

A lanthanum picrate complex of a 1,2-bisamide substituted calix[4]arene

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Abstract The synthesis and structural characterization of a lanthanum picrate complex of the proximally-substituted calix[4]arene bisamide, 5,11,17,23-tetra-tert-butyl-25,26-bis(diethylcarbamoylmethoxy)-27,28-dihydroxycalix[4]arene (**L**), is reported. The complex is formulated as $[\text{La}(\text{L-H})(\text{picrate})_2] \cdot 2.75\text{CH}_2\text{Cl}_2$ and crystallises with two inequivalent metal complexes in the unit cell. The differing dispositions of the picrate anions in the two complexes suggest that intramolecular interactions between the aromatic rings of the picrate and calixarene are less significant than the forces involved in the crystal packing of the complexes.

Keywords Calixarene · Lanthanide · Picrate · Crystal structure

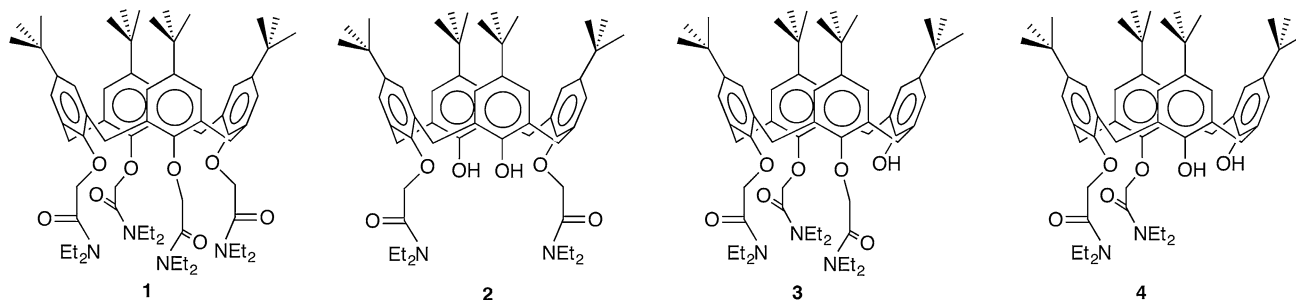
Introduction

Calixarene derivatives have proven to be readily accessible and versatile ligands, and they continue to be of interest as ionophores for ion selective electrodes and metal extraction, platforms for catalytic metal complexes, and “cluster keepers” [1–5]. While there are many ways that the calixarene framework can be functionalized, alkylation of the lower (phenolic) rim to introduce additional donor groups is perhaps the most readily accessible option, and many different examples are known. Here, we are interested in the introduction of amide moieties, which provide additional O-donor atoms particular suitable for “hard” metal cations. We reviewed the literature reporting structurally characterized calixarene-amide complexes in 2005 [6], with complexes of Group I and II, lanthanide, and transition metal cations all having been structurally characterized. Such complexes continue to be reported, most usually where the calixarene ionophore is employed for its functionality. For example, the tetraamide **1**, has been used to complex Group I and II cations to produce “naked” iodide anions, enabling the study of halogen bonding driven self-assembly between the anion, diiodoperfluoroalkanes and the calixarene [7, 8]. Other reports focus on the fundamental complexation behaviour of tetraamide calixarenes, combining structural studies with thermodynamic and/or computational techniques [9, 10]. The use of the amide moiety as a linker has included attaching coordinating [11] or fluorogenic [12] groups to the calixarene, or producing calix[4]azacrowns [13]. An amide/ester binding site has been used to create a redox-active tetrathiafulvalene-calixarene that responds to a cation binding event [14]. Our group has reported on the coordination chemistry of the trisamide **3** with lanthanides [15], and its use as the ionophore in lanthanide-based light-emitting polymeric materials [16, 17].

Dedicated to Professor Jack Harrowfield on the occasion of his 70th birthday.

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The majority of the calixarene-amide ionophores investigated to date are tetra-amides such as **1**, or 1,3-bisamides such as **2**. 1,2-substitution is much less common, although bisamide **4** has been reported [18]. Structurally characterized metal complexes of proximally substituted calix[4]arenes are limited to the phosphorus-coordinated palladium and nickel complexes of a bisphosphane ligand [19, 20], and a phenol-O coordinated bismuth complex of the 1,2-dibenzylated calix[4]arene [21]. Here we report the synthesis and structural characterization of a lanthanum complex of the bisamide calixarene **4**.

Materials and methods

The 1,2-bisamide **4** was isolated as a minor byproduct from the synthesis of the trisamide **2** [22], and gave ¹H NMR spectra consistent with the literature report [18]. The lanthanum picrate complex was crystallised as large yellow plates from dichloromethane/acetonitrile, following the procedure used for the lanthanum picrate complex of the partial cone conformer of tetraamide **1**. [23].

Crystallography

Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Mo K α radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97 [24]. The picrate ligands of the second molecule were disordered over two sets of sites with occupancies set at 0.5. As a result of possible close interactions, one methyl group of an ethyl group (C(216)) and oxygen atoms of a nitro group of a picrate anion (O(316, 317)) of molecule 1 and one solvent dichloromethane molecule were also disordered over two sites. Another dichloromethane solvent molecule was refined with occupancy set at 0.5 after trial refinement. The phenolic hydrogen atoms were included at positions consistent with hydrogen bonding interactions and refined with geometries restrained to ideal values. All remaining

hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for all non-hydrogen atoms.

Crystal data

[La(**4-H**)(picrate)₂] \cdot 2.75CH₂Cl₂: C_{70.75}H_{86.50}Cl_{5.5}LaN₈O₂₀; $M = 1702.86$, triclinic, $P\bar{1}$; $a = 12.9700(4)$, $b = 22.2552(5)$, $c = 27.6046(7)$ Å, $\alpha = 88.039(2)$, $\beta = 82.050(2)$, $\gamma = 88.378(2)^\circ$, $V = 7884.6(4)$ Å³, $Z = 4$; $D_c = 1.435$ g cm⁻³, $\mu = 0.802$ mm⁻¹, crystal size = $0.56 \times 0.31 \times 0.045$ mm³. 91,432 reflections collected, 51,269 unique ($R_{\text{int}} = 0.0523$), max., min. transmission = 0.965, 0.767. Data/restraints/parameters = 51269/428/2272; GoF = 1.148. $R1 = 0.1083$ ($I > 2\sigma(I)$), $wR2 = 0.2593$ (all data). Largest diff. peak and hole = 4.923 and -1.843 e.Å⁻³. CCDC 1034162.

Results and discussion

Combining lanthanum picrate hydrate with the proximally substituted bisamide-calixarene **4** in dichloromethane/acetonitrile resulted in the deposition of large yellow crystals suitable for a single crystal X-ray structure determination. The resulting structure is consistent with the formulation [La(**4-H**)(picrate)₂] \cdot 2.75CH₂Cl₂. There are two independent complex molecules present in the structure, and while there is appreciable disorder, the key features of the complex are clear. The two independent molecules are similar, with the La atoms being ten coordinate. The calixarene macrocycle is found in the cone conformation in each molecule, with a dichloromethane solvent molecule situated in the calixarene cavity. The metal coordination sphere of both molecules consists of the four calixarene phenol oxygen atoms, the two amide oxygen atoms and phenolic oxygen atoms and an oxygen atom from a nitro group from the two picrate ligands. In both molecules the coordination of the phenolic oxygen atoms are quite irregular even when considering the substitution pattern of the calixarene. The substituted phenol

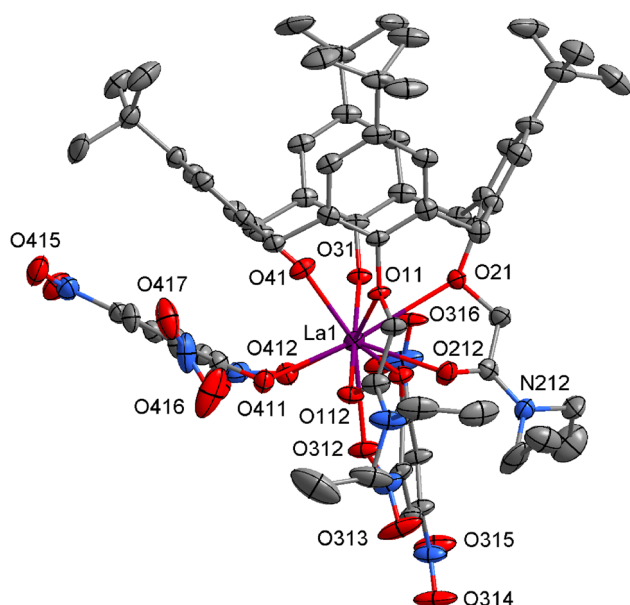


Fig. 1 Molecular structure of molecule 1 of $[\text{La}(\text{4-H})(\text{picrate})_2] \cdot 2.75\text{CH}_2\text{Cl}_2$. The CH_2Cl_2 molecule in the calix, hydrogen atoms and atoms of the disordered components have been omitted

oxygen–lanthanum distances are; $\text{La}(1)\text{--O}(21)$ 2.961(4), $\text{La}(1)\text{--O}(11)$ 2.697(4), $\text{La}(2)\text{--O}(51)$ 3.005(4), $\text{La}(2)\text{--O}(61)$ 2.787(4) Å. The free phenol oxygen atom distances deviate even more significantly; $\text{La}(1)\text{--O}(31)$ 2.665(4), $\text{La}(1)\text{--O}(41)$ 2.208(4), $\text{La}(2)\text{--O}(81)$ 2.585(4), $\text{La}(2)\text{--O}(71)$ 2.224(4) Å. The residual phenolic protons are thus tentatively assigned to

$\text{O}(31)$ and $\text{O}(81)$ and included accordingly with geometrical restraints. Consistent with this assignment, there are close approaches suggesting a hydrogen bond between these oxygen atoms, and a free nitro oxygen atom of a coordinated picrate in each case; $\text{O}(31)\dots\text{O}(316/8\text{-disordered})$ 2.835(13)/2.641(19), $\text{O}(81)\dots\text{O}(716)$ 2.731(11) Å.

The orientation of one of the picrates (41n) of molecule 1 is different to those in molecule 2 being oriented to be almost parallel to one of the calixarene Ph rings (inter-planar angle between the Ph rings C(4n) and C(41n) is $15.3(2)^\circ$, centroid to centroid = 3.81 Å, Fig. 1). Similarly disposed picrate anions have been observed in the lanthanide complexes of bisamide 2 [25, 26]. While the significance of aromatic ring interactions in picrate salts has been discussed [27], the fact that a similar orientation is not observed in molecule 2 suggests the interaction observed here may be a result of “crystal packing forces” rather than a particularly favourable interaction between the aromatic rings. The two picrate anions in molecule 2 are each disordered over two sets of sites, one pair being picrates (71n) and (81n) with the other components being labelled (72n) and (82n). The disorder results in the phenolic oxygen of (72n) of the second component to coordinate to the La(2) in approximately the same site as that of the first component but with the nitro oxygen atom bound at the phenolic site of (81n). For (82n), the coordination site of the nitro oxygen atoms are common with (81n) but the phenolic oxygen atoms bound at the site of the nitro group of 71n. The two components of the disordered molecule 2 are shown in Fig. 2.

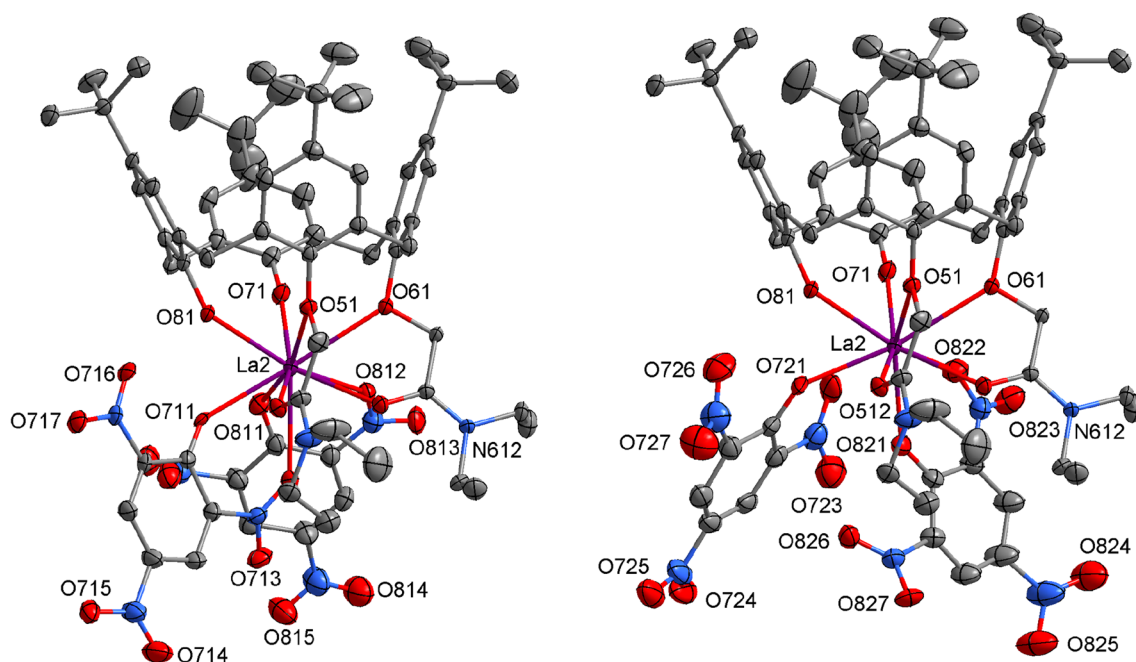


Fig. 2 Molecular structure of molecule 2 of $[\text{La}(\text{4-H})(\text{picrate})_2] \cdot 2.75\text{CH}_2\text{Cl}_2$ showing the two components of the disordered picrate anions. The CH_2Cl_2 molecule in the calix and the hydrogen atoms have been omitted for clarity

The lanthanum complex structurally characterized here illustrates that the unusual 1,2-substituted bisamide calixarene **4**, exhibits similar lanthanide coordination chemistry to the more widely studied 1,3-substituted ligand **2**. More detailed investigations are underway to study the coordination chemistry of this ligand with a broader range of metal cations.

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