A Novel Samarium(II) Complex Bearing a Dianionic Bis(phenolate) Cyclam Ligand: Synthesis, Structure and Electron-Transfer Reactions

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ABSTRACT: The reaction of the hexadentate dianionic 1,4,8,11-tetraazacyclotetradecane-based bis(phenolate) ligand, $(^{tBu2}ArO)_2Me_2$-cyclam^{2-}, with $[SmI_2(thf)_2]$ in thf resulted in ~~the~~ formation of the divalent samarium complex $[Sm(\kappa^6$-$\{(^{tBu2}ArO)_2Me_2$-cyclam$\})]$ (**1**). X-ray diffraction studies revealed that after recrystallization from *n*-hexane/thf complex **1** has a monomeric structure and does not contain thf molecules coordinated to the Sm(II) center. However, UV-vis and ^{1}H NMR spectroscopy of **1** evidenced the formation of thf-solvated complexes in neat thf. Reductive studies show that complex **1** can act as a single electron-transfer reagent and form well-defined Sm(III) species. The reaction of **1** with several substrates, namely, $TlBPh_4$, pyridine N-oxide, $OPPh_3$, $SPPh_3$ and bipyridines, are reported. Spectroscopic studies, including NMR, and single crystal X-ray diffraction data are in agreement with the formation of cationic Sm(III) species, monochalcogenide bridged Sm(III) complexes and Sm(III) complexes with bipyridine radical ligand, respectively.

Introduction

The propensity that divalent lanthanide complexes have to perform single electron redox processes is of great interest, since these reductions may lead to interesting chemical reactivity, as exemplified by the use of SmI_2 as a reducing agent in organic synthesis.[1,2] The synthesis of the soluble $[(C_5Me_5)_2Sm(thf)_2]$[3,4] and of the desolvated $[(C_5Me_5)_2Sm]$ complexes[5,6] have provided a wide variety of new chemistry for f-elements and demonstrated the importance of reductive chemistry in the lanthanide field.[7,8] Of great relevance is the reduction of the small molecules N_2, CO and CO_2 with these metallocenes.[9-11] Cyclopentadienyl derivatives continued to be successfully used as supporting ligands in Sm^{2+} chemistry, and recent studies

demonstrated that understanding the electronics and sterics of complexes is key to comprehend the redox behavior of organosamarium(II) complexes.[12,13] The recognized influence of steric and electronic factors in the stabilization and reactivity of Sm^{2+} ions has led to a continuous search for appropriate supporting ligands for the large Sm^{2+} ion, and to establish new Sm^{2+} - mediated transformations.

Among the reported non-cyclopentadienyl samarium compounds ligands, those bearing amines and bis(phenolate) moieties have received attention due to their ease of preparation and chemical versatility (both electronic and steric). However, this type of chelates have shown propensity to form Sm^{3+} species when reacting with a divalent samarium precursor,[14] and the isolation of Sm^{2+} complexes anchored on polyamine bis(phenolates) is scarce.[15,16] To our knowledge, only the tetrameric $[Sm^{II}L(HMPA)_2]_4$ (L = 1,4-bis(2-oxo-3-tert-butyl-5-methyl-benzyl)-piperazidine) and the trinuclear mixed-valent $[(Sm^{III})_2Sm_{II}(L)_4]$ (L = $[Bu^nN(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}But_2)_2]$) samarium complexes have been structurally characterized.[14, 16]

Recently, we have designed a new dianionic tetraazamacrocyclic-based bis(phenolate) ligand, $(^{tBu2}ArO)_2Me_2\text{-}cyclam^{2-}$, that was successfully used as a support ligand for mononuclear yttrium(III) and lanthanide(III) complexes, including $[Sm\{(^{tBu2}OAr)_2Me_2\text{-}cyclam\}Cl]$.[17] Our group also showed that this bulky and electron-rich $[O_2N_2N'_2]$ donor ligand allowed to isolate an unprecedented monomeric polyamine bis(phenolate) U(III) complex that promoted a high reactivity for the U^{3+} center.[18] Although the Sm(III)/Sm(II) redox potential of -1.55 V is significantly lower than the value reported for the U(IV)/U(III) redox couple, which is around -0.607 V,[19] the $(^{tBu2}ArO)_2Me_2\text{-}cyclam^{2-}$ ligand appears to be particularly well suited for the stabilization of low-valent samarium complexes. Herein, we report the first structural example of a monomeric Sm(II) complex anchored on polyamine

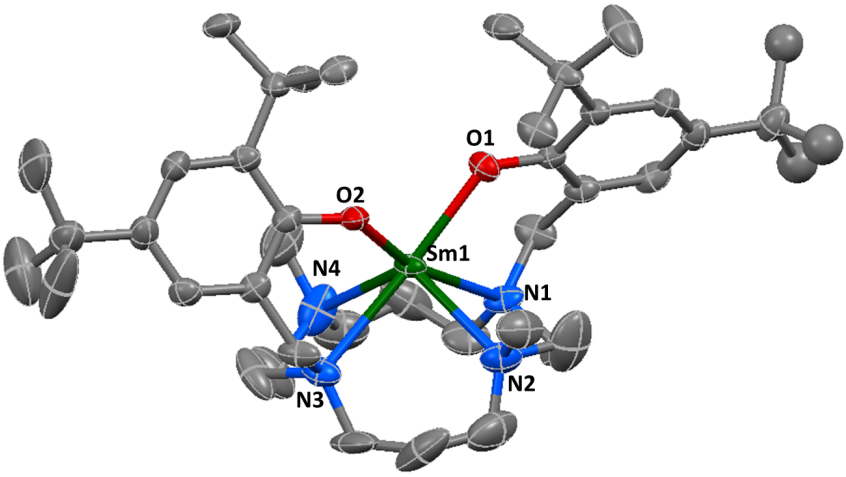
bis(phenolate) derivative and the first lanthanide(II) complex with this type of N,O donor ligand. Moreover, reactivity studies of the new divalent samarium complex with different oxidants were carried out, namely with $TlBPh_4$, pyridine N-oxide, $OPPh_3$, $SPPh_3$ and bipyridines, providing evidence that the new Sm(II) complex is able to engage in one-electron reduction of diverse substrates affording new Sm(III) complexes.

Results and Discussion

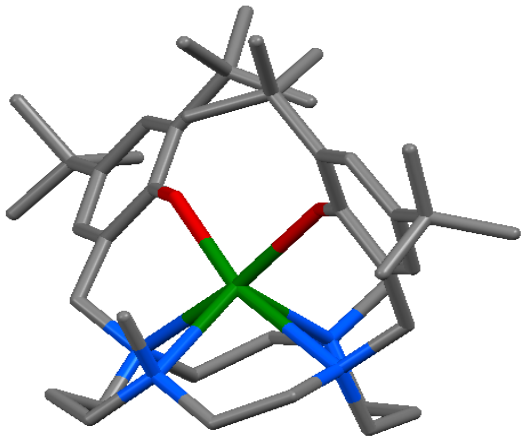
Synthesis and structure of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}]

The reaction of $[SmI_2(thf)_2]$ with one equivalent of $K_2(^{tBu2}O)_2$Me-cyclam, obtained *in situ* from the reaction of $H_2(^{tBu2}O)_2$Me-cyclam with excess of KH, was carried out in thf at room temperature. Evaporation of the solvent from the resulting green solution, followed by extraction with toluene and precipitation with *n*-hexane, allowed to isolate [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) as a dark brown microcrystalline solid in 74% yield. Complex **1** is soluble in thf, dme and aromatic solvents, and insoluble in *n*-hexane.

Single crystals were obtained from a dilute solution of **1** in a mixture of thf/*n*-hexane and analysed by X-ray diffraction that revealed that the metal complex crystallizes in the monoclinic $P2_1/c$ space group as monomeric molecular units, in which the divalent Sm center is six-coordinated by the κ^6-$O_2N_2N'_2$ donor ligand (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-}(Figure 1). Despite the use of thf as the reaction solvent, complex **1** does not contain thf molecules coordinated to the Sm(II) center.



(a)



(b)

Figure 1. (a) Solid-state molecular structure of [Sm{(^{tBu2}OAr)$_2$Me$_2$-cyclam}] (**1**) with thermal ellipsoids drawn at 40% probability level. Hydrogen atoms are omitted for clarity. (b) View of complex **1** showing the approximate C_2 symmetry in the solid state.

The coordination geometry of **1** is not regular and could be considered as a highly distorted trigonal prism, in which one of the three quadrangular faces is defined by the nearly coplanar four nitrogen atoms of the tetraazamacrocycle core,

with the samarium center sitting 1.394 Å above this plane. Although the crystallographic structure results in the absence of symmetry, the arrangement of the six donor atoms $O_2N_2N_2$' around the samarium(II) center in **1** approximates C_2 symmetry (Figure 1-b), that is reflected by the close values of the two *trans* N_{benzyl}-Sm-O angles (165.2(2) and 165.06(2)º) and the two *cis* N_{benzyl}-Sm-O angles (74.1(2) and 74.4(2)º). Two *cis* phenolate oxygens are coordinated to the Sm(II) with an O-Sm-O angle of 92.7(6)º, comparable to the one found for [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}Cl] (95.7(9)º),[17] and a dihedral angle between the two phenolate rings of 55.8(3)º.

The two Sm-O bond distances are similar, with a mean value of 2.343(8) Å, longer than those observed for the trivalent samarium complex [Sm{^{tBu2}ArO)$_2$Me$_2$-cyclam}Cl] (2.166(2) – 2.206(2) Å),[17] as expected for an increase of ionic radius from Sm^{3+} to Sm^{2+}.[20] The average Sm-O bond distances are comparable to the Sm-O(Ar) terminal distances found in the dimeric Sm(II) complexes [SmL(HMPA)$_2$]$_2$ supported by bridged bis(phenolate) ligands (L = 2,2'-methylene-bis(6-tert-butyl-4-methylphenoxide), 2.332(4) Å; L = 2,2'-ethylidene-bis(4,6-di-tert-butylphenoxide), 2.332(3) Å)[21] and with the average Sm-O(Ar) bond distances reported for the monomeric Sm(II) bis(aryloxide) complex [Sm(OAr)$_2$(thf)$_3$] (2.339(12) Å, 2.335(7) Å; Ar = $C_6H_2Bu^t_2$-2,6-Me-4).[22,23] The Sm-N bond distances range from 2.625(9) to 2.771(11) Å and are within the values reported for Sm ← :NR_3 dative bond, in particular with the Sm-N distances found for the Sm(II) cyclopentadienyl-triaazamacrocycle complex [Sm{$C_5Me_5SiMe_2$(^{i}Pr$_2$-tacn)}I] (2.663(10)-2.773(10) Å).[24]

Importantly, the combination of two phenolate arms and of the macrocycle effect impart sufficient steric protection to prevent the formation of polinuclear

species, allowing to structurally characterize the first monomeric Sm(II) complex stabilized by a polyamine bis(phenolate) derivative. Shen and co-workers have studied the reactions of Sm(II) with diamine bis(phenolate) ligands, although until now it was only possible to characterize in the solid state a tetrameric Sm(II) species stabilized by a piperazidine-bridged-bis(phenolate) ligand[16] or a trinuclear samarium mixed-valent complex $Sm^{III}_2Sm^{II}L_4$ with a tridentate amine bis(phenolate) ligand.[14] The sterically demanding bis(phenolate) tetraazamacrocycle ligand allows to easily obtain the unsolvated monomeric complex [Sm{^{tBu2}OAr)$_2$Me$_2$-cyclam}] (**1**). However, dissolution of the solid in thf results in a colour change from dark brown to dark green and removal of the solvent results in the back-formation of the dark brown solid **1**. Compound **1** seems to exhibit reversible solvatochromic behaviour as observed for other divalent samarium(II) complexes.[25] The analysis by UV-vis absorption spectroscopy of the samarium compound solutions in thf and in the non-coordinated solvent toluene results in distinct absorption spectra (Figure 2), consistent with the coordination of thf molecules when **1** is dissolved in this solvent.[25]

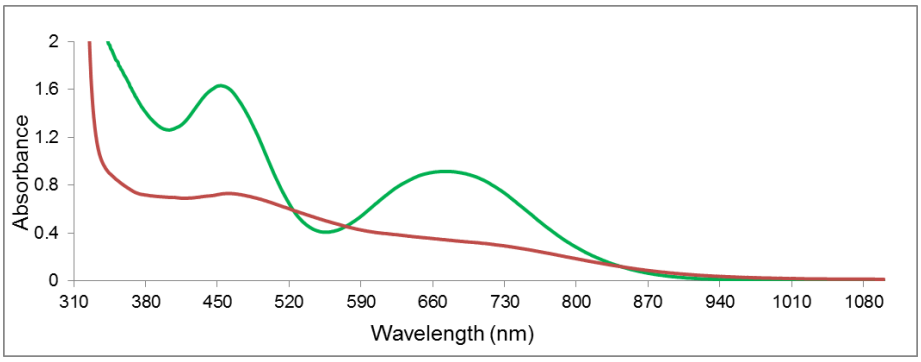


Figure 2 Electronic absorption spectra of **1** in toluene (red) and in tetrahydrofuran (green).

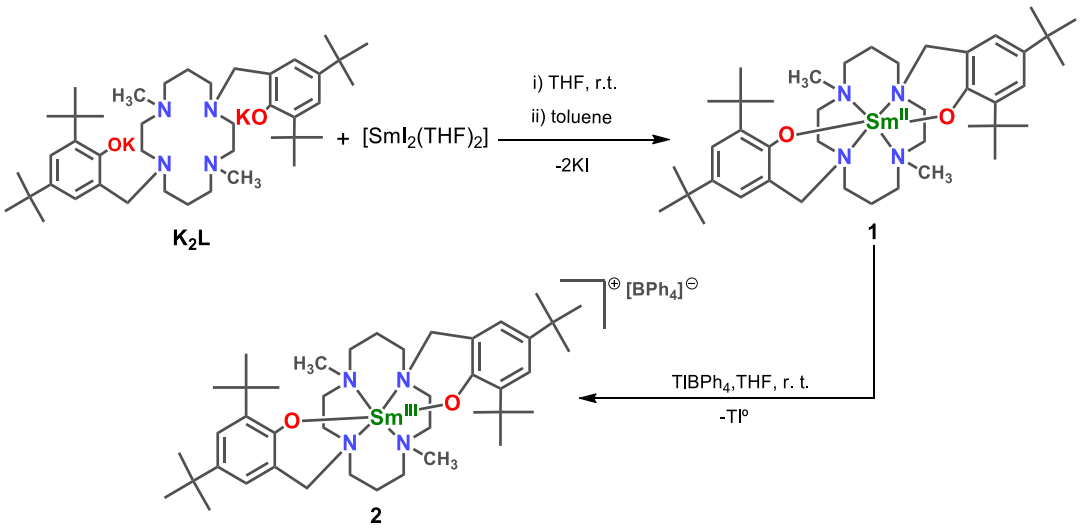
Several attempts were made to obtain single-crystals of the solvated complex suitable for X-ray diffraction analysis from thf solutions, however without success.

The ^{1}H NMR spectrum of **1** in the noncoordinating solvent toluene-d_8, at room temperature, displays only two well defined resonances at -0.34 and -6.02 ppm assignable to the *tert*-butyl groups of the ligand (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-}, and a few broad signals (see Fig. S1 in Supporting Information), suggesting a conformation exchange process of complex **1** in solution, that can be attributed to the 14-member macrocycle core flexibility. Cooling the solution allowed obtaining a low-temperature paramagnetic ^{1}H NMR spectrum, consistent with an average C_2-symmetric structure (see Fig. S2 in Supporting Information), corresponding to the approximate C_2 symmetry found in the solid-state structure of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**). Thus, at -40ºC one resonance is observed at 187.9 ppm for the two methyl NCH$_3$ groups and two resonances at -1.62 and -14.03 ppm assignable to two non-equivalent *tert*-butyl groups of the two equivalent phenolate motifs of the ligand. In addition, 12 signals are observed from 63.43 to -70.76 ppm and assignable to the remaining twenty-eight aromatic, benzylic and tetrazamacrocycle methylenic ligand protons.

The ^{1}H NMR of **1** was also run in the coordinating solvent thf-d_8 and, as in toluene-d_8, at room temperature is very simple and structural uninformative; a resonance at -1.40 ppm was assigned to *tert*-butyl protons (Fig. S3 in Supporting Information). As the temperature of the sample is decreased, the signals of the macrocycle core start to emerge and the *tert*-butyl protons split into four distinct resonances in a 9:9:9:9 ratio. At -40ºC, it is possible to observe a considerably resolved spectrum with 34 paramagnetically shifted resonances, ranging from 112.63 to -72.82 ppm (Fig. S4 in Supporting Information). Four relatively sharp signals at

1.34, -0.78, -1.49 and -2.36 ppm are assigned to four *tert*-butyl groups of two inequivalent phenolate arms of the ligand, and two resonances for the methyl NCH_3 protons of the ligand are observed at low field (112.6 and 86.8 ppm). The remaining 28 resonances integrate to 1H each, and correspond to the aromatic protons, to the diastereotopic benzylic protons and to the twenty methylenic protons of the tetraazamacrocycle core, for which the assignment remains equivocal. This NMR pattern is consistent with an asymmetric structure in solution, in contrast with the C_2 symmetry observed in toluene-d_8 and the approximate C_2 symmetry obtained in the solid state. This solution behaviour suggests that in neat thf some solvation takes place and thf binds to the divalent samarium complex **1**, which was also evidenced by UV-vis absorption spectroscopy.

Note that the reduction potential of the systems M^{3+}/M^{2+} can be enhanced upon coordination by organic molecules, as exemplified by samarium(II) species (*cf.* Sm^{3+}/Sm^{2+}, $E_{1/2} = -1.55$ V, and $Sm^{III}Cp_3/Sm^{II}Cp_3^-$, −2.50 V).[26] Successful isolation of the non-cyclopentadienyl monomeric complex **1** with the bulky $\{O_2N_2N'_2\}^{2-}$ donor ligand prompts us to study the reducing properties of this new coordinatively unsaturated Sm(II) center, and first reactivity studies with some substrates explored by Evans and co-workers for $[(C_5Me_5)_2Sm(thf)_2]$ and $[Sm(C_5Me_5)_2]$ were performed. The results will be discussed herein by direct comparison with the abovementioned studies.



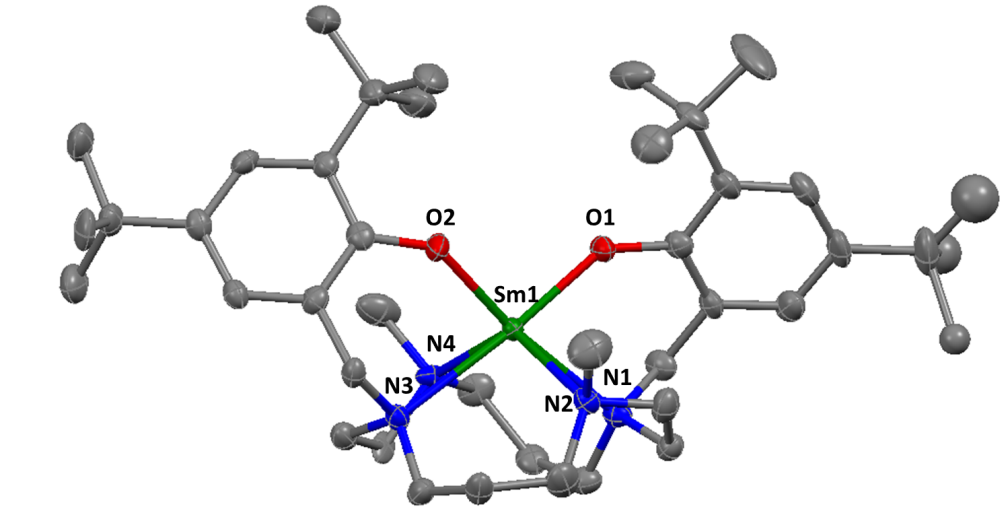
Scheme 1. Synthesis of **1** and **2**

Reactivity of 1 with $TlBPh_4$: generation of cationic species. Cationic samarium(III) complexes can be synthesized by one-electron oxidation of the corresponding divalent complex with $MBPh_4$ (M = Ag, Tl),[27-29] including the preparation of the Sm(III) bis(aryloxide) complex $[Sm(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(dme)_2][BPh_4]$.[28] This methodology was tested with the divalent samarium(II) compound $[Sm\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}]$ (**1**) using the thallium salt as oxidant. Thus, $TlBPh_4$ was added to a solution of **1** in thf and then the colour of the mixture changed from green to a grey suspension, indicative of formation of a Tl precipitate (Scheme 1). After removing the Tl, the yellow solution obtained was layered with *n*-hexane and compound **2** was obtained as a lightly yellow precipitate in 58% yield. The elemental analysis and MS are consistent with the formation of $[Sm\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}][BPh_4]$. The Electrospray Ionization (ESI) mass spectrum shows a molecular ion in the positive mode with *m/z* 814.2 corresponding to the cation $[Sm\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}]^+$ and in the negative mode gives a molecular ion with *m/z* 319.2 corresponding to the anion $[BPh_4]^-$. Complex **2** is soluble in

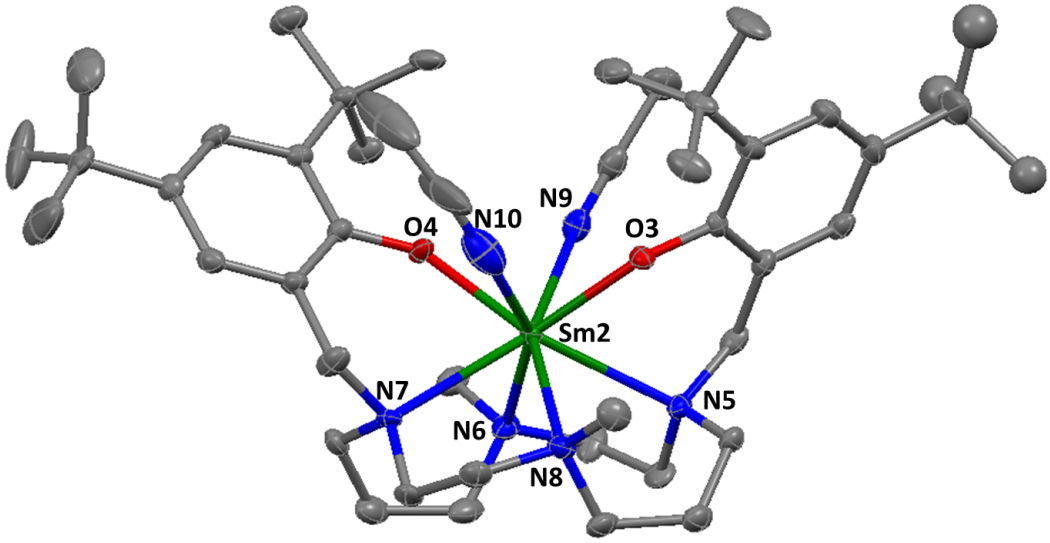
tetrahydrofuran and acetonitrile, insoluble in dichloromethane and in the nonpolar solvents toluene and n-hexane.

Several attempts were made to isolate crystals of **2** in thf suitable for X-ray diffraction, however without success. Crystallization from acetonitrile resulted in colourless crystals, for which X-ray diffraction analysis revealed the presence of two independently refined Sm(III) cationic species in the asymmetric unit: $[Sm\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}]^+$ (**2a**) and $[Sm\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(CH_3CN)_2]^+$ (**2b**), and two $[BPh_4]^-$ anions, confirming the ionic nature of compound **2** (see Fig. SX in supporting Information). Each cationic unit shows a tetraazamacrocycle anchor bearing two phenolate side arms coordinated to the Sm(III) center in a κ^6-$O_2N_2N_2$' mode. The molecular structure of **2a** is a solvent-free hexa-coordinate Sm(III) cationic complex in a distorted octahedral geometry (Figure **3-a**), in which the phenolate arm oxygens are mutually *cis* with a O-Sm-O bond angle of 97.18(12)º, comparable to that one found for the Sm(II) precursor, and with dihedral angle between the two phenolate rings of 46.9(2)º.

The samarium cation **2b** shows a bis(acetonitrile) adduct eight-coordinate in a distorted square antiprismatic geometry (Figure **3-b**). The almost coplanar four nitrogens atoms of the macrocycle define one of the quadrangular faces, and the other one is defined by the two phenolate oxygens and the two coordinated acetonitrile nitrogens.



(a)



(b)

Figure 3. Solid-state molecular structure of compound **2**: cationic unit **2a** (a) and cationic unit **2b** (b) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and $[BPh_4]^-$ anions are omitted for clarity.

Selected structural parameters for compounds **1**, **2a** and **2b** are presented in Table 1. Comparatively to the solvent free cation **2a**, the O-Sm-O bond angle in the octacoordinate molecule **2b** is slightly open (111.08(12)º) in order to accommodate

the two acetonitrile molecules, and the two phenolate rings are arranged with a dihedral angle of 66.2(2)º. The average Sm-O bond distances are smaller (**2a**: 2.155(14); **2b**: 2.190(4) Å) than the one observed for the Sm(II) precursor **1** (2.343(8) Å), as expected for a decrease of the ionic radii for Sm(III),[20] and compare with the average Sm-O bond distance of the trivalent complex [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}Cl] (2.18(2) Å).[17] The Sm-O bond distances of **2a** are also comparable with the distances found for the bis(phenolate) [Sm(^{tBu2,Me}ArO)$_2$(dme)$_2$][BPh$_4$] (2.147(3) and 2.114(3) Å).[27] In the case of the hexacoordinate cation [Sm{(^{tBu}ArO)$_2$Me$_2$-cyclam}]$^+$ (**2a**), the respective average Sm-N(benzyl) and Sm-N(CH$_3$) bond distances of 2.64(2) and 2.53(2) Å are smaller than those observed for the hexacoordinate Sm(II) precursor (Table 1), in accordance with the smaller Sm(III) ionic radius. The observation of two independent Sm(III) cationic structures in the asymmetric unit demonstrated that the (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-} ligand set is suitable for the stabilization of unsolvated and solvated cationic Sm(III) bis(phenolate) cyclam complexes.

Table 1. Selected bond lengths (Å) and angles (deg) of **1** and **2**.

		2	
	1	**cation 2a**	**cation 2b**
Sm-O	2.341(6); 2.345(6)	2.147(3); 2.167(3)	2.202(3); 2.176(3)
Sm-N_{benzyl}	2.723(8); 2.771(8)	2.624(4); 2.664(4)	2.686(4); 2.650(4)
Sm-N_{CH3}	2.625(9); 2.719(11)	2.505(4); 2.546(4)	2.640(4); 2.689(4)
Sm-$N_{acet.}$	-	-	2.685(5); 2.756(7)
O-Sm-O	92.6(2)	97.20(13)	111.11(13)
N_{benzyl}-Sm-N_{benzyl}	117.9(2)	110.06(13)	125.35(13)
N_{CH3}-Sm-N_{CH3}	118.3(3)	131.43(13)	105.94(13)
O-Sm-$N_{benzyl(trans)}$	165.1(2)	172.54(13)	149.40(12)
	165.6(2)	174.16(13)	146.40(13)
$N_{acet.}$-Sm-$N_{acet.}$	-	-	114.10(16)

The room-temperature ^{1}H NMR spectrum of **2** in acetonitrile-d_3 or thf-d_8 shows only four well-define resonances for the ligand (see Fig. S5 and S6 in Supporting Information), which were attributed to the *tert*-butyl and aromatic protons of the bis(phenolate) cyclam ligand, and three resonances (7.26, 6.83 and 6.98 ppm) with an integration of 2:2:1 assigned to the aromatic protons of the $[BPh_4]^-$ anion. The observation of few and broad resonances for the $(^{tBu2}ArO)_2Me_2$-cyclam^{2-} ligand means that the complex is undergoing exchange that is rapid on the NMR time scale. Variable temperature ^{1}H NMR studies in acetonitrile-d_3 solution above the melting point did not slow down the exchange process and structural information of complex **2** could not be obtained in this solvent. On the other hand, when the temperature is decreased in thf-d_8 the resonances of the *tert*-butyl protons of the $(^{tBu2}ArO)_2Me_2$-cyclam^{2-} ligand split in four inequivalent resonances, and at -30ºC they can be observed at 1.87, 1.82 and 1.01 ppm with an area ratio of 9:9:18 (two ^{t}Bu group

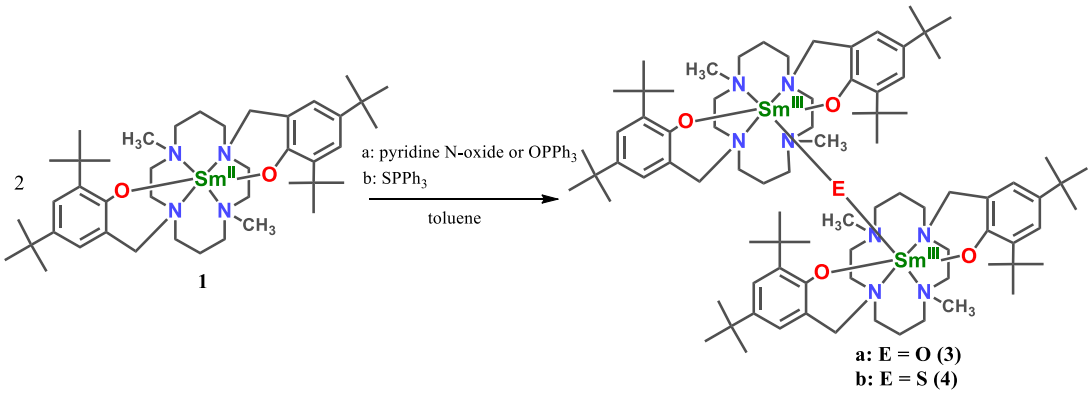
proton resonances are overlapping), implying that the molecule has a C_1 symmetry. The NCH_3 protons of the ligand emerge as two signals at -4.48 and -6.85 ppm in an area ratio of 3:3, and additionally and in agreement with an asymmetric molecule, the ^1H NMR spectrum at -30ºC contains four resonances at 12.08, 9.00, 7.41 and 5.94 ppm, in a ratio of 1:1:1:1, assignable to the diastereotopic benzylic protons NCH_2Ar, four resonances at 9.08, 9.04, 7.76 and 7.65 ppm, in a ratio of 1:1:1:1, assignable to the phenolate ligand aromatic protons and 20 resonances ranging from 7.35 to -2.53 ppm for the tetraazamacrocycle methylenic protons (See Fig. S7 in Supporting Information). Albeit some proton resonances of the tetraamine bis(phenolate) ligand are overlapping, chemical shifts were assigned on the basis of two-dimensional ^1H-^1H COSY and ^1H-^{13}C HSQC NMR experiments. Moreover, the pattern of the ^{13}C NMR spectrum of **2**, at low-temperature, for the secondary carbons, that was identified indirectly from a ^1H-^{13}C HSQC experiment, also points out to a C_1 symmetric samarium complex in solution (see Table S1 for ^1H and ^{13}C chemical shits, partially assigned, in Supporting Information). The chemical shifts of the three resonances corresponding to the aromatic anion $[BPh_4]^-$ protons are not significantly affected by the temperature and are observed in the diamagnetic zone, implying that the anion is completely outer-sphere in complex **2** and is not interacting with the paramagnetic metal center.

The identification by X-ray diffraction of two distinct cationic structures for **2**, one unsolvated (**2a**) and the other one with two coordinated acetonitrile molecules (**2b**), puts on the possibility of coordinating to the cation $[Sm\{(^{tBu2}ArO)_2Me_2$-cyclam$]^+$ up to two molecules of a Lewis base. In the case of the more bulky thf molecule, we can hypothesize that in neat thf one molecule is coordinated to the samarium cation giving an asymmetric seven-coordinate Sm(III) complex with a ^1H

NMR pattern similar to the one observed for the seven-coordinate Sm(III) complex [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}Cl].[17]

Reactivity of 1 with chalcogen-atom transfer reagents. A few reported complexes containing a Sm-O-Sm unit were prepared by reactions of Sm(II) complexes with oxygen transfer reagents, such as NO, N_2O, pyridine *N*-oxide, epoxybutane and nitrobenzene.[30-32] To address the possibility of isolating an oxo-bridged complex, the reaction of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1)** with 0.5 equiv of pyridine N-oxide was first attempted in benzene-d_6. The addition of this substrate to the brown benzene-d_6 solution caused a colour change to yellow and the ^{1}H NMR showed a mixture of products with a predominant paramagnetic species and the expected pyridine by-product. The reaction was scaled up in toluene by reacting 2 equiv of the divalent samarium complex **1** with 1 equiv of pyridine N-oxide (Scheme 2). The oxidation complex [({(^{tBu2}ArO)$_2$Me$_2$-cyclam}Sm)$_2$(μ-O)] (**3**) was isolated as a white microcrystalline solid in 40% yield, after workup and recrystallization from thf/diethyl ether. Complex **3** is soluble in aromatic solvents and tetrahydrofuran, and slightly soluble in diethyl ether and *n*-hexane. In contrast, to the reaction of [Sm(C$_5$Me$_5$)$_2$(thf)$_2$] with triphenylphosphine oxide, that conducted to the formation of the adduct [Sm(C$_5$Me$_5$)$_2${OPPh$_3$}(thf)],[30] **3** can also be prepared by oxidation of **1** with OPPh$_3$ in toluene at room temperature; however the separation of the triphenylphosphine by-product from the oxo-bridged disamarium complex proved to be difficult due to the similar solubility of the compounds. The isolation of the Sm(III) complex **3,** using pyridine N-oxide as oxygen transfer reagent has shown to be a better process.

The sulphur analogue of **3**, [({(^{tBu2}ArO)$_2$Me$_2$-cyclam}Sm)$_2$(μ-S)] (**4**), could be obtained in toluene from the reaction of **1** with $(C_6H_5)_3P{=}S$, by reductive cleavage of the S=P bond (Scheme 2). The reaction occurs at room temperature with slow colour change to yellow. Complex **4** could not be isolated as a clean product by this route, however, a few colourless crystals were isolated from the mixture in n-hexane, and X-ray crystallographic analysis permitted to confirm the formation of [({(^{tBu2}ArO)$_2$Me$_2$-cyclam}Sm)$_2$(μ-S)] (**4**).



Scheme 2: Synthesis of **3** and **4**.

To our knowledge, **4** is the second example of a monosulfide bridged disamarium complex crystallographically characterized. The [{Sm(C$_5$Me$_5$)$_2$(thf)}$_2$(μ-S)] complex was also obtained by the sulfur atom transfer reaction of triphenylphosphane sulphide with the divalent complex [Sm(C$_5$Me$_5$)$_2$(thf)$_2$].[33] A few other examples of dinuclear metal complexes containing the bridged monosulphide, S^{2-}, with yttrium and other lanthanide metals have been reported.[34-36]

Single crystals of the oxo-bridged disamarium complex **3** were obtained from slow concentration of a tetrahydrofuran /diethyl ether solution and also analysed by single crystal X-ray diffraction. The oxo-bridged samarium complex **3** crystallized in the monoclinic space group $C_{2/c}$, with two thf molecules in the lattice, and resides on twofold rotation axis. The monosulfide bridged samarium **4** crystallized in the

centrosymmetric monoclinic space group $P2_1/n$ with *n*-hexane in lattice. The structures of **3** and **4** are represented in Figure 4 and Figure 5 and comparative relevant parameters are presented in Table 2.

In the monoxide and monosulphide bridged disamarium complexes **3** and **4**, the ligand $(^{tBu2}ArO)_2Me_2$-cyclam^{2-} coordinates to each metal in a κ^5 mode through the two oxygen phenolates and three of the nitrogen macrocycle amines. The two Sm(III) centres are connected by the E^{2-} ligand coordinated in the axial position of distorted octahedra. This highlights the hemilabile behaviour and flexibility of the $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ chelate which can adopt different metal ion coordination modes, depending on the coordination environment. Indeed, this behaviour was also observed for other lanthanides and uranium complexes.[17,18]

The average Sm-O and Sm-S bond distances in the $[(\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}Sm)_2(\mu\text{-E})]$ complexes **3** and **4**, are consistent with the 0.44 Å difference in radii between O^{2-} and S^{2-},[20] increase from 2.138(1) Å (E = O) to 2.61(2) Å) (mean value, E = S).

The Sm-O3 bond length in **3** is slightly longer than the ones found for the precisely linear complexes $[\{Sm(C_5Me_5)_2\}_2(\mu\text{-O})]$ (2.094(1) Å)[30] and $[\{(Me_3Si)_2N\}_2(thf)Sm]_2(\mu\text{-O})]$ (2.0819(2) Å),[32] and more comparable with the Sm-O distances found for the more sterically crowed complexes $[\{Sm(C_5Me_4{}^iPr)_2\}_2(\mu\text{-O})]$ (2.116(3) Å) and $[\{Sm(C_5Me_5)_2(NC_5H_5)\}_2(\mu\text{-O})]$ (2.151(2) Å),[37] in which the Sm-O-Sm angle is deviated from linearity. Complex **3** exhibits a Sm-O-Sm angle of 157.80º, and as expected for a larger chalcogen atom, the Sm-S-Sm angle in **4** increases (176.89º). An increase of the Sm…Sm distances is also observed (**3**: 4.196(1) Å; **4**: 5.213(1) Å). The average Sm-S bond distance and Sm-S-Sm angle can be compared with the corresponding parameters described for the only mono-sulfide

bridged samarium complex reported, [{(Sm(C_5Me_5)$_2$(thf)}$_2$(μ-S)] (2.664(2) Å, 170.0(1)º),[33] however, the Sm-S distance in **4** is slightly shorter compared with the bridged metallocene, in which each Sm(III) centre is formally eight coordinate.

In complex **3,** the two [{(^{tBu2}ArO)$_2$Me$_2$-cyclam}Sm]$^+$ units are identical, as the second unit is generated by symmetry, and exhibit a mean value for the Sm-N bond distances of 2.69(4) Å. In the case of the dimer **4**, the two macrocycle ligands show different chirality at the coordinated N amines for each metal center (Sm1: SSS; Sm2: RRR), with similar average Sm-N bond distances (Sm1: 2.72(6) Å; Sm2: 2.73(9) Å). The shortening of the Sm-O(phenolate) distances in **3** and **4** (av: 2.211(14) Å for **3** and 2.165(6) Å for **4**), when compared to those in precursor **1**, also indicates the oxidation of Sm(II) to Sm(III).

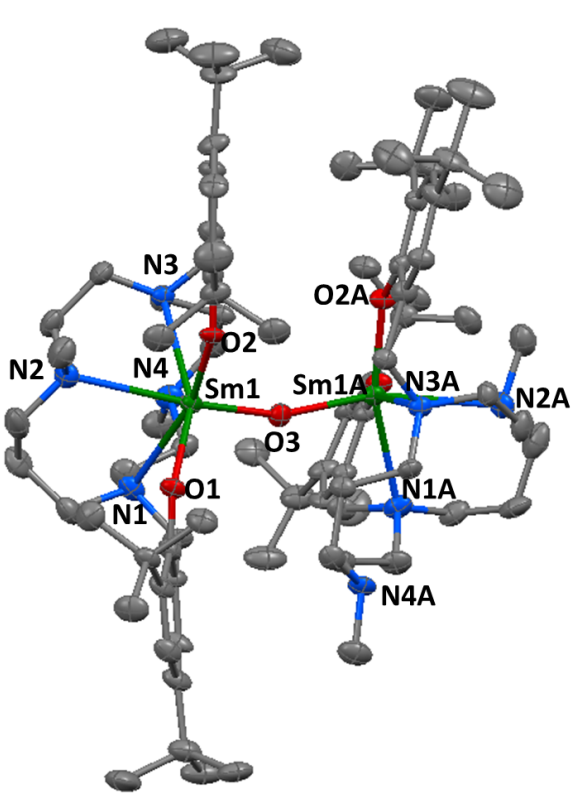


Figure 4. Solid-state molecular structure of [{Sm(κ^5-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})}$_2$(μ-O)] (**3**) in **3**.(C_4H_8O)$_2$ with thermal ellipsoids drawn at 40% probability level. Hydrogens atoms and cocrystallized solvent are omitted for clarity.

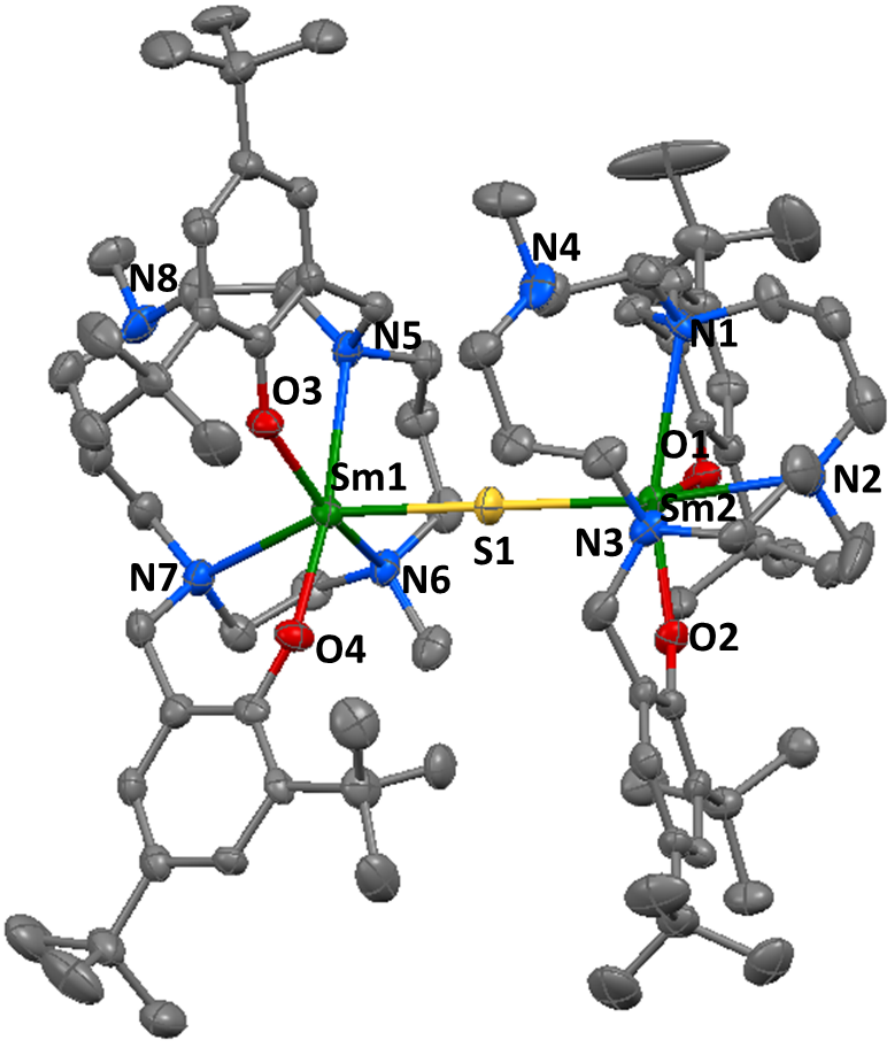


Figure 5. Solid-state molecular structure of [{Sm(κ^5-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})}$_2$(μ-S)] (**4**) with thermal ellipsoids drawn at 40% probability level. Hydrogens atoms and cocrystallized solvent are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (deg) of **3** and **4**.

	3	**4**
Sm-E	2.138(1)	2.592(2), 2.622(2)
Sm-O	2.201(4), 2.222(3)	2.164(4), 2.167(4), 2.163(4), 2.167(4)
Sm-N_{benzyl}	2.649(4), 2.729(5)	2.786(5), 2.673(5), 2.835(5), 2.694(5)
Sm-N_{CH3}	2.776(5)	2.693(5), 2.653(5)
O-Sm-O	101.84(16)	102.88(15), 102.47(16)
N_{benzyl}-Sm-N_{benzyl}	103.56(14)	104.82(14), 100.30(15)
Sm-E-Sm	157.80	176.89(8)
N_{benzyl}-Sm-E	97.51(11), 95.61(17)	99.76(11), 99.98(12), 88.20(11), 150.91(12)
N_{CH3}-Sm-E	159.07(10)	166.56(12), 84.99(12)

The solution ^{1}H and ^{13}C NMR of **3** at room temperature is consistent with the dimeric structure observed in the solid-state. Four separate ^{t}Bu resonances, two separate AB spin systems for the benzylic protons and two ^{13}C resonances at 172 and 171.9 assignable to the Ar*C*-O phenolate carbons can be observed, consistent with two distinct phenolate groups coordinated to each samarium center and with two equivalent [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] units.

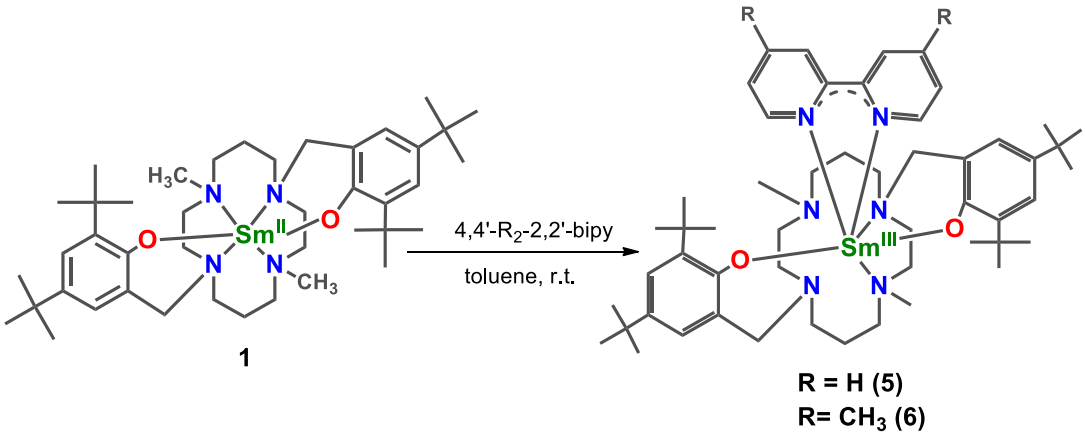
As mentioned above, compound [({Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}})$_2$(μ-S)] **(4)** was not isolated cleanly. The formation of **4** is accompanied by the formation of other products as well as by the by-product triphenylphospane, and the extreme solubility of the product mixture prevented the isolation of pure samples. As such, the NMR spectra of unpurified reaction mixtures revealed to be of difficult assignment as some resonances were overlapping. The reaction of

[Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) with $SPPh_3$ can offer only indications of reactivity, rather than complete characterisation of **4**.

Reaction of 1 with bipyridines. Another possibility to test the reactivity of the new Sm(II) complex **1** is the reaction with N-aromatic heterocycle compounds, such as bipyridines. These molecules, in addition of being chelating N-donors, are redox-active ligands with potential to act as electron acceptors and ability to oxidize electropositive metals. Complexation studies of lanthanocenes(II) with bipyridine ligands have been extensively explored, and depending on the metal reduction potential and the electronic properties of the coordinated ligands, the bipy ligands can be either neutral or radical-anionic.[38-46] 2,2'-bipyridine is known to be reduced by [Sm(C_5Me_5)$_2$(thf)$_2$] affording the [Sm^{III}(C_5Me_5)$_2$(bipy$^{\cdot-}$)] complex,[38] in which the bipyridil is a monoanionic radical ligand and the samarium is trivalent. Recently, it was also reported the reduction of the 2,2'-bipyridine with the Lewis base-free complex [Sm(Cp^{Bn5})$_2$].[46]

Thus, reactivity of our bis(phenolate) cyclam samarium(II) complex with two bipyridines was studied and the results are discussed here. The reduction potentials of the bipyridines used in this work are -2.10 V and -2.15 V for 2,2'-bipyridine and 4,4'-Me_2-2,2'-bipyridine (referred to SCE), respectively.[47,48] The addition of one equiv of 2,2'-bipyridine or one equiv. of the substituted one to a dark brown toluene solution of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) conducted immediately to a change of solution colour to dark orange or to dark red, respectively, at room temperature, from which we could isolate the complexes [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(R_2-bipy$^{\cdot-}$)] (R = H (**5**), CH_3 (**6**)) in 73 and 77%, respectively (Scheme 3). Both complexes are soluble in aromatic solvents, tetrahydrofuran, diethyl ether and sparingly soluble in *n*-

hexane. **5** and **6** were characterized by elemental analysis, NMR, IR and UV/Vis spectroscopy. In the case of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(Me$_2$-bipy$^{\cdot-}$)] (**6**) it was possible to confirm the structure by X-ray diffraction studies.



Scheme 3: Synthesis of **5** and **6**.

In the room-temperature ^{1}H NMR spectra of **5** and **6** in toluene-d_8, the compounds resonate in a large chemical shifts window (**5**: 13 to -240 ppm; **6**: 161 to -242 ppm), although the proton chemical shifts of the {(^{tBu2}ArO)$_2$Me$_2$-cyclam}$^{2-}$ ligand are not significantly shifted from a typical Sm(III) bis(phenolate) cyclam ^{1}H NMR chemical shift window (13 to -7 ppm).[17] Complex **5** and **6** exhibit similar split patterns and proton chemical shifts for the ancillary ligand (see Fig. S9 and S10 in Supporting Information): four resonances, integrate 9H each, assignable to four ^{t}Bu groups (**5**: 1.74, 1.64, -0.21 and -0.66 ppm; **6**: 1.77, 1.66, -0.22 and -0.69) and 25 resonances assignable to the methyl NCH$_3$ protons, aromatic protons, diastereotopic benzylic protons and to the 20 methylenic protons of the macrocycle core of the bis(phenolate) cyclam ligand, which were identified with the support of one ^{1}H-^{13}C HSQC NMR experiment. This pattern is consistent with asymmetric structures in solution. In accordance with a C_1 symmetry, the remaining 8 and 7 resonances were attributed to the bipyridine ligand**,** for **5** and **6**, respectively. The bipyridine

resonances are shifted from their diamagnetic values and experience exceedingly large paramagnetic shifts, with two resonances appearing far upfield (**5**:-233.8 and -239.8 ppm ; **6**: -235.9 and -242 ppm). These ^{1}H NMR data suggest that the large bipy chemical shifts are dominated by a radical rather than the paramagnetic Sm(III) center as observed for the [$(4f)^5$-$(\pi^*)^1$] ground-state electronic configuration Sm(III) complex [$Sm(C_5Me_5)_2(tpy)$] (tpy= 2,2',6',2''-terpyridine).[49]

In the ^{13}C NMR spectra only the resonances corresponding to the coordination of (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-}, in asymmetric mode, are observed. The carbon chemical shits of the 2,2'-bipyridyl radicals in **5** and **6** are NMR silent at room temperature. Evans et al did not report the chemical shifts for the bipyridyl carbons of [$Sm(C_5Me_5)_2(bipy^{\cdot-})$][38] and Jonh et al also mentioned that the terpyridyl carbons in the ^{13}C spectrum of [$Sm(C_5Me_5)_2(tpy)$] were not observed.[49]

Consistent also to one single electron reduction of the 2,2'-bipyridine ligands by the bis(phenolate) cyclam Sm(II) complex, and consequently to the oxidation of the metal ions to Sm(III), the infrared spectra exhibit absorption bands in the 900-1000 cm^{-1} (**5**: 943 cm^{-1}; **6**: 955 cm^{-1}) and 1490-1600 cm^{-1} regions, which are characteristic of reduced bipyridil systems,[50] and differ from neutral bipyridine complexes, and are also observed for the radical bipyridine complexes [$Sm(C_5Me_5)_2(bipy^{\cdot-})$] and [$Sm(C_5Bn_5)_2(bipy^{\cdot-})$] (Bn= benzyl).[38,46] The colours of **5** and **6** in toluene solutions are intense and the UV-visible absorption spectra were collected (Figure S11 in Supporting Information). The UV-vis-NIR spectra clearly exhibit three distinct regions with strong absorption bands (λ_{max} (**5**): 906, 806, 528, 497 and 396 nm; λ_{max} (**6**): 874, 779, 545, 511 and 402 nm), which are characteristic of the presence of the bipyridil monoanion and of lanthanide complexes containing a radical bipyridine in the coordination sphere.[38,39] As the IR data, the electronic

spectra support the formation of the Sm(III) species containing radical-anion bipyridines [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(R$_2$-bipy$^{\cdot-}$)] (R = H (**5**), CH$_3$(**6**)).

Dark-red crystals of [Sm{(^{tBu2}ArO)$_2$Me-cyclam}(Me$_2$-bipy$^{\cdot-}$)] (**6**) were grown by concentrating a toluene/n-hexane solution. However, the complex is highly air- and moisture-sensitive and the crystals decomposed rapidly, giving rise to a X-ray diffraction structure of poor quality. Nevertheless, the crystallographic data allowed an unambiguous identification of the product as **6** (Figure 6), supporting all the conclusions drawn from NMR, UV-vis and IR spectroscopy.

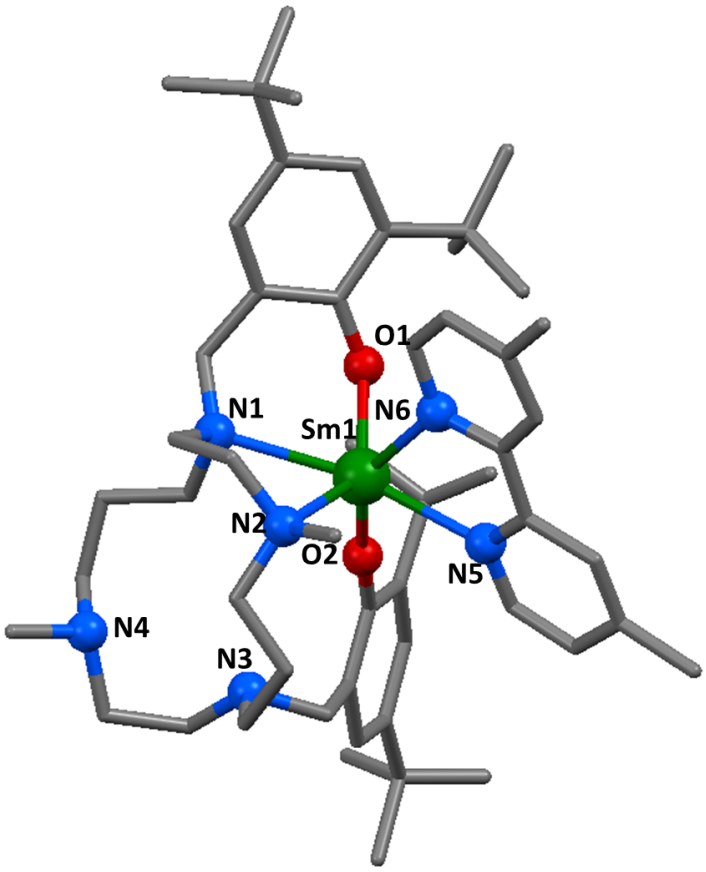


Figure 6. Diagram of the solid-state structure of [Sm(κ^4-{(^{tBu2}ArO)$_2$Me$_2$-cyclam}](Me$_2$-bipy•-)] (**6**). The hydrogens atoms have been removed for clarity.

Some structural parameters will be discussed here. The structure revealed a six-coordinate samarium center, with the $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ ligand binding in a κ^4 mode, through the two phenolate oxygens atoms and two nitrogen amines of the tetraazamacrocycle moiety, and two nitrogen atoms of the bipyridyl. The samarium-nitrogen distances for the 4,4'-Me_2-2,2'-bipy ligand of 2.48(3) and 2.50(3) Å are slightly longer than the ones found for the $[Sm(C_5Me_5)_2(bipy^{\cdot-})]$ (2.427(2) and 2.436(2) Å) and $[Sm(C_5Bn_5)_2(bipy^{\cdot-})]$ (Bn= benzyl; 2.437(2) Å and 2.439(2) Å), however they are shorter than the coordination bond distances Sm←:NR_3 of the macrocycle moiety of the bis(phenolate) cyclam ligand in **6** (2.62(2) and 2.71(3) Å) and shorter than those values found in the six coordinated complex $[SmI_2$(3,5-dimethylpyridine)$_4]$ for the neutral coordinated pyridines (Sm−N =2.708(10) Å).[51]

Comparison of the C-C bond connectivity distances between the two pyridine fragments in **6** (1.44(4) Å) and the free 4,4'-dimethyl-2,2'-bipyridine ligand (1.493(1) Å)[52] shows that the distance shortens in **6**, in accord with occupation of the π* LUMO and indicative that the reduction of the bipyridine ligand has occurred. The shortening of the Sm-O bond distances in **6** (2.15(2) and 2.20(2) Å) compared to those in the precursor **1** indicates the oxidation of the Sm(II) to the Sm(III).

Serendipitous oxygenation during recrystallization of **5** in toluene/*n*-hexane resulted in identification of colourless crystals from amongst the dark-orange crystalline solid of 5, whose X-ray diffraction analysis confirmed to be the oxo-bridged samarium structure **3**.

Following **5** and **6** solutions in toluene-d_8 (or benzene-d_6) by ^{1}H NMR analysis, during days, also evidenced the formation of the oxo-bridged complex $[(\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}Sm)_2(\mu\text{-O})]$ (**3**) as a side product, presumably also arising

from the unintentional exposure to very small amounts of O_2, showing that the bipyridil samarium complexes are very reactive.

Conclusions

Monomeric divalent samarium complex supported by the bulky bis(phenolate) cyclam chelate (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-} is readily accessible by simple metathesis reaction between Sm(II) diiodide and the dipotassium ligand salt. Although the Lewis base free complex [Sm{^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) is easy to isolate at room temperature in the solid state, spectroscopic studies in solution demonstrated that the six-coordinate complex features intermolecular interactions with thf molecules, consistent with the existence of additional labile coordination sites.

Due to strong reduction potential of the Sm(II), the cationic species [Sm(κ^6-{(^{tBu2}ArO)$_2$Me$_2$-cyclam)][BPh$_4$] was formed by one electron oxidation with TlBPh$_4$. ~~The~~ High reduction power of the divalent samarium complex has been demonstrated in the oxidation with the pyridine-N-oxide, OPPh$_3$ and SPPh$_3$, which afforded the E^{2-} containing species [Sm(κ^5-{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(μ-E)] (E = O, S), and in the reactions with two bipyridines that conducted to the formation of the radical species [Sm(κ^4-{(^{tBu2}Ar)$_2$Me$_2$-cyclam})(R$_2$-bipy$^{\cdot-}$)] (R = H, Me).

Furthermore, our studies revealed that the bulky ligand (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-} is adequate for stabilizing low-valence metals[18], and in addition the ligand hemilabile behavior allowed to access a diversity of Sm(III) coordination environments by electron transfer reactions.

Experimental

General Considerations. All reactions were performed under an inert atmosphere of nitrogen with the rigorous exclusion of oxygen and water (< 2 ppm) using standard Schlenk techniques or a nitrogen-filled glovebox.

Tetrahydrofuran, toluene and *n*-hexane were pre-dried using 4Å molecular sieves, distilled from Na alloy under nitrogen, and deoxygenated, immediately prior use. Tetrahydrofuran-d_8, benzene-d_6 and toluene-d_8 were dried over sodium-benzophenone. Acetonitrile and acetonitrile-d_3 were distilled from P_2O_5 under nitrogen and maintained in contact with molecular sieves several days before use.

$[SmI_2(thf)_2]$ (dark blue) was prepared by reaction of small pieces of metal with 1,2-diiodoethane in thf.[53] $H_2(^{tBu2}ArO)_2Me_2$-cyclam was prepared as previously reported and $K_2(^{tBu2}ArO)_2Me_2$-cyclam was prepared *in situ* upon reaction of $H_2(^{tBu2}ArO)_2Me_2$-cyclam with excess of KH in thf.[17] $TlBPh_4$ was precipitated as a white solid by mixing aqueous solutions of $NaBPh_4$ and $TlNO_3$.The compound was then washed with hot water followed by *n*-hexane and dried under vacuum for 48 h. All other reagents were purchased from commercial suppliers and dried in vacuum during 24 h. ^1H and ^{13}C NMR spectra were recorded in Varian 300 MHz or Bruker AVANCE II 300, 400 or 500 MHz instruments. ^1H and ^{13}C chemical shifts were referenced to external $SiMe_4$ using the residual proton or carbon of the solvents as an internal standards. IR spectra were recorded as Nujol mulls between CsI round cell windows on a Bruker Tensor 27 spectrophotometer. CHN elemental analyses were performed using a CE Instruments EA1110 automatic analyser. Electrospray ionization mass spectrometry (ESI/MS) was performed using a quadrupole ion trap (Bruker HCT); the samples were prepared under N_2 with dry solvents and an air-tight syringe was filled inside an inert atmosphere glove-box and carried in a closed vessel

under N_2 before injection. UV-vis-NIR spectra were recorded in the range 300–1100 nm at room temperature on a Shimadzu UV 1800 Spectrometer in 10 mm quartz cuvettes; the solvent background was corrected.

Synthesis of [Sm{($^{t\text{Bu2}}$ArO)$_2$Me$_2$-cyclam}] (1). Excess of potassium hydride (105 mg, 2.62 mmol) was added to a solution of H$_2$($^{t\text{Bu2}}$ArO)$_2$Me$_2$-cyclam (500 mg, 0.751 mmol) in thf (20 mL). After stirring for 16 h at room temperature, the resulting colourless solution was separated by centrifugation and added to a solution of [SmI$_2$(thf)$_2$] (412 mg, 0.751 mmol) in thf (15 mL). The solution turned green and KI precipitated. After stirring over 16 h at room temperature, the reaction mixture was centrifuged, the supernatant was decanted off, and the solvent was removed under reduced pressure. Toluene (20 mL) was added to extract the compound and the solution was layered with *n*-hexane (20 mL). The resulting microcrystalline brown-chocolate solid was separated by centrifugation, washed with *n*-hexane and dried under vacuum. Compound **1** was isolated in 74% yield (449 mg, 0.552 mmol). Brown crystals suitable for XRDA were grown from a dilute solution of **1** in thf/n-hexane. ^{1}H NMR (300 MHz, toluene-d_8, 23 °C): δ(ppm) -0.34 (s, C(CH_3)$_3$), -3.77 (br), -6.02 (s, C(CH_3)$_3$), -10.65, -14.47, -27.04, -29.91 (br). Not all of the ligand ($^{t\text{Bu2}}$ArO)$_2$Me$_2$-cyclam^{2-} resonances were observed a 23ºC. ^{1}H NMR (300 MHz, toluene-d_8, -40 °C): δ (ppm) 187.98 (6H, NCH_3), 63.43 (2H), 54.03 (2H) 14.59 (2H), -1.06 (2H), -1.62 (18H, C(CH_3)$_3$), -4.58 (2H), -9.23 (2H), -10.93 (4H), -14.03 (18H, C(CH_3)$_3$), -16.91 (4H), -21.86 (2H), -46.90 (2H), -63.00 (2H), -70.76 (2H). ^{1}H NMR (thf-d_8, 300 MHz, 25 °C): 1.22, -1.19 (br), -1.40 (C(CH_3)$_3$), -2.96 (br), -15.77 (br). ^{1}H NMR (300 MHz, thf-d_8, -40 °C) δ (ppm) 112.63 (3H, NCH_3), 86.57 (3H, NCH_3), 55.34 (1H), 47.68 (1H), 32.89 (1H), 30.86 (1H), 27.38 (1H), 17.41 (1H), 9.59 (1H),

6.02 (1H), 1.34 (C(CH_3)$_3$), 0.60 (1H), 034 (1H), -0.005 (1H), -0.78 (C(CH_3)$_3$), -1.49 (C(CH_3)$_3$), -1.82 (1H), -2.36 (C(CH_3)$_3$), -4.79 (1H), -6.15 (2H), -7.23 (1H), -11.41 (2H), -13.45 (1H), -21.58 (1H), -22.12 (1H), -22.87 (1H), -2518 (1H), -25.78 (1H), -26.18 (1H), -27.39 (1H), -52.06 (1H), -7282 (1H). Anal. Calcd for $C_{42}H_{70}N_4O_2Sm$: C 62.02; H 8.67; N 6.89. Found C 61.88; H 8.71; N 6.86.

Synthesis of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (2). TlBPh$_4$ (97 mg, 0.185 mmol) was added to a green solution of **1** (150 mg, 0.184 mmol) in thf (20mL). The reaction mixture was stirred during 20 h at room temperature and the solution turned pale yellow and a grey solid precipitated (metallic thallium). The mixture was centrifuged, concentrated and then *n*-hexane was added. After 3 days, a slightly yellowish white microcrystalline solid of **2** precipitated and was isolated from the mother liquor by decantation, washed with *n*-hexane and dried under vacuum. Yield: 58% (122 mg, 0.108 mmol). ^{1}H NMR (300 MHz, acetonitrile-d_3, 25 °C): δ (ppm) 9.05 (2H, Ar-*H*), 7.96 (2H, Ar-*H*), 7.26 (8H, br, *m*-Ph-BPh$_4$), 6.98 (8H, t, *o*-Ph-BPh$_4$), 6.83 (4H, t, *p*-Ph-BPh$_4$), 5.74 (br), 4.36 (br), 1.92 (18H, s, C(CH_3)$_3$), 1,33 (18H, s, C(CH_3)$_3$), 0,65 (br), -0,42 (br), -1,71 (br), -3,16 (br). ^{1}H RMN (300 MHz, thf-d_8, 25 °C) δ (ppm) 8.98 (2H, Ar-*H*), 7.71 (2H, Ar-*H*), 7.23 (8H, largo, *m*-Ph-BPh$_4$), 6.83 (8H, t, *o*-Ph-BPh$_4$), 6.70 (4H, t, *p*-Ph-BPh$_4$), 1.84 (18H, s, C(CH_3)$_3$), 1.12 (18H, s, C(CH_3)$_3$), -0.88 (br), -1.50 (br), -5.41 (br). ^{1}H NMR (300 MHz, thf-d_8, -30 °C) δ (ppm) 12.08 (1H, br, ArCH_2N), 9.08 (1H, s, Ar-*H*), 9.04 (1H, s, Ar-*H*), 9.00 (br, 1H, ArCH_2N) 7.77 (1H, s, Ar-*H*), 7.64 (1H, s, Ar-*H*), 7.51-7.28 (2H, br, ArCH_2N+CH_2), 7.20 (8H, br, *m*-Ph-BPh$_4$), 6.84 (8H, t, 7.3 Hz, *o*-Ph-BPh$_4$), 6.72 (4H, t, 7.1 Hz, *p*-Ph-BPh$_4$), 5.94 (1H, br, ArCH_2N), 5.21 (1H, CH_2), 4.75 (1H, CH_2), 4.33 (1H, CH_2), 3.63 (1H, br, CH_2), 3.50 (1H, br, CH_2), 3.14 (1H, br, CH_2), 2.90-1.90

(6H, br, CH_2), 1.87 (9H, s, C(CH_3)$_3$), 1.82 (9H, s, C(CH_3)$_3$), 1.15 (1H, br, CH_2), 1.01 (18H, s, C(CH_3)$_3$), -0.55-(-0.98) (4H, br, CH_2), -1.11 (1H, d, CH_2), -2.53 (1H, CH_2), -4.48 (3H, s, NCH_3), -6.85 (3H, s, NCH_3). Anal. Calcd for $C_{66}H_{90}BN_4O_2Sm$: C 69.99; H 8.01; N 4.95. Found: C 69.59; H 8.34; N 4.77. ESI-MS (*m/z):* 814.2 $[SmL]^+$ (calc. 814.47); 319.2 $[BPh_4]^-$ (calc. 319.17).

Synthesis of [(Sm{($^{t\mathrm{Bu}2}$ArO)$_2$Me$_2$-cyclam})$_2$(μ-O)] (3). A solution of pyridine oxide (12 mg, 0.123 mmol) in toluene (1 mL) was added to a brown solution of **1** (200 mg, 0.246 mmol) in toluene (15 mL). After stirring during 18 h at room temperature, the solution turned brown-yellow. The solvent was removed under vacuum and then the solid residue was dissolved in thf/diethyl ether (5 mL; 1:1). After slow evaporation of the solvent, a slightly yellow microcrystalline solid precipitated and **3** was isolated by decantation and dried in vacuum. Yield: 40% (80 mg, 0.049 mmol). Suitable crystals for X-ray diffraction analysis were obtained in the same way. ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ (ppm) 24.56 (1H, NCH_2Ar), 15.28 (1H, NCH_2Ar), 12.23 (1H, CH_2), 9.90 (1H, Ar-*H*), 8.72 (3H, Ar-*H*+2CH_2), 8.21 (2H, Ar-*H*+NCH_2Ar), 7.74 (1H, Ar-*H*), 4.53 (1H, CH_2), 3.77 (1H, NCH_2Ar), 3.09 (1H, CH_2), 2.12 (9H+1H, C(CH_3)$_3$+CH_2), 2.02 (9H, C(CH_3)$_3$), 1.80 (2H, CH_2), 0.10 (1H, CH_2), -0.13 (7H, s, NCH_3 + CH_2), -0.47 (9H, s, C(CH_3)$_3$), -0.53 (9H, s, C(CH_3)$_3$), -1.24 (1H, CH_2), -1.59 (1H, CH_2), -1.87 (1H, CH_2), -2.87 (1H,CH_2), -4.55 (1H, CH_2), -6.50 (1H, CH_2), -7.49 (1H, CH_2), -8.97 (1H, CH_2), -9.75 (1H, CH_2), -13.29 (1H, CH_2). ^{13}C RMN (100 MHz, benzene-d_6, 25 °C): δ (ppm) 172.01 (Ar*C*-O), 171.85 (Ar*C*-O), 136.93 (Ar*C*), 136.73 (Ar*C*), 134.06 (Ar*C*), 132.99 (Ar*C*), 132.77 (Ar*C*), 132.48 (Ar*C*), 131.39 (Ar*C*-H), 130.28 (Ar*C*-H), 124.99 (Ar*C*-H), 124.65 (Ar*C*-H), 82.67 (Ar*C*H$_2$N), 77.18 (Ar*C*H$_2$N), 62.55 (*C*H$_2$),

59.46 (*C*H_2), 58.23 (*C*H_2), 56.32 (*C*H_2), 52.84 (*C*H_2), 46.48 (2C, *C*H_2), 45.20 (*C*H_2) 41.66 (2C, N*C*H_3), 35.33 (*C*$(CH_3)_3$), 35.13 (*C*$(CH_3)_3$), 34.93 (*C*$(CH_3)_3$), 34.82 (*C*$(CH_3)_3$), 33.01 (C(*C*$H_3)_3$), 32.92 (C(*C*$H_3)_3$), 29.30 (C(*C*$H_3)_3$), 28.75 (C(*C*$H_3)_3$), 22.88 (*C*H_2), 18.35 (*C*H_2). Anal. Calcd for $C_{84}H_{140}N_8O_5Sm_2$: C 61.41; H 8.59; N 6.82. Found: C 60.72; H 8.54; N 6.74.

Synthesis of [Sm{(^{t}Bu2ArO)$_2$Me$_2$-cyclam}]$_2$(μ-S) (4). A solution of $SPPh_3$ (36 mg, 0.122 mmol) in toluene (1 mL) was added to a brown solution of **1** (200 mg, 0.246 mmol) in toluene (15 mL). After stirring during 18 h at room temperature, the solution turned slightly yellow and the solvent was removed under vacuum. The solid residue was extracted with n-hexane and concentrated. Very few X-ray suitable crystals were obtained by slow concentration of an *n*-hexane solution of the mixture. The pure compound was not isolated preventing further characterization. We were not able to find a recrystallization solvent to overcome this problem.

Synthesis of [Sm{(^{t}Bu2ArO)$_2$Me$_2$-cyclam}(bipy)] (5). A toluene solution (2 mL) of 2,2'-bipyridine (39 mg, 0.250 mmol) was added to a brown solution of **1** (203 mg, 0.250 mmol) in toluene (15 mL) at room temperature. The solution turned orange-brown immediately. After 2 h of stirring at room temperature, the orange-brown solution was taken to dryness under vacuum and the solid was washed with *n*-hexane and dried under vacuum. Yield: 73% (177 mg, 0.183 mmol). ^{1}H NMR (500 MHz, toluene-d_8, 25 °C): 12.54 (1H, ArC*H*$_2$N), 11.48 (2H, bipy), 9.59 (1H, ArC-*H*), 8.23 (1H, C*H*$_2$), 8.12 (1H, ArC-*H*), 7.72 (1H, ArC-*H*), 7.54 (1H, ArC-*H*), 4.62 (1H, C*H*$_2$), 4.46 (1H, C*H*$_2$), 4.22 (1H, C*H*$_2$), 3.85 (1H, C*H*$_2$), 3.32 (1H, C*H*$_2$), 2.53 (2H, C*H*$_2$), 2.00-1.10 (8H), 1.74 (9H, C(*CH*$_3)_3$), 1.64 (9H, C(*CH*$_3)_3$), 1.10-0.80 (2H, CH$_2$),

0.98 (6H, NCH_3), -0.21 (9H, C(CH_3)$_3$), -0.66 (9H, C(CH_3)$_3$), -1.00 (1H, CH_2), -4.16 (1H, CH_2), -5.68 (1H, CH_2), -6.56 (1H, CH_2), -6.69 (1H, CH_2), -16.83 (1H, bipy), -20.79 (1H, bipy), -164.6 (1H, bipy), -170.1 (1H, bipy), -233.8 (1H, bipy), -239.8 (1H, bipy). ^{13}C {1H} NMR (125 MHz, toluene-d_8, 25 °C): δ (ppm) 166.66 (Ar*C*-O), 157.58, (Ar*C*-O), 138.53 (Ar*C*), 137.27 (ArC), 136.83 (ArC), 135.58 (ArC), 132.97 (ArC), 130.13 (Ar*C*-H), 127.90 (Ar*C*-H), 124.64 (Ar*C*-H), 12.30 (Ar*C*-H), 75.60 (*C*H$_2$), 72.29 (*C*H$_2$), 69.51 (*C*H$_2$), 61.95 (*C*H$_2$), 54.27 (*C*H$_2$), 53.64 (*C*H$_2$), 51.17 (3C, *C*H$_2$), 43.50 (*C*H$_2$), 42.67 (N*C*H$_3$), 35.58 (C(*C*H$_3$)$_3$), 34.51 (*C*(CH$_3$)$_3$), 34.31 (*C*(CH$_3$)$_3$), 34.15 (*C*(CH$_3$)$_3$), 33.92 (C(*C*H$_3$)$_3$), 33.33 (C(*C*H$_3$)$_3$), 31.91 (C(*C*H$_3$)$_3$), 22.85 (*C*H$_2$), 17.91 (*C*H$_2$). IR (CsI, nujol, ν cm^{-1}): 1600 (m), 1493 (w), 1414 (m), 1377 (s), 1360 (s), 1292 (s), 1239 (m), 943 (m), 877 (m), 746 (w), 724 (M), 641 (w), 524 (w). ESI-MS (*m/z*): 815.0 [SmL]$^+$ (calc. 814.47); 971.1 [SmLbipy]$^+$ (calc. 970.54). Anal. Calcd for $C_{52}H_{78}N_6O_2Sm$: C 64.42; H 8.11; N 8.67. Found: C 64.38; H 8.36; N 8.55.

Synthesis of [Sm{(^{t}Bu2ArO)$_2$Me$_2$-cyclam}(Me$_2$-bipy)] (6). A toluene solution (2 mL) of 4,4'-dimethyl-2,2'-bipyridine (45 mg, 0.244 mmol) was added to a brown solution of **1** (198 mg, 0.244 mmol) in toluene (15 mL) at room temperature. Immediately the solution turned red-brown. After 2 h of stirring at room temperature, the solvent was removed under vacuum and the residue solid was washed with n-hexane. The remaining solid was dissolved in 5 mL of toluene/-hexane, concentrated to yield a red-brown microcrystalline solid. The precipitate was decanted, washed with n-hexane and dried under vacuum. Yield: 69% (169 mg, 0.0169 mmol). Red-black crystals were obtained by slow evaporation of a toluene/*n*-hexane solution of **6**.

^{1}H NMR (500 MHz, toluene-d_8, 25 °C): δ (ppm) 160.6 (3H, CH_3-bipy), 159.6 (3H, CH_3-bipy), 24.13 (1H, bipy), 18.82 (1H, bipy), 12.73 (1H, CH_2), 9.49 (1H, ArC-*H*), 8.35 (1H, CH_2), 8.15 (1H, ArC-*H*), 7.74 (1H, ArC-*H*), 7.56 (1H, ArC-*H*), 4.65 (1H, CH_2), 4.32 (1H, CH_2), 3.87 (1H, CH_2), 3.38 (1H, CH_2), 2.56 (1H, CH_2), 2.15-1.10 (9H, CH_2), 1.77 (9H, C(CH_3)$_3$), 1.66 (9H, C(CH_3)$_3$), 0.98 (6H, NCH_3), -0.22 (9H, C(CH_3)$_3$), -0.69 (9H, C(CH_3)$_3$), -0.90 (1H, CH_2), -4.11 (1H, CH_2), -5.68 (1H, CH_2), -6.71 (1H, CH_2), -42.82 (1H, bipy), -44.64 (1H, bipy), -235.9 (1H, bipy), -242.0 (1H, bipy). ^{13}C {1H} NMR (125 MHz, toluene-d_8, 25 °C): 168.41 (Ar*C*-O), 158.55 (Ar*C*-O), 138.65 (Ar*C*), 137.44 (Ar*C*), 137.07 (Ar*C*),, 135.73 (Ar*C*), 133.21 (Ar*C*), 130.02 (Ar*C*-H), 128.99 (Ar*C*-H), 124.81 (Ar*C*-H), 123.28 (Ar*C*-H), 75.99 (*C*H$_2$), 70.17 (*C*H$_2$), 69.67 (*C*H$_2$), 59.93 (*C*H$_2$), 54.45 (*C*H$_2$), 53.77 (*C*H$_2$), 51.37 (3C, CH$_2$), 43.61 (*C*H$_2$), 42.81 (N*C*H$_3$), 35.59 (C(*C*H$_3$)$_3$), 34.72 (*C*(CH$_3$)$_3$), 34.64 (*C*(CH$_3$)$_3$), 34.52 (C(*C*H$_3$)$_3$), 34.38 (*C*(CH$_3$)$_3$), 33.57 (C(*C*H$_3$)$_3$), 32.02 (C(*C*H$_3$)$_3$), 23.08 (*C*H$_2$), 17.09 (*C*H$_2$). Anal. Calcd for $C_{54}H_{82}N_6O_2Sm$: C 65.01; H 8.28; N 8.42. Found: C 65.18; H 8.53; N 8.58. ESI-MS (*m/z)*: 814.2 [SmL]$^+$ (calc. 814.47); 998.7 [SmLMe$_2$bipy]$^+$ (calc. 998.57). IR (CsI, nujol, ν cm^{-1}): 1598 (m), 1566 (m), 1377 (s), 1297 (s), 1262 (s), 1211 (s), 954 (s), 877 (s), 744 (m), 527 (m).

X-Ray diffraction analysis

Crystallographic and experimental details of data collection and crystal structure determinations for the compounds are given in Table S2 (Supporting Information). Suitable crystals of compounds **1-4** and **6** were selected and coated in FOMBLIN oil under an inert atmosphere. Crystals were then mounted on a loop and the data were collected using graphite-monochromated Mo Kα (α=0.71073 Å) on a Bruker AXS-KAPPA APEX II area detector at 150 K. Cell parameters were retrieved using

Bruker SMART and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.[54] The structures were solved by direct methods using either SHELXS-97[55]or SIR 97[56] and refined using full-matrix least squares refinement against F^2 using SHELXL-97[55]. In the former case, all programs are included in the package of programs WINGX-version 1.64.05.[57] All non-hydrogen atoms were refined anisotropically, unless it was mentioned in the cif files of the structures, and all hydrogen atoms were placed in idealized positions and allowed to refine riding on the parent carbon atom. In complexes **1**-**4** some carbons of the ligand are disordered and a constraint model was used (see cif files in Supporting Information). CIF files were deposited at the Cambridge Crystallographic Data Centre under the reference CCDC numbers: 1438772 (1), 1438773 (2), 1438774 (3), 1438775 (4) and 1438776 (6).

Acknowledgements

We thank Adelaide Cruz for experimental assistance. The work was supported by Fundação para a Ciência e a Tecnologia (FCT) under the Ciência 2008 Programme, RNEM-Portuguese Mass Spectrometry Network and through the projects PTDC/QUI-QUI/109846/2009, RECI/QEQ-QIN/0189/2012 and UID/Multi/04349/2013. K. V. L. thanks the Russian Foundation for Basic Research for support of his work through the grant 15-33-20536.

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