unusual self-assembly phenomenon that the cationic Ln10 cluster layers are separated by the layers of cocrystal H8TBC8A2− ligands. As far as we know, these two clusters represent the largest pure lanthanide clusters supported by H8TBC8A ligands. The photoluminescent analyses show that compound 1 shows a broad emission band at visible region, while compound 2 exhibits the characteristic emissions of Nd3+ ion at the near-infrared region. The magnetic properties of both compounds were also examined, indicating strong antiferromagnetic interactions between the Ln(III) centers and/or depopulation of the Stark sublevels of the Ln(III) ions. Further work on using other calixarene or phosphonate ligands in the synthesis of high-nuclearity lanthanide coordination complexes with interesting structures and physicochemical attributes is underway.

Acknowledgments

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Appendix A. Supplementary material

CCDC-1004493 and -1004494 contain the supplementary crystallographic data for compounds 1 and 2 in this paper. These data can be obtained free for charge via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.01.035.

References


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