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Review

Transition metal and lanthanide cluster complexes constructed with thiacalix[n]arene and its derivatives☆

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Contents

Abstract

This review deals with the formations, structures, and properties of transition metal and lanthanide clusters supported by thiacalix[n]arene and its oxidized derivatives, sulfinylcalix[4]arene and sulfonylcalix[4]arene. Each thiacalix[n]arene possesses donor atoms both on the lower rim position (phenol oxygen atoms) and on the cyclic framework itself (–S–, –SO–, or $–SO_2–$), and behaves as a multidentate multi-nucleating ligand to support the formation of a phenoxo-bridged cluster core. For first row transition metals, calix[4]arenes offer a platform for assembling the metal ions *via* four fac-tridentate coordination sites, and planar tri- and tetra-nuclear clusters are formed. A larger and more flexible thiacalix[6]arene could bind up to five metal ions inside the coordination cavity formed when it adopts the pinched cone conformation. Sulfonylcalix[4]arene shows a strong affinity to lanthanide ions through phenoxo and sulfonyl oxygen donors, and yields a variety of cluster compounds involving di-, tetra-, octa-, and dodeca-nuclear cores, achieved by controlled synthetic conditions.

Keywords: Thiacalix[n]arene; Sulfinylcalix[4]arene; Sulfonylcalix[4]arene; Transition metal; Lanthanide; Cluster

1. Introduction

Calix[n]arenes are widely investigated in host–guest chemistry, supra-molecular chemistry, and molecular recognition chemistry [1–3]. The original calix[n]arenes are macrocyclic compounds in which n phenol groups were connected by n methylene groups to make a ring structure (see Scheme 1), and can include small molecules in the hydrophobic cavity formed by the phenol aromatic rings. The introduction of heteroatoms vested calixarenes with the remarkable ability to coordinate metal ions, and a novel kind of host–guest chemistry is now expanding in scope on the basis of this coordination bonding. In most cases, ligating groups such as alcohols and amines were introduced at the upper and lower rim positions of the calixarene [4–9]. In 1997, Myano et al. reported a new and simple method for synthesizing

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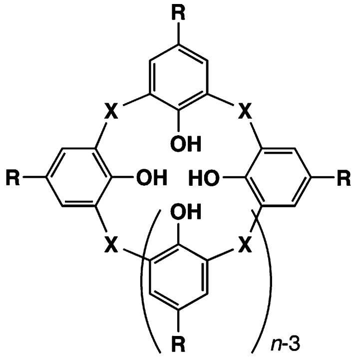


	X	*n*	R
calix[*n*]arene	CH_2	≥ 4	
thiacalix[*n*]arene (H_n**tca[*n*]**)	S	4, 6, 8	^{t}Bu
sulfinylcalix[*n*]arene (H_n**soca[*n*]**)	SO	4	^{t}Bu
sulfonylcalix[*n*]arene (H_n**so$_2$ca[*n*]**)	SO_2	4	^{t}Bu

Scheme 1. Calix[*n*]arenes.

p-*tert*-butylthiacalix[*n*]arene (H_n**tca[*n*]**) from the reaction of *p*-*tert*-butylphenol with sulfur [10], and oxidized derivatives including *p*-*tert*-butylsulfinylcalix[*n*]arenes (H_n**soca[*n*]**) and *p*-*tert*-butylsufonylcalix[*n*]arenes (H_n**so$_2$ca[*n*]**) were soon synthesized (see Scheme 1) [11], leading to new coordination compounds. *p*-*tert*-Butyl groups introduced for better solubility in organic solvents could easily be converted into sulfonic acid groups to give water-soluble calixarenes [12,13]. The sulfonic acid groups at the *p*-positions also acted as donor atoms to form coordination bonds with metal ions, and formation of infinite 1D or 2D structures with complicated structures were reported (Fig. 1) [13–17]. The focus of this paper is on discrete molecules and complex ions, and the discussion will be limited to *p*-*tert*-butylthiacalix[*n*]arene and its derivatives. The frameworks of the calixarenes are flexible, and they can adopt several conformations. For example, four are known for the calix[4]arenes: the cone; partial cone; 1, 2-alternate; and 1, 3-alternate conformations. Fig. 2 shows typical coordination modes of the original calix[4]arene and thiacalix[4]arene in the cone conformation. In most cases, methylene-bridged calix[4]arenes behaved as tetradentate ligands, bonding to one metal ion *via* four phenol (or phenoxo) oxygen atoms [18]. Due to the C–S bonds in thiacalix[4]arene being longer than the corresponding C–C bonds in calix[4]arene and the greater number of donor atoms in thiacalix[4]arene, it could simultaneously offer four tridentate chelating sites involving one sulfur atom and two adjoining phenoxo oxygen atoms (Fig. 2(b)). Because of their multidentate nature and flexibility in conformation, thiacalix[*n*]arene and its derivatives could be used as templates for generating metal-containing assemblages with a variety of structures. In this paper, the formation, crystal structures, and some discriminative properties of large cluster complexes supported by **tca**[*n*]$^{n-}$ **soca[4]**$^{4-}$, and **so$_2$ca[4]**$^{4-}$ will be summarized.

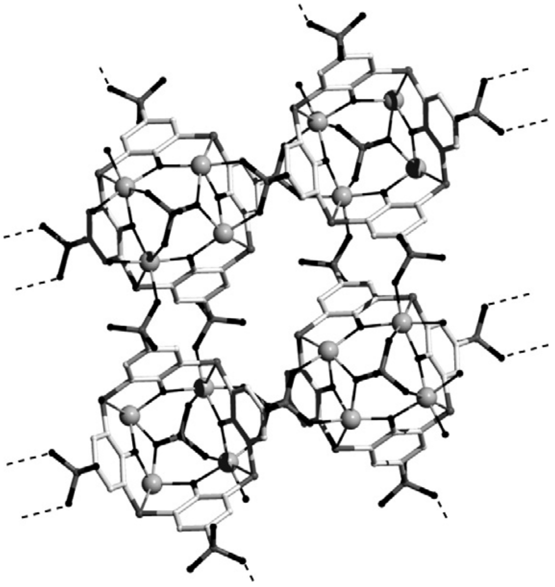


Fig. 1. Crystal structure of two-dimensional infinite complex constructed with tetra-cobalt(II) clusters supported by *p*-sulfonatothiacalix[4]aiene. The atoms depicted here are: Co, sphere; S, gray; O, black; C, white (Ref. [16]).

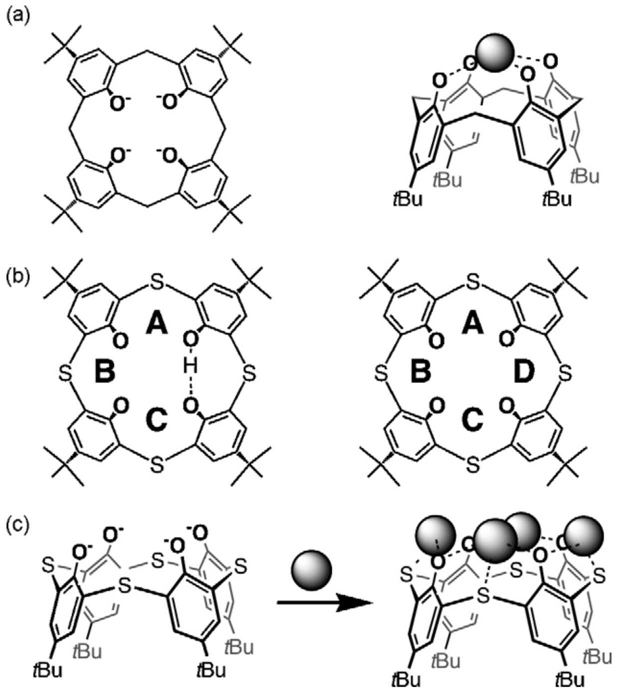


Fig. 2. (a) A tetradentate coordination site formed on calix[4]arene in the cone conformation (left), and formation of a mono-nuclear moiety surrounded by tetra-anionic calix[4]arene (right), (b) three and four coordination sites formed on H**tca[4]**$^{3-}$ (left) and **tca[4]**$^{4-}$ (right), respectively and (c) formation of tetranuclear cluster core supported by **tca[4]**$^{4-}$ in the cone conformation.

2. Cluster complexes supported by thiacalix[*n*]arene

Thiacalix[*n*]arene (H_n**tca[*n*]**) can bind metal ions both by its hard oxygen atoms and soft sulfur atoms. For hard species such as alkali metal ions and zirconium(IV), **tca[*n*]**$^{n-}$ coordinated only *via* its phenoxo oxygen atoms to give, e.g., [$\mathrm{Zr_2}$(**tca[4]**)$_2$(HOMe)$_2$] [19], [$\mathrm{Na_6}$(**tca[4]**)$_2$(dmf)$_2$]$^{2-}$ [20], [$\mathrm{K_2}$($\mathrm{H_3}$**tca[4]**)$_2$($\mathrm{OEt_2}$)$_2$$\mathrm{H_2O}$] [21], [$\mathrm{Rb_4}$($\mathrm{H_3}$**tca[4]**)$_4$($\mathrm{H_2O}$)(dmf)$_{10}$] [21], and [$\mathrm{Li_2}$($\mathrm{H_2}$tca[4])(thf)($\mathrm{H_2O}$)$_2$] [21]. In these complexes, the coordination mode of H_{4-m}**tca[4]**$^{(4-m)-}$ was the same as for the original calix[4]arene (Fig. 2(a)) [4–9,18,22,23], and these will not be discussed further. An infinite two-dimensional compound with the formula [K_4(H_4**tca[8]**)] was obtained by the reaction between KH and a very large macrocyclic compound, H_8**tca[8]** [24]. In this compound, long potassium–sulfur contacts (up to 3.56 Å) were reported.

2.1. Cluster complexes supported by thiacalix[4]arene

Thiacalix[4]arene behaves as a tris- or tetrakis-tridentate ligand for late transition metal ions including manganese(II) [25]; cobalt(II) [26]; copper(II) [27]; and zinc(II) (Fig. 3) [26]; and other metal ions such as mercury(II) (Fig. 4) [28] and neodymium(III) (Fig. 5) [29]. The motifs of these clusters were similar: a phenoxo bridged tri-nuclear or tetra-nuclear cluster core was sandwiched by two H**tca[4]**$^{3-}$ or two **tca[4]**$^{-}$ units. The calixarene adopted the cone conformation, with the four-phenoxo oxygen atoms and four sulfur atoms oriented in a plane (Fig. 2(c)). One sulfur atom could coordinate to a metal ion together with two adjoining phenoxo oxygen atoms in a *fac* configuration (Fig. 2(b)), forming four tridentate sites related by a pseudo four-fold axis, resulting in a square cluster core. In the tri-nuclear cluster, the metal-free site was occupied by a proton hydrogen bonded to two adjoining phenoxo groups (Fig. 2(b), left). Manganese(II), cobalt), mercury(II), and neodymium(III) ions were hexa-coordinated by an $(O_2S)_2$ donor set from two calixarenes in a distorted trigonal prismatic arrangement. Each neodymium(III) ion was further ligated by two dmf or dmso molecules, and a μ_4-hydroxo group which capped the sides of the trigonal prism. The zinc(II) ions were penta-coordinated by an O_3S_2 donor set (Fig. 3).

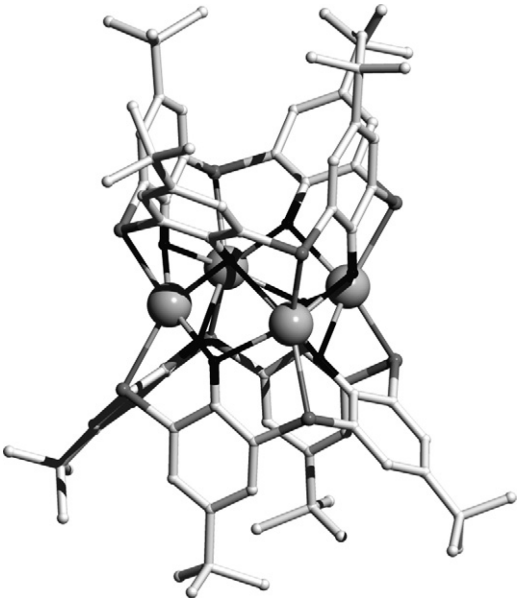


Fig. 4. Crystal structure of tetra-mercury(II) cluster supported by **tca[4]**$^{4-}$. The atoms depicted here are: Hg, sphere; S, gray; O, black; C, white (Ref. [28]).

2.2. Cluster complexes supported by thascalix[6]arene

A larger thiacalix[6]arene (H_6**tca[6]**) [29–33] was a more flexible ligand than the thiacalix[4]arene, and could bind up to five metal ions *via* oxygen and sulfur atoms to form a phenoxy-bridged cluster-core. A deca-copper(II) cluster complex with the formula [Cu_{10}(**tca[6]**)$_2$(μ_3-O)$_2$(μ_3-OH)$_3$(μ-AcO)], supported by two tca[6]$^{6-}$ and other ligands (O^{2-}, OH^-, and AcO^-), was synthesized by the reaction of $Cu(AcO)_2$ with H_6**tca[6]** (Fig. 6) [34]. The complex involved a crystallographic two-fold axis which connected two penta-copper(II) cores. The flexible **tca[6]**$^{6-}$ adopted a "pinched-cone" conformation having a

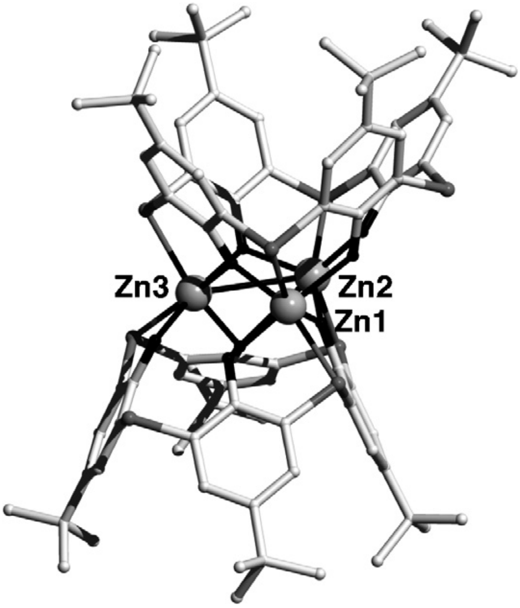


Fig. 3. Crystal structure of tri-zinc(II) cluster supported by **tca[4]**$^{4-}$. Zn, sphere; S, gray; O, black; C, white (Ref. [26]).

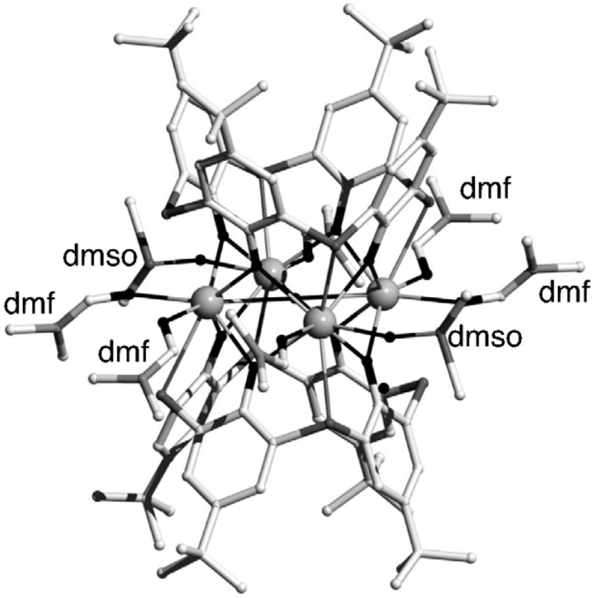


Fig. 5. Crystal structure of tetra-neodymium(III) cluster supported by **tca[4]**$^{4-}$. The atoms depicted here are: Nd, sphere; S, gray; O, black; C, white (Ref. [29]).

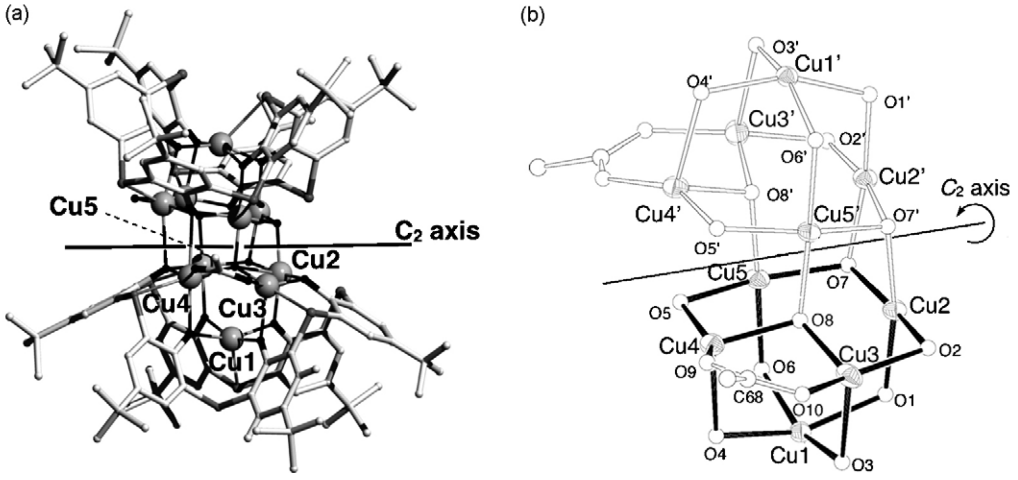


Fig. 6. (a) Crystal structure of deca-copper(II) cluster supported by two **tca[6]**$^{6-}$ moieties. The atoms depicted here are: Cu, sphere; S, gray; O, black; C, white AND (b) Ortep diagram of deca-copper(II) cluster core (Ref. [34]).

pocket-like cavity surrounded by six phenoxo oxygen atoms and six sulfur atoms (Fig. 7, left). Five copper(II) ions were included in this pocket, forming a square pyramid (Fig. 6. right, drawn with filled bonds). The apical Cu1 was located in the center of the oxygen square (O1, O3, O4, and O6; 1.941 (2)–2.0154(19) Å). The four basal copper atoms (Cu2–Cu5) were placed above the phenoxo oxygen atoms with standard Cu–O distances of 1.9660(19) and 2.0125(18) Å (Cu2 and Cu5) or longer distances of 2.208(2) and 2.276(2) Å (Cu3 and Cu4). Around the crystallographic two-fold axis, the two penta-copper(II) units were connected *via* O7 and O8 to form the deca-copper(II) cluster. Each copper(II) atom was further coordinated by a sulfur atom from **tca[6]**$^{6-}$, and the copper atoms as a whole were considered to adopt a distorted square-pyramidal configuration. This cluster was soluble in non-polar chloroform and dichloromethane, and it maintained the core structure even in acidic EtOH solution, as confirmed by ESI mass spectroscopy (a clear signal at $m/z = 2946.79$ was observed, corresponding to $[\mathrm{Cu}_{10}(\mathbf{tca[6]})_2(\mathrm{O})(\mathrm{OH})_4(\mathrm{AcO})(\mathrm{H_2O})]^+$).

Investigation of the magnetic behavior of this deca-copper(II) cluster revealed that a ferromagnetic interaction occurred with $\theta = 7.9(2)$ K based on the Curie-Weiss model. As each copper(II) ion adopted a pyramidal coordination geometry, the magnetic orbital ($d_{x^2-y^2}$) lay in the basal plane. The dihedral angles between the basal planes of two adjoining two copper ions were estimated to lie between 77.08(12)° and 89.09(7)°, advantageous for orthogonality between neighboring magnetic orbitals [35]. Although some antiferromagnetic pathways were possible in the core, the overall magnetic behavior of the complex is ferromagnetic.

The copper(II) ion is one of the most flexible ions in coordination geometry, more so than other transition metal ions such as cobalt(II) and nickel(II). The reaction of cobalt(II) acetate or nickel(II) acetate with H$_6$**tca[6]** resulted in the formation of different kinds of clusters depending on the rigidity of the coordination geometry of the metal ions [36].

In the penta-cobalt(II) cluster complex $[\mathrm{Co}_5(\mathbf{tca[6]})(\mu_4\text{-OH})(\mu\text{-AcO})(\mu\text{-OMe})(\mathrm{MeOH})_4]^-$ (Fig. 8), **tca[6]**$^{6-}$ also adopted a pinched-cone conformation forming a pocket-like structure with four phenoxo oxygen atoms (O1, O3, O1*, and O3*) in a square planar arrangement. The apical cobalt(II) ion (Co3) was located slightly below this O$_4$ plane (0.670(2) Å) and was additionally coordinated by two sulfur atoms (S1 and S4). Hence Co3 was in a distorted trigonal prism with two trigonal planes defined by O1/O1*/Sl and O3/O3*/S4. The basal cobalt(II) ions (Co1, Co2, Co1*, and Co2*) were located above the phenoxo oxygen atoms in an octahedral coordination. Each of these ions was coordinated by two phenoxo oxygen atoms (O1–O3); a sulfur; a μ_4-hydroxo (O4); a μ_2-methoxo or a μ_2-acetate (O5 or O6); and a methanol oxygen. An acetate counterion formed hydrogen bonds with the μ_4-hydroxo group ($\mathrm{O4}\cdots\mathrm{O_{acetate}} = 3.020(9)$ Å), whose hydrogen atom was found by differential Fourier synthesis.

A similar reaction of Ni(AcO)$_2$ with H$_6$**tca[6]** resulted in the formation of a completely different cluster from the previous copper and cobalt clusters, though the reaction conditions were very similar. In the resulting tetra-nickel(II) complex, $[\mathrm{Ni}_4(\mathrm{H}_2\mathbf{tca[6]})(\mathrm{AcO})_4(\mu\text{-dmf})(\mathrm{dmf})_2]$ (Fig. 9), di-protonated H$_2$**tca[6]**$^{4-}$ adopted a cone conformation having a planar arrangement of the donor atom set (O1, O2, S1, S2, and so on), and held four nickel(II) ions arranged in a zigzag chain manner on the donor plane. The H$_2$**tca[6]**$^{4-}$ anion bound Ni1 *via* a phenoxo oxygen (O1) and a sulfur (S1, 2.4309(5) Å) and Ni2 *via* two phenoxo oxygen atoms (O1 and O2) and a sulfur (S2, 2.4271(6) Å). The nickel(II) ions were additionally bridged by two acetate ions (Ni1···Ni2) or two acetate ions and a dmf

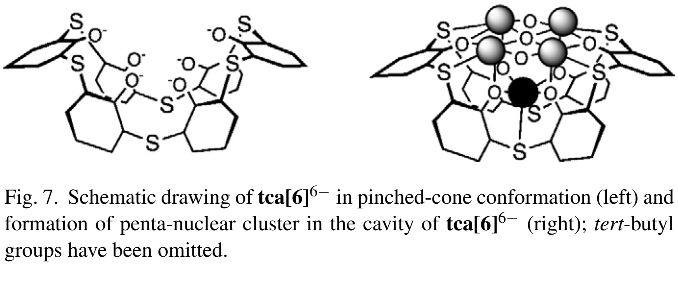


Fig. 7. Schematic drawing of **tca[6]**$^{6-}$ in pinched-cone conformation (left) and formation of penta-nuclear cluster in the cavity of **tca[6]**$^{6-}$ (right); *tert*-butyl groups have been omitted.

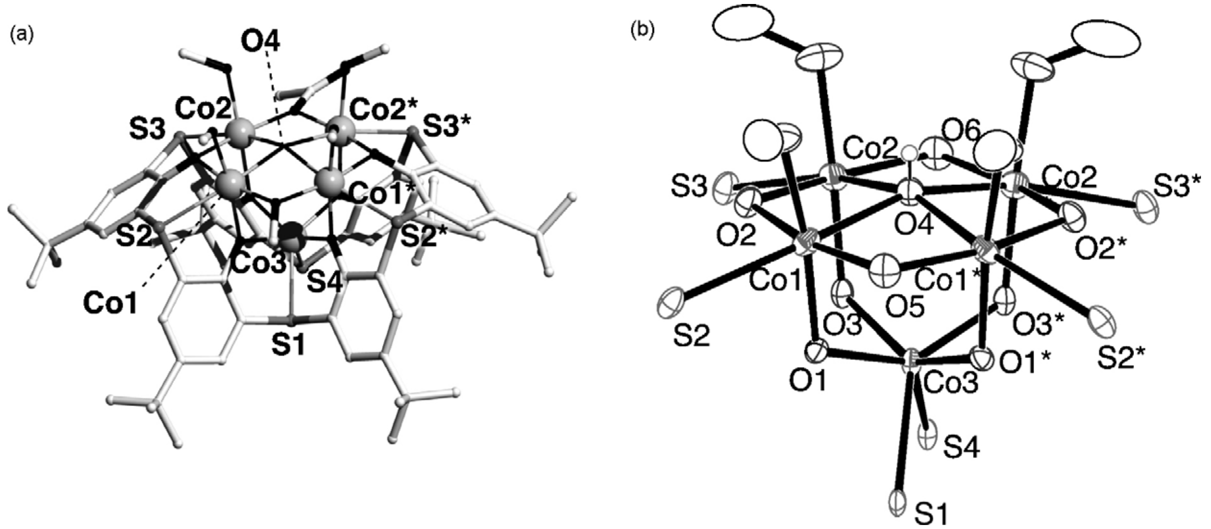


Fig. 8. (a) Crystal structure of the cationic part of the penta-cobalt(II) complex supported by **tca[6]**$^{6-}$. The atoms depicted here are: Co, sphere; S, gray; O, black; and C, white and (b) ORTEP diagram of penta-cobalt(II) core with thermal ellipsoids at 40% probability (Ref. [36]).

oxygen (Ni1···Ni1*). A dmf molecule was encapsulated in the cavity of conic H_2**L**$^{4-}$ which bridged Ni1 and Ni1* *via* O9. Two sulfur (S3 and S3*) and two phenol oxygen atoms (O3 and O3*) of H_2**tca[6]**$^{4-}$ were free from coordination

In the previous copper and cobalt complexes, pinched-conic **tca[6]**$^{6-}$ supplied five or six donor atoms to complete the coordination geometry around the apical metal positions. Copper(II) and cobalt(II) ions can take square pyramidal or trigonal prismatic coordination, and here they adopted a distorted coordination geometry at the apex. On the other hand, nickel(II) ions usually cannot adopt such distorted geometries, and thus a penta-nickel(II) complex similar to the copper(II) and cobalt(II) complexes did not form. The calixarene took the cone conformation in the absence of the apical metal ions, and four nickel(II) ions were placed on the donor surface of H_2**tca[6]**$^{4-}$.

Since the tetra-nickel(II) complex included four coordination-free donor atoms (S3, S3*, O3 and O3*), this complex itself could be expected to act as a ligand *via* these sites. The reaction of the tetra-nickel(II) complex with manganese(II), cobalt(II), or copper(II) acetate in a 1:1 molar ratio induced a cluster core rearrangement and yielded a pyramidal mixed-metal cluster complex almost quantitatively (Fig. 10). The resulting [MNi$_4$(**tca[6]**)(μ_4-OH)(μ-AcO)$_2$(AcO)(H_2O)$_2$(ROH)] (*M* = Mn, Co, or Cu, and R = Et, Et, or H, respectively) had a similar core structure to that of the previously described deca-copper(II) or penta-cobalt(II) clusters. In all complexes, the apical position of the pyramidal clusters was occupied by the second metal ion. When **tca[6]**$^{6-}$ adopted the pinched cone conformation, the chelating effect for the apical position would be expected to be stronger than that for basal metal ions because the latter were bound to **tca[6]**$^{6-}$ *via* three donor atoms whereas the former was surrounded by six donor atoms. Hence it was assumed that, in the early stages of formation of homo-metallic complexes, the thiacalix[6]arene bound the first metal ion *via* an O_4S or O_4S_2 donor set to take on the pinched-cone conformation, followed by other metal ions being taken up in the pocket formed (Scheme 2, **I** → **II**). On the other hand, in the reaction of the tetra-nickel(II) cluster with the second metal ion, the insertion of the metal ion into the apical position would have forced the calixarene

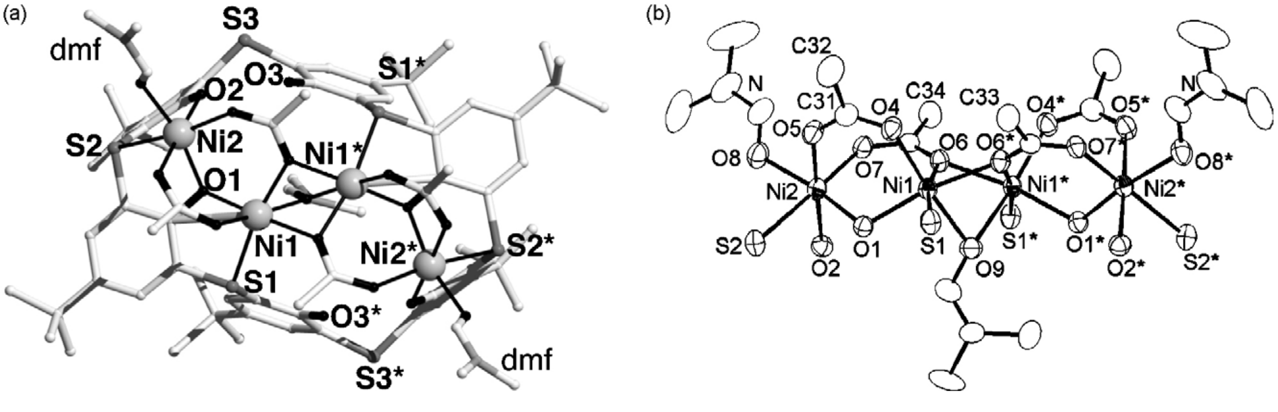


Fig. 9. (a) Top view of the crystal structure of the tetra-nickel(II) complex formed with H_2**tca[6]**$^{4-}$. Ni, sphere; S, gray; O, black; and C, white. (b) Side view of the ORTEP diagram of the tetra-nickel(II) core with thermal ellipsoids at 40% probability (Ref. [36]).

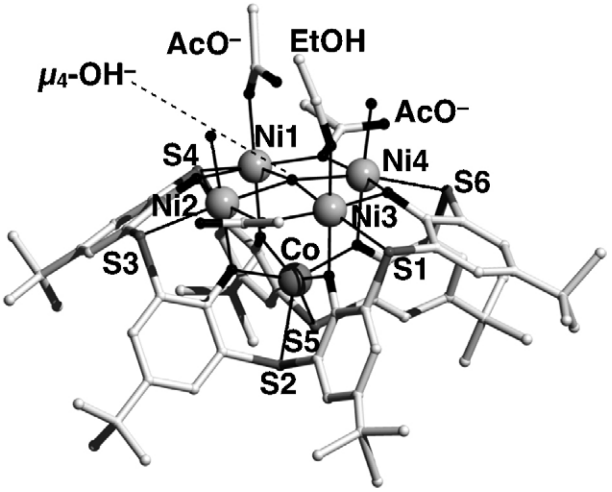
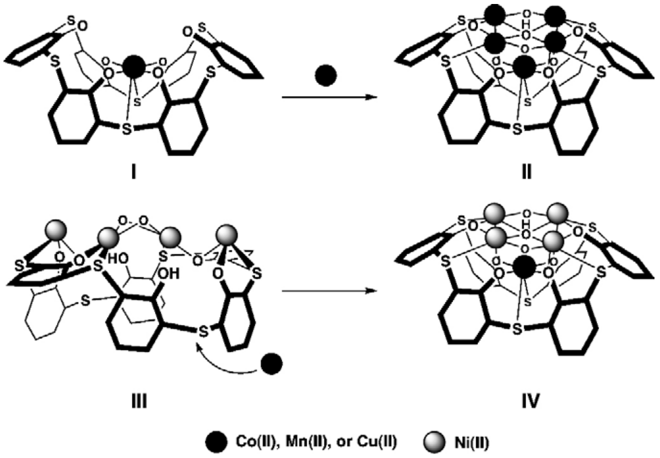


Fig. 10. Crystal structure of the mono-cobalt(II) tetra-nickel(II) complex. The atoms depicted here are: Ni, light gray sphere; Co, dark gray sphere; S, gray; O, black; C, white (Ref. [36]).



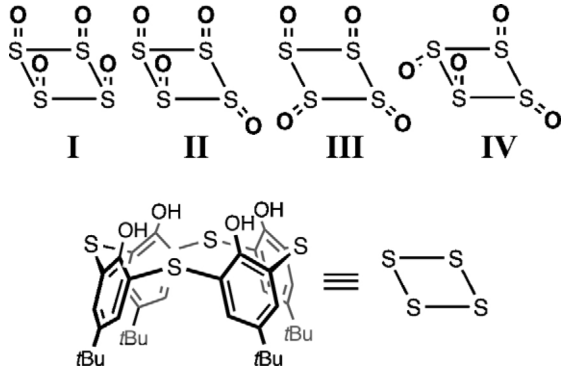
Scheme 2. Proposed mechanism for the formation of cluster cores.

to adopt the pinched-cone conformation because of its strong chelating affinity to manganese(II), cobalt(II), and copper(II) ions. In this conformation, four nickel(II) ions were no longer able to adopt the zigzag arrangement, and the core rearranged to the square planar shape with the involvement of a small bridging μ$_4$-hydroxo group (Scheme 2, **III** → **IV**). This result demonstrated a novel synthetic method for the formation of a position-selective mixed-metal array by a sequence of step-by-step bottom-up reactions.

3. Cluster complexes supported by sulfinylcalix[4]arene

The controlled oxidation of thiacalix[*n*]arene yielded the corresponding sulfinylcalix[*n*]arenes. Since the syntheses of thiacalix[*n*]arenes with $n > 4$ were rather difficult and the yields were extremely low, sulfinylcalix[4]arene was the only compound for which cluster formation was reported.

The abilities of thia-, sulfinyl-, and sulfonylcalix[4]arenes to extract metal ions were investigated. Thiacalix[4]arene was classified as a soft to intermediate extracting reagent whereas sulfonylcalix[4]arene showed a strong affinity for hard metal ions [11], in keeping with the softness or hardness of their respective donor atoms. Sulfinylcalix[4]arene, with its four sulfoxide moieties, ligated metal ions irrespective of hardness or softness, forming coordination compounds with both hard and soft metal ions *via* O and S donor atoms, respectively, of the S = O group. There have been two very recent reports describing cluster formation with **soca[4]**$^{4-}$ as a ligand [25,37].



Scheme 3. Schematic drawing of four configurational isomers of H$_4$**soca[4]** in the cone conformation.

One feature distinguishing **soca[4]**$^{4-}$ from **tca[4]**$^{4-}$ and **so$_2$ca[4]**$^{4-}$ was its stereo isomerism arising from the displacement of the S = O group from the plane of the four sulfur atoms, and four configurational isomers were identified (Scheme 3). This resulted in a very complicated process of cluster formation. In the reports of cluster syntheses with **soca[4]**$^{4-}$, manganese(II) and copper(II) ions were employed because of their flexible coordination geometries, as well as the intermediate character of the copper(II) ion with regard to softness and hardness.

The solvothermal reaction of H$_4$**soca[4]** (conformation **I**) with manganese(II) chloride in the presence of pyridine resulted in a tetra-manganese(II) complex, [Mn$_4$(**soca[4]**)$_2$], whose structure was very similar to that of the previous manganese(II) cluster [Mn$_4$(**tca[4]**)$_2$], with an O$_3$ donor set instead of O$_2$S [25]. Antiferromagnetic interactions between adjoining manganese(II) ions through bridging phenoxo oxygen atoms were also reported.

The reaction of copper(II) acetate with H$_4$**soca[4]** in configuration **I**, **II**, or **IV** in a 4:1 ratio gave single crystals of [Cu$_4$(**soca[4]**)(OAc)$_3$(μ-OH)] for **I** and **III**, and [Cu$_4$(**soca[4]**)(OAc)$_3$(μ-MeO)(MeOH)] for **IV**, both containing a tetracopper(II) core [37].

The crystal structures of [Cu$_4$(**soca[4]**)(OAc)$_3$(μ-OH)] (Fig. 11) in the **I** and **III** configurations were very similar, with different apical donor atoms for Cu3 and Cu4 (O for the former and S for the later). The **soca[4]**$^{4-}$ ligand adopted the cone conformation to provide four *fac*-tridentate coordination environments for the Cu$_4^{\mathrm{II}}$ core. All four copper(II) ions were in a square-pyramidal penta-coordinate geometry: Cu3 and Cu4 had four basal oxygen atoms from two phenols and two acetate ions and one apical oxygen (**I**) or sulfur (**III**) from a sulfinyl group,

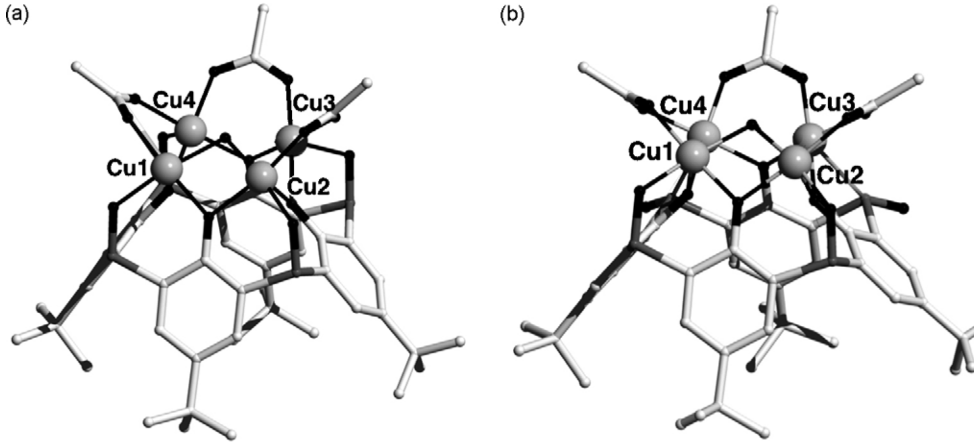


Fig. 11. Crystal structures of [Cu_4(**soca[4]**)$(OAc)_3$(μ-OH)] with configurations **I** (a) and **III** (b). The atoms depicted here are: Cu, sphere; S, gray; O, black; C, white (Ref. [37]).

while Cu1 and Cu2 had four basal oxygen atoms from phenol, sulfinyl, acetate and μ-OH^- groups and one axial oxygen from a phenol moiety.

The structure of [Cu_4(**soca[4]**)$(OAc)_3$(μ-MeO)(MeOH)] with the **IV** configuration was more complicated than that of the previous clusters because of the asymmetrical coordination of **soca[4]**$^{4-}$ (Fig. 12). Cu2, Cu3 and Cu4 were in a square pyramidal geometry, whereas Cu1 was in an octahedral geometry. The apical donors of Cu2 and Cu4 were phenoxo and sulfinyl oxygen atoms, with basal sites occupied by (μ-OH)(μ-OAc) for the former and $(\mu\text{-OAc})_2$ for the latter. The apical site of Cu2 was occupied by sulfurs from sulfinyl groups.

The magnetic interactions between copper(II) ions in the cores were investigated for [Cu_4(**soca[4]**)$(OAc)_3$(μ-OH)] with the **III** configuration. The tetramer could be considered a magnetically independent dimer of copper(II) dimers, with Cu1/Cu2 and Cu3/Cu4 pairs. Both antiferromagnetic and ferromagnetic interactions occurred in the tetra-nuclear core, and based on the bridging structures, the antiferromagnetic interactions were assigned to the former and the ferromagnetic to the latter.

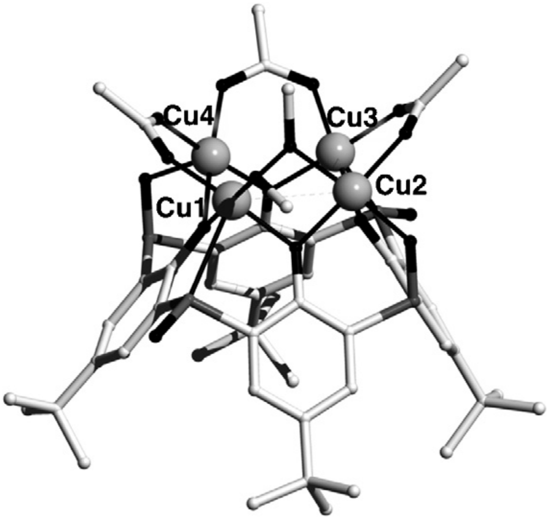


Fig. 12. Crystal structure of [Cu_4(**soca[4]**)$(OAc)_3$(μ-MeO)(MeOH)] with configuration IV. The atoms depicted here are: Cu, sphere; S, gray; O, black; C, white (Ref. [37]).

4. Cluster complexes supported by sulfonylcalix[4]arene

For the same reasons as for the sulfinylcalix[*n*]arene, sulfonylcalix[4]arene (H_4**so$_2$ca[4]**) was the only compound of its class known to have been used as a ligand. H_4**so$_2$ca[4]** possessed four phenol and eight sulfonyl oxygen atoms, and showed strong affinity for late first row transition metal ions as well as for lanthanide ions.

4.1. Transition metal complexes supported by sulfonylcalix[4]arene

The reaction of H_4**so$_2$ca[4]** with cobalt(II) acetate or nickel(II) acetylacetonate resulted in di-nuclear complexes, [M_2(**so$_2$ca[4]**)$(dmf)_4(H_2O)_2$] (Fig. 13), with acetate ions or acetylacetonate ions behaving as bases to remove the protons from H_4**so$_2$ca[4]** [38]. In these complexes, **so$_2$ca[4]**$^{4-}$ adopted the 1,2-alternate conformation and coordinated to metal ions in a tridentate *fac*-fashion *via* a sulfonyl oxygen and two adjoining phenoxo oxygen atoms. This *fac*-tridentate mode was the common manner of coordination of H_{4-m}**so$_2$ca[4]**$^{(4-m)-}$ with first row transition metal ions, and the same coordination was also

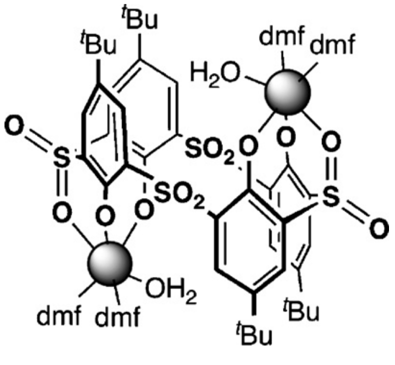


Fig. 13. Molecular structure of di-nuclear complexes, [M_2(**so$_2$ca[4]**)$(dmf)_4$ $(H_2O)_2$].

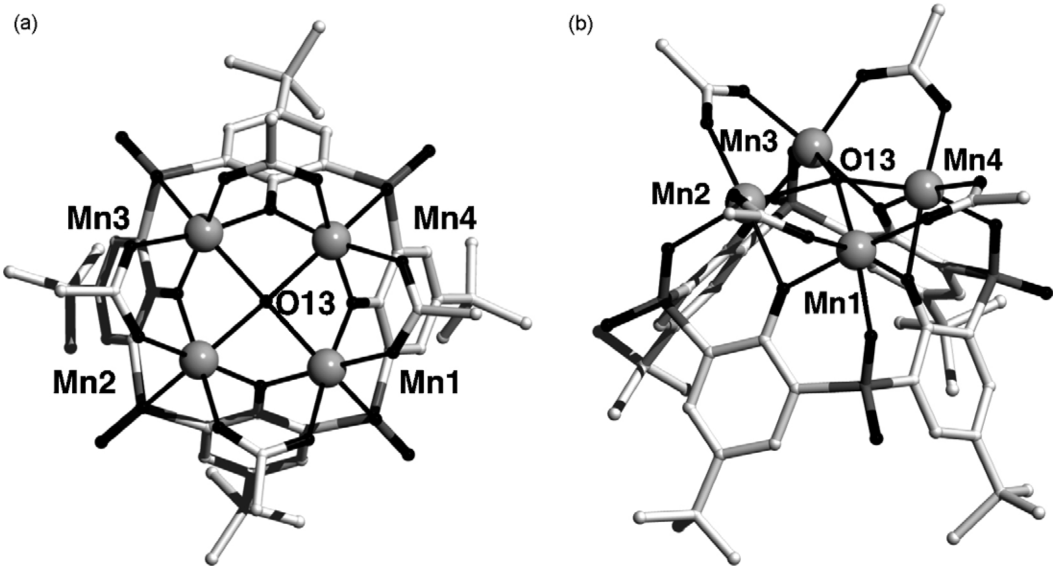


Fig. 14. Crystal structure of $[Mn_4(\mathbf{so_2ca[4]})(AcO)_4(OH)]^-$. (a) Top view and (b) side view. The atoms depicted here are: Mn, sphere; S, gray; O, black; C, white (Ref. [40]).

found in the zinc(II) complex $[Zn(H_2\mathbf{so_2ca[4]})(tacn)]$ [39]. Even when an excess of cobalt(II) acetate or nickel(II) acetylacetonate was used, cluster complexes with higher nuclear numbers were not obtained as crystalline compounds with this procedure.

Tetra-nuclear clusters were obtained by the reaction of $H_4\mathbf{so_2ca[4]}$ with an excess of metal acetate in the presence of Me_4N^+ as a counter cation. The resulting square mono-anionic clusters, $[M_4(\mathbf{so_2ca[4]})(OH)(OAc)4]^-$ (M = Mn(II), Co(II), Ni(II)) [40], are shown in Fig. 14. The structure was similar to one half of the tetra-nuclear cluster formed by $\mathbf{tca[4]}^{4-}$ or the tetra-copper(II) clusters formed by $\mathbf{soca[4]}^{4-}$ mentioned above. Four phenoxo and four axial sulfonyl oxygen atoms formed an almost flat surface with slight deviations from an ideal plane (for M = Mn, the deviations were in the range from −0.132(3) to 0.220(3) Å), and $\mathbf{so_2ca[4]}^{4-}$ acted as a tetrakis-tridentate ligand through these eight oxygen atoms to form a square arrangement of four metal ions. The metal ions were further bridged by four chelating acetate ions and one μ_4-hydroxo ion to complete the hexa-coordination of each metal center. Although each whole molecule of the complex was crystallographically independent, the molecule was highly symmetrical with a pseudo four-fold axis lying on the μ_4-OH^- group. For the nickel(II) cluster, the μ_4-ligand was assigned to disordered OH^- and OMe^- groups, and the structures were analyzed as a superposition of two molecules, $[Ni_4(\mathbf{so_2ca[4]})(AcO)_4(\mu_4\text{-}OH)]^-$ and $[Ni_4(\mathbf{so_2ca[4]})(AcO)_4(\mu_4\text{-}OMe)]^-$, with 67% and 33% probability, respectively. The presence of μ_4-OMe bridged species was also confirmed by mass spectroscopy. The formation of the μ_4-OMe bridged complex was explained by the greater basicity of nickel(II) compared to manganese(II) or cobalt(II).

The tetranuclear clusters were stable enough to maintain their core structures even in highly dilute solution (~10 μM), as confirmed by mass spectroscopy, and moreover, formation of $[M_4(\mathbf{so_2ca[4]})(AcO)_3(O)(H_2O)_2]^-$ species $(=[M_4(\mathbf{so_2ca[4]})(AcO)_4(\mu_4\text{-}OH)]^- - AcOH + 2H_2O)$ was observed. This indicated that bridging acetate ions could be removed in a ligand exchange reaction, yielding certain derivative complexes even under mild conditions. An exchange reaction of bridging acetate with benzoate was performed for all complexes. Soon after the mixing of $[M_4(\mathbf{so_2ca[4]})(OH)(OAc)_4]^-$ with an excess of benzoic acid (1:5 molar ratio) at ambient temperature, the formation of $[Mn_4(\mathbf{so_2ca[4]})(AcO)_{4-n}(BzO)_n(OH)]^-$ (n = 2–4) and $[Mn_4(\mathbf{so_2ca[4]})(AcO)_{3-m}(BzO)_m(O)(H_2O)_2]^-$ (m = 2–3) was confirmed by FT-MS, and the reaction ultimately yielded pure $[Mn_4(\mathbf{so_2ca[4]})(BzO)_4(OH)]^-$ clusters.

Metal–metal interactions were investigated by means of magnetic susceptibility measurements, and it was revealed that both ferro- and antiferromagnetic interactions occurred in the nickel(II) complex depending on the Ni–O–Ni bridging angle.

4.2. Lanthanide cluster complexes supported by sulfonylcalix[4]arene

Lanthanide ions show strong affinity toward oxygen donor atoms, and the reaction of $H_4\mathbf{so_2ca[4]}$ with lanthanide acetate resulted in a variety of cluster families depending on reaction conditions such as reaction ratio, solvents, acidity/basicity of the solution, and presence/absence of co-ligands [41–43].

As described previously, $H_2\mathbf{so_2ca[4]}^{2-}$ and $\mathbf{so_2ca[4]}^{4-}$ behaved as *fac*-tridentate ligands for divalent transition metal ions such as manganese(II), cobalt(II), nickel(II), and zinc(II) (the ionic radius for these species is in the range 0.87–0.97 Å). Since lanthanide(III) ions have larger ionic radii (1.02–1.23 Å for octa-coordination), the calixarene could show different coordination modes with lanthanide ions from those involving transition metal ions.

The reaction of gadolinium(III) acetate with $H_4\mathbf{so_2ca[4]}$ in a 2:1 ratio gave crystals of a large lanthanide cluster, $[Gd_8(\mathbf{so_2ca[4]})_4(AcO)_8(EtOH)_4(H_2O)_4]$, in good yield [41].

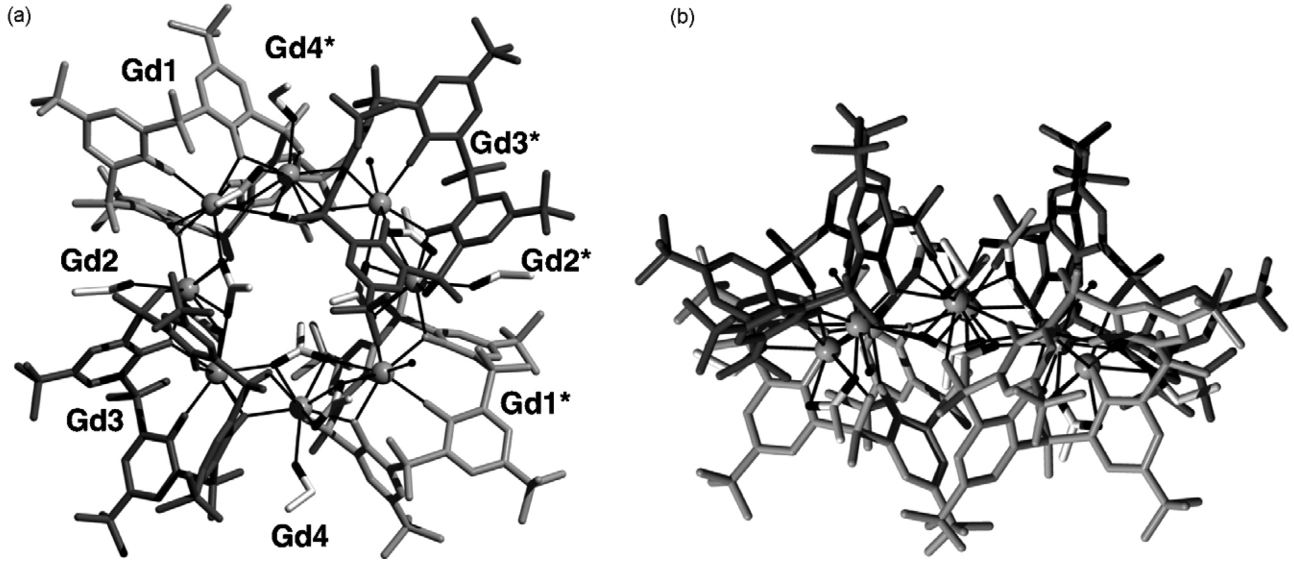


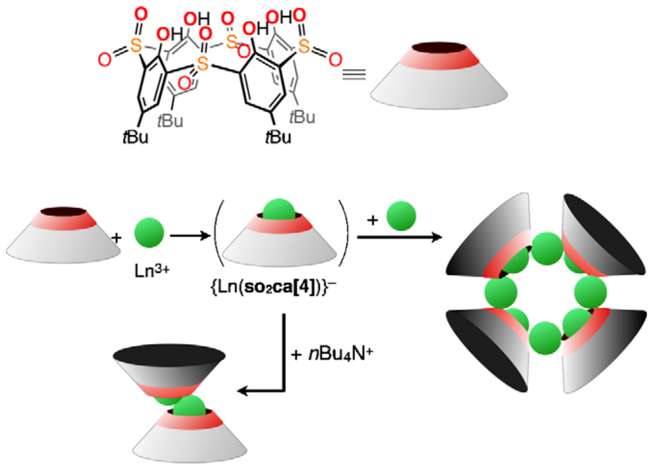
Fig. 15. Crystal structure of Gd$_8$ wheel. (a) Top view and (b) side view of the molecule with two crystallographically independent **so$_2$ca[4]**$^{4-}$ ligands depicted as gray and dark gray frames. Other atoms depicted here are: Gd, sphere; O, black; C, white (Ref. [41]).

The structure of this large cluster was confirmed by X-ray analysis (Fig. 15). The complex possessed a wheel-like core of eight gadolinium(III) ions supported by four **so$_2$ca[4]**$^{4-}$ and eight acetate groups. The diameter of the Gd$_8$ cluster core (Gd1$\cdots$Gd1*) was 9.8 Å. The **so$_2$ca[4]**$^{4-}$ ligand bridged three gadolinium(III) ions, acting as a tetradentate ligand for Gd1 and Gd3 *via* four phenoxo oxygen atoms, and also as a bis-bidentate chelating ligand for adjoining gadolinium(III) ions (Gd2 and Gd4) to form the wheel. Acetate ions also bridged two or three gadolinium(III) ions. The gadolinium(III) octagon core was slightly bent (Fig. 15(b)), deviating from the ideal plane by −0.97 and 0.98 Å. Gd1 and Gd3 were octa-coordinate, whereas Gd2 and Gd4 were nona-coordinate, with each coordination sphere completed by EtOH and water. When samarium(III) was used instead of gadolinium(III), an Sm$_8$ wheel was obtained, isostructural with the Gd$_8$ wheel.

A similar reaction of H$_4$**so$_2$ca[4]** with Nd(AcO)$_3$·4H$_2$O or Pr(AcO)$_3$·4H$_2$O in a 1:2 ratio resulted in a similar wheel, [M$_8$(**so$_2$ca[4]**)$_4$(AcO)$_4$(MeOH)$_4$(H$_2$O)$_8$] (M = Nd or Pr). The Nd$_8$ and Pr$_8$ wheels showed slight differences in the chelating mode of **so$_2$ca[4]**$^{4-}$ and bridging behavior of acetate ions compared to the Gd$_8$ wheel, probably arising from the slight difference in ionic radii between the Gd/Sm and Nd/Pr pairs. The Nd$_8$ core in the Nd$_8$ wheel was flatter than the Gd$_8$ core, with a deviation from the ideal plane of 0.2296(2) Å, and a diameter of 10.5 Å.

The wheels were thought to have been formed in a stepwise manner, as indicated by a mass spectroscopic study (Scheme 4). Since the calix[4]arene acted as a tetra-dentate ligand toward the large metal ions *via* four phenoxo oxygen atoms, the reaction of a lanthanide with H$_4$**so$_2$ca[4]** first gave a cone-shaped mono-nuclear precursor, {Ln(**so$_2$ca[4]**)}$^-$, which could act as a "metal-involving ligand" *via* phenoxo and sulfonyl oxygen atoms directed outward from the cone. Reaction with further equivalents of metal ion resulted in the formation of the cyclic tetramer of **so$_2$ca[4]**$^{4-}$.

Using a similar precursor, a larger dodeca-lanthanide wheel [Ho$_{12}$(**so$_2$ca[4]**)$_6$(mal)$_4$(AcO)$_4$(H$_2$O)$_{14}$] (Fig. 16) was synthesized by the introduction of the malonate dianion (mal^{2-}) as a co-ligand [42]. This wheel was synthesized by the reaction of Ho(AcO)$_3$·nH$_2$O with H$_4$**so$_2$ca[4]** and malonic acid in a 4:2:1 ratio. The molecule could be considered a wheel of six {Ho(**so$_2$ca[4]**)}$^-$ moieties alternating with six {Ho(H$_2$O)$_2$}$^{3+}$ moieties, similar to the previous octa-lanthanide wheels. The presence of mal^{2-} groups introduced considerable complexity in the structure. One malonate group (mal(A) in Fig. 16) chelated Ho4 to form mono-nuclear {Ho(**so$_2$ca[4]**)(mal)(H$_2$O)}$^{3-}$ moieties (fragment **A**$^{3-}$, **so$_2$ca[4]**$^{4-}$ frameworks in light gray). The other malonate di-anion (mal(B)) bridged two Ho^{III} ions (Ho2 and Ho2′), and the resulting di-nuclear {(Ho(**so$_2$ca[4]**)(AcO))$_2$(mal)}$^{6-}$ unit (depicted as **so$_2$ca[4]**$^{4-}$ in dark gray) further acted as a bis-tridentate ligand for Ho1 to form the tri-nuclear moiety



Scheme 4. Step-by-step formation of the lanthanide wheel and dimer from a mono-nuclear precursor, {Ln(**so$_2$ca[4]**)}$^-$.

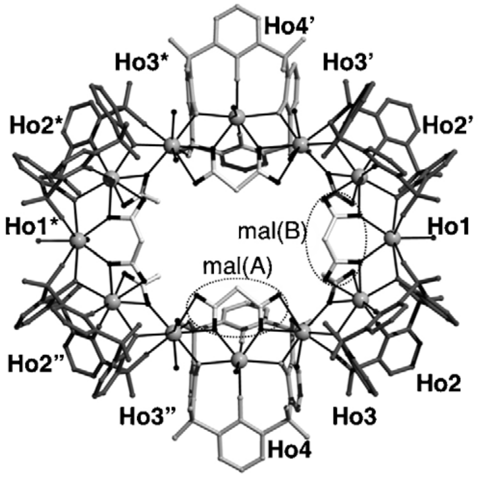


Fig. 16. Crystal structure of HO$_{12}$ wheel. Top view of the molecule with two crystallographically independent **so$_2$ca[4]**$^{4-}$ ligands depicted as light gray and dark gray frames (*tert*-butyl groups have been omitted). Other atoms depicted here are: Ho, sphere; O, black; C, white (Ref. [42]).

$\{(Ho(H_2O)_2)(mal)(Ho($**so$_2$ca[4]**$)(AcO))_2\}^{3-}$, which contained Ho1, Ho2, and Ho2′ (fragment $\mathbf{B}^{3-}$). The remaining four holmium(III) ions (Ho3) formed cationic $\{Ho(H_2O)_2\}^{3+}$ moieties (fragment $\mathbf{C}^{3+}$). The alternating arrangement of these fragments, $\mathbf{A}^{3-}$–$\mathbf{C}^{3+}$–$\mathbf{B}^{3-}$–$\mathbf{C}^{3+}$–$\mathbf{A}^{3-}$–$\mathbf{C}^{3+}$–$\mathbf{B}^{3-}$–$\mathbf{C}^{3+}$–, resulted in a dodeca-nuclear wheel. The coordination mode of **so$_2$ca[4]**$^{4-}$ was very similar to that in the octa-lanthanide wheels. The longest Ho···Ho separation reached 17.7562(16) Å, and the dimensions of the whole molecule were 3 nm × 3 nm × 2 nm, taking into account the Van der Waals radii.

Attempts at synthesis of an octa-holmium(III) wheel similar to the previous gadolinium(III) wheel failed due to the smaller ionic radius of holmium(III) ion (1.02 Å), possibly causing steric repulsion between the methyl groups of acetate ligands in the core. The malonate anion was introduced to avoid the methyl–methyl repulsion. However, it led to the formation of a larger wheel with a more complicated sequential structure. The nanoscale lanthanide wheel structures synthesized here were very sensitive to small changes in the coordination distances of the lanthanide ions, and adoption of appropriate co-ligands was essential for construction and control of structures of this type.

In the previous syntheses, the acetate ions acted as bridging ligands and as a base to deprotonate the phenol group of the calixarene. As a consequence of the mild reaction conditions, the resultant complex involved neutral terminating ligands such as water and alcohol molecules. Reactions of H$_4$**so$_2$ca[4]** with lanthanide acetate in the presence of base gave different kinds of lanthanide clusters [41,43]. When the ligand was reacted with lanthanide acetate and *n*Bu$_4$NOH in the ratio of 1:1:2, di-nuclear complexes $(Bu_4N)_2[\{Ln($**so$_2$ca[4]**$)(H_2O)_2\}_2]$ were obtained (Ln = Gd [41], Eu, and Tb [43]). These three complexes were isostructural (Fig. 17) and were regarded as dimers of the mono-nuclear precursor mentioned above (Scheme 4), $\{Ln($**so$_2$ca[4]**$)\}^{-}$, in which pinched-conic **so$_2$ca[4]**$^{4-}$ behaved as a tetradentate ligand *via* four phenoxo oxygen atoms (Fig. 17(b)). The assembly of two of these units resulted in the formation of a di-nuclear cluster core sharing two phenoxo oxygen atoms from two units.

Further reaction of $(n\mathrm{Bu}_4N)_2[Ln_2($**sa$_2$ca[4]**$)_2(H_2O)_4]$ with $Ln(AcO)_3 \cdot nH_2O$ and *n*Bu$_4$NOH in a 1:2:4 molar ratio afforded cubane-type complexes $(n\mathrm{Bu}_4N)_4[Ln_4($**so$_2$ca[4]**$)_2(OH)_4(AcO)_4]$ with Ln = Gd, Eu and Tb, as pale yellow crystals with relatively high yield [43]. These cubanes were again isostructural, and the crystal structure of the Tb$_4$ cubane is shown in Fig. 18. The cubane complexes could be regarded as assemblages of two smaller $\{Ln_2($**so$_2$ca[4]**$)\}^{2+}$ units, in which a conical **so$_2$ca[4]**$^{4-}$ behaved as a bis-tridentate ligand bonding *via* two phenoxo and one sulfonyl oxygen atom to each

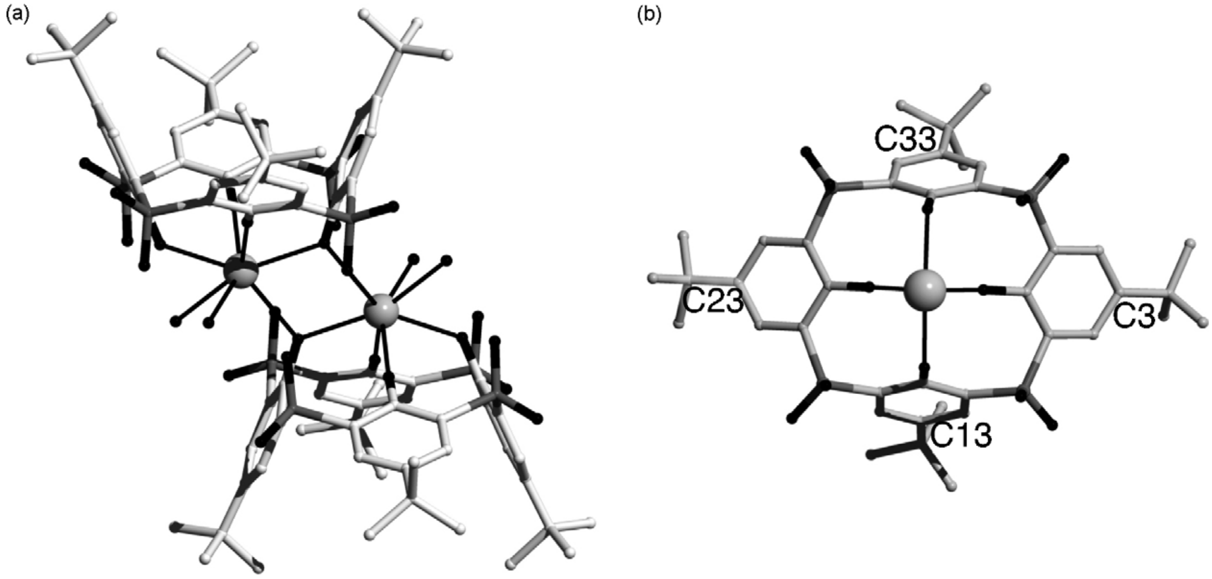


Fig. 17. Crystal structure of $[\{Tb($**so$_2$ca[4]**$)(H_2O)_2\}_2]^{2-}$ (a) Side view of the molecule and (b) mono-nuclear core involving one calixarene ligand and one Tb^{III} ion. The atoms depicted here are: Tb, sphere; S, gray; O, black; C, white (Ref. [43]).

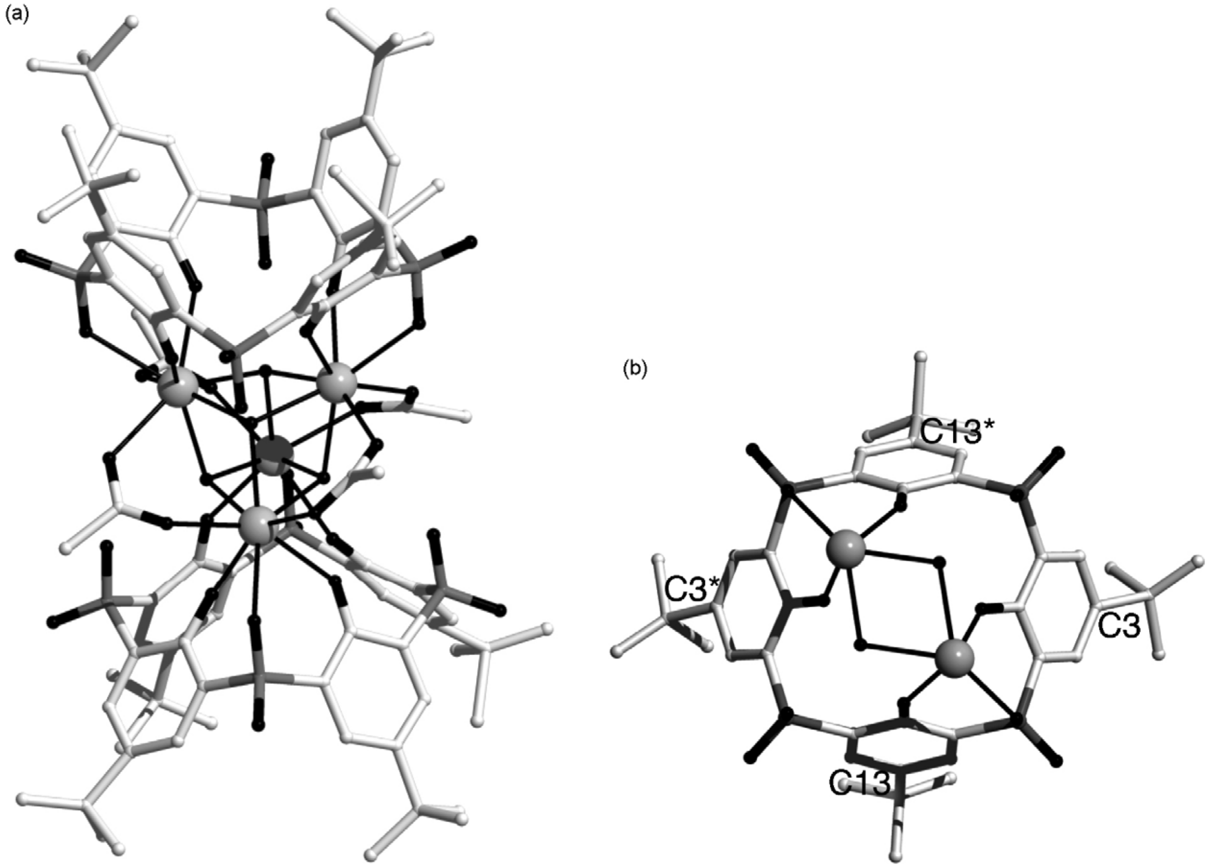


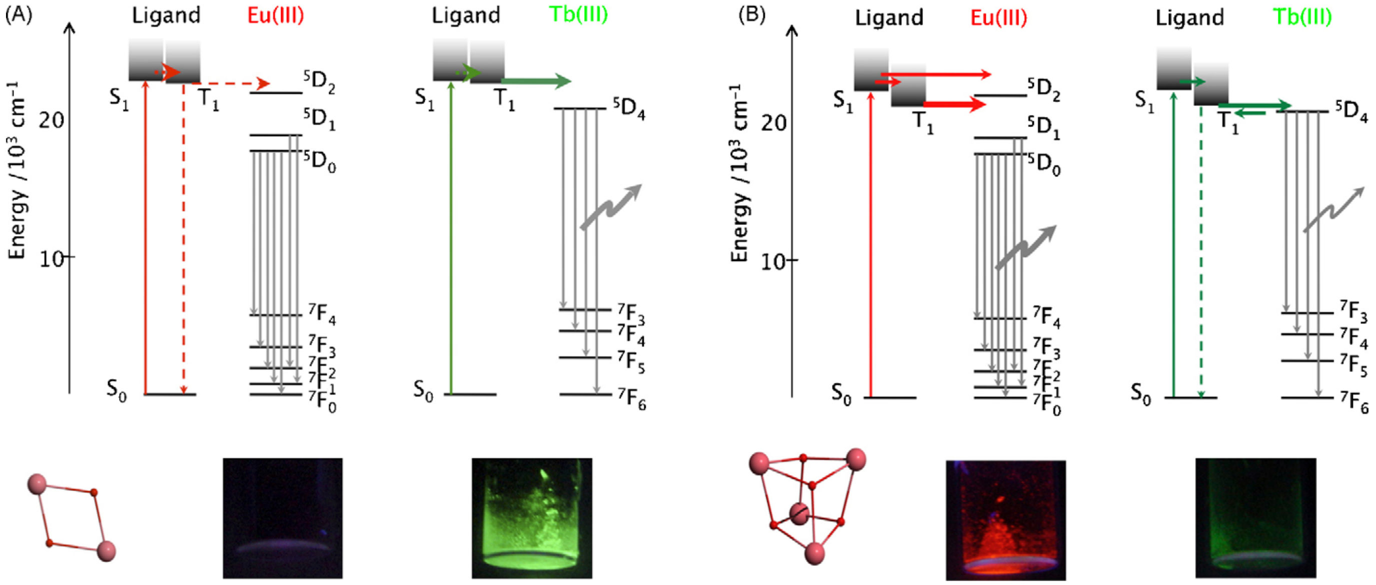
Fig. 18. Crystal structure of $[Tb_4(so_2ca[4])_2(OH)_4(AcO)_4]^{4-}$. (a) Side view of the molecule and (b) di-nuclear core involving one ligand and two Tb^{III} ions. The atoms depicted here are: Tb, sphere; S, gray; O, black; C, white (Ref. [43]).

lanthanide ion. This coordination was very similar to that of first row transition metal ions. The two units assembled in a cubane cluster supported by four μ_3-hydroxo and four bridging acetate ligands.

One of the peculiar properties of lanthanide ions is their luminescence enhancement by irradiation of ligands. Since the f–f* excitations are forbidden, energy transfer from the excited levels of ligand(s) is commonly used to create more strongly luminescent lanthanide complexes. The sulfonylcalix[*n*]arenes might be better antenna chromophores for UV and near-UV excitation than the original methylene-bridged calixarenes [44,45], since the sulfonylcalixarene possesses a large and flexible π-conjugated system extending over the entire ligand, whereas each phenol π-conjugated system in the original calixarene is isolated by methylene groups. The π–π* transition bands of methylene-bridged and sulfonyl-bridged calixarenes were found at around 290 nm (*p-tert*-butylcalix[5]arene [45]) and 350 nm (*p-tert*-butylsulfonylcalix[4]arene, [43]), respectively. Even though the ring size of the latter was smaller than that of the former, the excited singlet level of the sulfonylcalix[4]arene was located lower than in calix[5]arene and closer in energy to the excited level of lanthanide ions. Moreover, it was found that the energies of the excited singlet and triplet levels could be controlled by slight changes in the conformation of the sulfonylcalixarene. The **so$_2$ca[4]**$^{4-}$ ligand in di-nuclear complexes adopted a pinched-cone conformation with a distance ratio $d_{C13–C33}/d_{C3–C23}$ of 0.71 (Fig. 17(b)), whereas in the cubane system the cone conformation had $d_{C13–C13^*}/d_{C3–C3^*} = 0.83$ (Fig. 18(b)). TD-DFT calculations on idealized models of dimer and cubane systems including Lu(III) suggested that the effectively higher symmetry of the ligand in the cubane system was reflected in the greater overall delocalization of the occupied MOs and consequently, in a lower transition energy to the delocalized LUMO (Fig. 19). In turn, the occupied MOs in the di-nuclear system were less delocalized, and the energy of the transition to the delocalized LUMO was higher in this system.

The difference in π–π* transition energies of these two systems was confirmed by the absorption at 340 nm for dimer systems and 356 nm for cubane systems, the latter exhibiting a bathochromic shift compared to the former. The di-gadolinium(III) system exhibited phosphorescence from the ligand at 468 nm (21,400 cm^{-1}) accompanied by a shoulder at 457 nm (21,900 cm^{-1}), whereas the cubane system showed phosphorescence at lower energy, namely at 482 nm (20,700 cm^{-1}). The excited T_1 level of the cubane system was slightly lower in energy than that of the dimer system.

This slight difference in ligand-based T_1 levels led to drastic differences in the luminescent properties of terbium(III) and europium(III) dimer and cubane systems (Scheme 5). The Tb dimer showed strong luminescence in the solid state ($\lambda_{ex} = 365$ nm), though the related Eu dimer did not show any luminescence at room temperature. On the other hand, the cubane complexes



Scheme 5. Energy diagram for the Eu dimer and Tb dimer complexes (top); Eu cubane and Tb cubane (bottom), respectively (Ref. [43]).

exhibited the opposite trend: the Eu cubane luminesced strongly, whereas the Tb cubane only showed very weak luminescence under the same experimental conditions. These observations are summarized in Scheme 5, which shows that the ligand T_1 state and the excited Ln(III)* state were located close to each other in these systems, and therefore the exact energies of these states determined the luminescence properties of each complex.

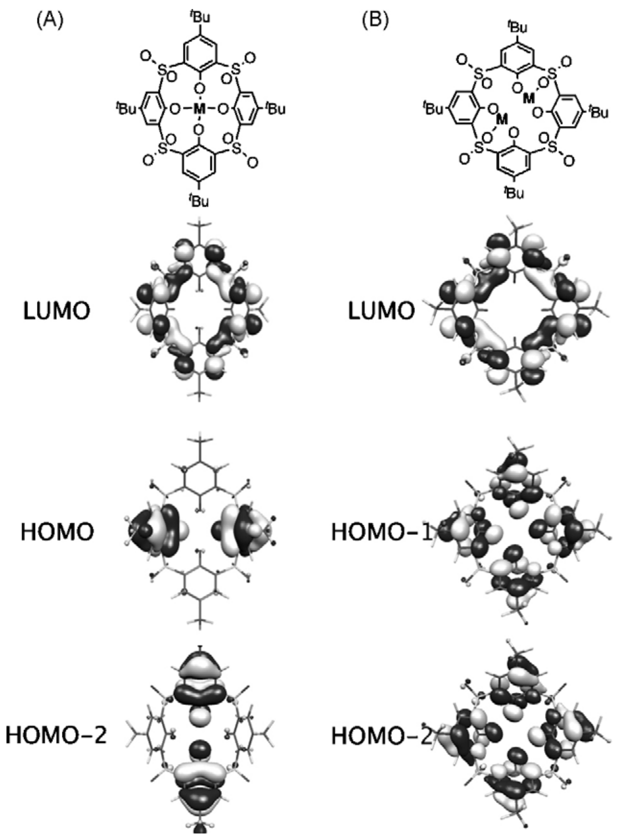


Fig. 19. Frontier MOs of idealized models of one-half of the di-nuclear system in the pinched cone conformation (a) and the cubane system in the cone conformation (b).

In summary, in a new functionality, sulfonylcalixarenes act as good antenna chromophores for UV and near-UV light. Due to the large π-conjugated system of the ligand spanning the entire molecule, this functionality was controllable by conformational changes without the need for any chemical modifications.

5. Conclusions

The cluster-forming ability of thiacalix[*n*]arene and its derivatives as multidentate and multi-nucleating ligands have been summarized. In contrast to ordinary calixarenes, each of these new calixarenes involved donor atoms on the framework of the macrocycle itself, lending it a potent ability to act as a template for metal assemblages. In most cases, these novel calixarenes offered coordination sites with octahedral geometry for the smaller first row transition metal ions. The new calix[4]arenes behaved as a platform for the formation of a tri- or tetra-nuclear cluster core located on the plane of a set of eight donor atoms. When thiacalix[6]arene adopted a pinched cone conformation, a coordinative cavity was formed with a set of twelve donor atoms, able to bind up to five transition metal ions at once in a pyramidal cluster core. Sulfonylcalix[4]arene produced a variety of cluster families with lanthanide ions depending on the reaction conditions. The formation of dimers, wheels, and cubanes was achieved by stepwise construction, which was advantageous for tailored molecular design. This calixarene showed new functionality as an antenna chromophore for UV and near-UV irradiation based on the pronounced delocalization of its π conjugated system over the entire molecule, affording a chromophore whose properties could be tuned by small changes in conformation.

Acknowledgements

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