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# Synthesis and structural characterization of polynuclear divalent ytterbium complexes supported by a bis(phenolate) cyclam ligand



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#### ABSTRACT

A new  $[O_2N_2N'_2]$  1,4,8,11-tetraazacyclotetradecane-based bis(phenol) chelate,  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (**2**), containing methyl groups in the phenolate rings, has been synthesized and fully characterized. The studies of the coordination chemistry of the hexadentate dianionic ligands,  $(^{R2}ArO)_2Me_2$ -cyclam<sup>2–</sup> (R = <sup>t</sup>Bu, Me), with [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] are reported. The reaction of  $K_2(^{tBu2}ArO)_2Me_2$ -cyclam with [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] in 1:1 ratio in thf led to the formation of a divalent ytterbium complex that is highly unstable and propitious to the formation of Yb(III) species, while the metathesis reaction of the less bulky ligand ( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2–</sup> with [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] showed a preference for the stabilization of polynuclear divalent ytterbium complexes. The reaction of the potassium salt of this ligand,  $K_2(^{Me2}ArO)Me_2$ -cyclam, with 1.5 and 2 equiv. of [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] in thf led to formation of [Yb<sub>3</sub>( $\mu$ -{( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam})]<sub>2</sub>[I (**4**) and [Yb<sub>2</sub>( $\mu$ -{( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam}])<sub>2</sub>[thf)<sub>2</sub>] (**5**), respectively. The trimer (**4**) and dimer (**5**) were characterized by elemental analysis, UV-Vis and NMR spectroscopy and single-crystal X-ray diffraction. These are the first examples of ytterbium(II) complexes incorporating bis(phenolate) cyclam ligands.

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#### 1. Introduction

Lanthanide ions are characterized by being stabilized by bulky or high-coordination number ligands. Nevertheless, the control of lanthanide complexes properties and geometries can be achieved by meticulous ligand design and selection [1,2]. Amine bis(phenolate) ligands are dianionic chelates that have received considerable attention in lanthanide(III) chemistry over the last decade, and some of these complexes have displayed remarkable catalytic activities on the ring-opening polymerization of cyclic esters [3]. Despite their conceptually similar synthesis to the trivalent lanthanide complexes, the access to divalent lanthanide amine bis(phenolate) compounds is still scarce [4-8]. Though the +2 oxidation state is known for all of the lanthanides except radioactive Pm [9], the molecular chemistry with the amine bis (phenolate) ligands has been restricted to the classical three Ln<sup>2+</sup> ions, the ones with the less negative Ln<sup>3+</sup>/Ln<sup>2+</sup> reduction potential (Sm<sup>2+</sup>: -1.55 V, Eu<sup>2+</sup>: -0.35 V, Yb<sup>2+</sup>: -1.15 V). These Ln(II) complexes were explored as starting materials to access trivalent Ln complexes using mild oxidizing agents, some of them demonstrating attractive catalytic activity and the ability of activating organic molecules [4,7,10].

A number of trends have been observed, which indicate that steric encumbrance of the phenolate ligand along with metal selection play an important role in influencing the stability in solid-state and solution of the lanthanide(II) amine bis(phenolate) complexes. It was also reported that modification of the shape, of the steric bulkiness of the amine bis(phenolate) ligands, as well as the reactional conditions, could crucially affect the structures of the corresponding Ln(II) complexes [4,7a,10].

In our previous work, we demonstrated that the dianionic bulky tetraazamacrocyclic-based bis(phenolate) ligand ( $^{tBu2}ArO$ )<sub>2</sub>-Me<sub>2</sub>-cyclam<sup>2-</sup> provides steric protection against the formation of polynuclear species, allowing to stabilize and structurally characterize the hexa-coordinate solvent-free samarium complex [Sm {( $^{tBu2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam}] [10], which was the first example of a lanthanide(II) complex bearing a bis(phenolate) tetraazamacrocycle derivative. Moreover, this [O<sub>2</sub>N<sub>2</sub>N<sub>2</sub>'] donor displays the advantage of hemilabile behavior of the tetraazamacrocycle core, allowing to access a diversity of Sm(III) coordination environments by electron transfer reactions [10].

Additionally, the flexibility of the macrocycle core of the ligand ( $^{\text{(Bu2}}\text{ArO})_2\text{Me}_2\text{-cyclam}^{2-}$  allowed to the formation of monomeric trivalent rare earth complexes [Ln{( $^{\text{(Bu2}}\text{ArO})_2\text{Me}_2\text{-cyclam}$ Cl], in which the ligand bonding mode varied from hexadentate to pentadentate depending on the size of the rare earth metal ion [11]. The ligand coordinates to the smaller Yb(III) in a  $\kappa^5\text{-O}_2\text{N}_2\text{N}'$ 



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mode and with the larger Sm(III) ion in a  $\kappa^6\text{-}O_2N_2N_2'$  bonding mode.

These results have inspired us to extend the coordination chemistry of the dianionic macrocycle derivative ligands to ytterbium (II). The Yb(II) ion, with its large ionic radius (1.02 Å, coordination number 6) [12], should allow coordination of the sterically bulky ligand ( $^{tBu2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup>. Herein, we report our attempts on the synthesis and isolation of monomeric bis(phenolate) cyclam Yb(II) complexes with the dianionic ligands ( $^{R2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup> (R =  $^{tBu}$ , Me). We also demonstrate that the new and less bulky ligand ( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup> is adequate for the formation of polynuclear Yb(II) complexes, and the synthesis and molecular structures of the trimeric and dimeric divalent ytterbium complexes of formula [Yb<sub>3</sub>( $\mu$ -{( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam})<sub>2</sub>I] and [Yb<sub>2</sub>( $\mu$ -{( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam})<sub>2</sub>I] and [Yb<sub>2</sub>( $\mu$ -{( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam})<sub>1</sub>Z(thf)<sub>2</sub>], respectively, are described.

#### 2. Results and discussion

#### 2.1. Ligand synthesis

The *tert*-butyl *trans*-disubstituted tetraazamacrocycle  $(H_2(^{tBu2}ArO)_2Me_2$ -cyclam)  $(H_2L^1)$  (**1**) was prepared according to the previously reported method [11]. To prepare the methylated derivative a similar synthetic protocol was employed. The 1,8-bis (2-hydroxy-3,5-dimethylbenzyl)-4,11-dimethyl-1,4,8,11-tetraaza-cyclotetradecane  $(H_2(^{Me2}ArO)_2Me_2$ -cyclam) (**2**) was prepared with a 78% yield, by N-alkylation of 1,8-dimethylcyclam with 2-hydroxy-3,5-dimethylbenzyl using aqueous formaldehyde and 2,4-dimethylphenol in refluxing methanol, in a typical Mannich reaction (Scheme 1). This simple synthetic approach allows to incorporate different R groups in the phenol rings and to form ligands with different steric and electronic profiles.

The identity of  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (2) was confirmed by elemental analysis, ESI-MS and by NMR spectroscopy. Compound 2 is soluble in tetrahydrofuran and chlorinated solvents, presents low solubility in aromatic solvents and is insoluble in n-hexane.

The <sup>1</sup>H NMR spectrum of **2** in benzene- $d_6$  at room temperature (see Fig. S1 in ESI) revealed the resonances corresponding to the aromatic (6.92 and 6.75 ppm), hydroxyl (10.03 ppm) and methyl substituents (2.25 and 1.91 ppm) protons of the phenolate groups, along with a signal at 2.44 ppm for the NCH<sub>3</sub> protons and very broad resonances for the benzylic and methylene macrocycle protons. However, when a chloroform- $d_1$  solution of **2** was cooled until -40 °C, all resonances of the bis(phenol) cyclam derivative became well resolved (see Fig. S2 in ESI). Ten diastereotopic macrocyclic protons and two diastereotopic benzyl protons have been assigned with the help of a <sup>1</sup>H-<sup>13</sup>C HSQC experiment at -40 °C (see Fig. S5 in ESI). Moreover, the observation of one set of resonances for the <sup>Me2</sup>ArOH groups and one for the NCH<sub>3</sub> shows that

the *trans*-substituents are magnetically equivalent, as expected for **2**. As observed in the <sup>1</sup>H NMR spectrum of **1** [11], the OH proton resonance of **2** appears shifted to high frequencies, suggesting that the <sup>Me2</sup>ArOH groups also establish hydrogen bonds with the nitrogen atoms of the cyclam ring. The carbon NMR data (see Figs. S3 and S4 in ESI) corroborate the <sup>1</sup>H NMR conclusions and, as whole, the NMR results are compatible either with the presence of a molecule with  $C_2$  symmetry or with a  $C_i$  species, with an inversion center in the middle of the cyclam ring, in agreement with the solidstate molecular structure (see Fig. 1).

The structure of **2**, determined by X-ray diffraction analysis of single crystals grown from a tetrahydrofuran solution, shows that it crystallizes in the monoclinic C2/c space group with one-half of the molecule in the asymmetric unit cell. The molecular structure and selected parameters are shown in Fig. 1.

The structure of **2** is similar to the one observed for the *tert*butyl compound  $H_2(^{tBu2}ArO)_2Me_2$ -cyclam (**1**). The two phenolate arms are pointing in the opposite direction with respect to the mean plane containing the 14-membered ring and the cyclam unit adopts a rectangular (4,3,4,3) conformation with C2, C5 and symmetry related carbon atoms at the corners of the rectangle [13]. Each phenolate arm is folded toward the cyclam unit with the torsional angle N1–C7–C8–C13 of 62.2(2)°, allowing the nitrogen atoms lone pairs to interact with the phenolic protons via weak hydrogen bonds (N1...O1 3.035(2) Å, N1...H1 2.412 Å, N2...O1 2.828(2) Å, N2...H1A 2.070 Å), also suggested by the <sup>1</sup>H NMR analysis.

#### 2.2. Synthesis of the divalent ytterbium complexes

Direct metathesis reactions of a lanthanide diiodide and the potassium salt of a ligand is a particularly facile synthetic route for the synthesis of divalent lanthanide complexes. Thus, we added a fresh thf solution of  $K_2(^{tBu2}ArO)_2Me_2$ -cyclam, prepared in situ by reaction of **1** with KH, to a thf solution of [YbI<sub>2</sub>(thf)<sub>2.5</sub>], in a 1:1 M ratio and at room temperature. The color of the solution changed immediately from yellow to a strong orange, indicating that reaction took place. After workup, the orange solid was analyzed by NMR spectroscopy, in thf- $d_8$ , and, according to the data obtained, the compound was found to be diamagnetic, indicating that the vtterbium ion is in the +2 oxidation state. Moreover, the <sup>1</sup>H and <sup>13</sup>C NMR at room temperature revealed only one chemical environment for the phenolate groups consistent with a  $C_2$  symmetric compound in solution (see Fig. S7 in ESI), that could be attributed to a monomeric ytterbium(II) complex analogous to the recently reported samarium complex [Sm{(<sup>tBu2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam}] [10]. However, elemental analyses failed to give reproducible data and deduction about the metal-ligand stoichiometry proved to be difficult.



Scheme 1. Synthesis of the H<sub>2</sub>(<sup>R2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam pro-ligands via Mannich condensations.



**Fig. 1.** (a) Molecular structure of  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (**2**). Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N1–C7 1.466(2), N1–C1 1.461(2), N1–C5 1.463(2), N2–C6 1.462(2), N2–C2 1.459(2), N2–C3 1.463(2), C13–O1 1.366(2), C1–N1–C5 111.60(13), C3–N2–C2 110.83(13), C7–N1–C1 111.99(13), C7–N1–C5 110.37(13), C6–N2–C3 111.46(14), C6–N2–C2 109.60 (13). (b) Conformation of the cyclam ring in **2** (hydrogens are omitted for clarity).

A thf- $d_8$  solution of the compound was monitored by <sup>1</sup>H NMR during one day and showed that the ytterbium compound **3** is propitious to oxidation, as proton resonances appeared shifted from the diamagnetic zone and consistent with the formation of paramagnetic trivalent ytterbium species. The initially orange solution became more yellow, also indicative of oxidation to Yb(III). The

orange ytterbium compound **3** has high solubility in thf, is sparingly soluble in toluene and insoluble in n-hexane. Several attempts to grow crystals from a variety of solvent systems were unsuccessful and most of the time conducted to decomposition products and oils.

The Yb<sup>3+</sup>/Yb<sup>2+</sup> redox potential (-1.15 vs. NHE) is less negative than the one of Sm<sup>3+</sup>/Sm<sup>2+</sup> (-1.55 vs. NHE), and a higher stability for the ytterbium compounds could be expected. However, in the absence of any X-ray crystallographic analysis, it is difficult to know the exact structure of the ytterbium(II) complex **3** and understand its poor stability.

In order to isolate a less soluble and perchance more crystalline ytterbium complex, we performed the reaction of [YbI<sub>2</sub>(thf)<sub>2.5</sub>] with the potassium salt of the methyl substituted bis(phenol) cyclam, H<sub>2</sub>(<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam, in a 1:1 M ratio in tetrahydrofuran and at room temperature. After workup, the elemental analysis was not consistent with the formulation of the expected complex [Yb{(Me2ArO)Me2-cyclam}] and the <sup>1</sup>H NMR spectrum of the crude product in thf- $d_8$  indicated the presence of a new diamagnetic species and of K<sub>2</sub>(<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam. Orange crystals were isolated upon crystallization from a tetrahydrofuran solution of the mixture and the trinuclear cationic structure  $[Yb_2(\mu-{(M^{e2}ArO)_2Me_2-}$ cyclam})<sub>2</sub>Ybl]I (4) was determined by X-ray diffraction analysis (see below). The reaction of [YbI<sub>2</sub>(thf)<sub>2.5</sub>] with excess of  $K_2(^{Me2}ArO)_2Me_2$ -cyclam was also attempted in thf, nevertheless the reaction conducted again to the formation of the Yb(II) trimeric compound 4.

The rational synthesis of the solvent-free trimer **4** could be performed by the reaction of  $[YbI_2(THF)_{2.5}]$  with  $K_2(^{Me2}ArO)_2Me_2$ -cyclam in a 1.5:1 M ratio in thf, with 43% yield after workup (Scheme 2).

The apparent preference of the (<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2–</sup> ligand for the formation of polynuclear complexes of the type 1.5:1 (M: L), a behavior never found before in the coordination chemistry of polyamine bis(phenolate) ligands with lanthanides, led us to increase the amount of metal relative to the ligand. Thus, the potassium salt of the ligand (**2-K**) was also treated with 2 equiv. of [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] in thf, and the reaction conducted to the formation of the dinuclear ytterbium(II) complex **5** with two residual iodide ligands (Scheme 2). The structure of complex **5** was investigated by solution NMR spectroscopy and the solid-state molecular structure was unambiguously established by single-crystal analysis of orange needles, obtained from a concentrated tetrahydrofuran solution.

Both Yb(II) complexes, **4** and **5**, are extremely air-sensitive orange solids and are soluble in thf and insoluble in hydrocarbon solvents. The solubility of **4** is lower than that of compound **5**, a difference that may be correlated to their structures, since **4** is a cationic species and **5** presents thf molecules coordinated to one of the metal centers. The elemental analyses were in good agreement with the formulation of both complexes.

#### 2.3. Solution NMR spectroscopy of the Yb(II) complexes

The room-temperature <sup>1</sup>H NMR spectrum of **4** in thf- $d_8$  is structurally uninformative, as we observed only one set of resonances for the methyl and aromatic phenolate protons and a few broad resonances for the macrocycle core of the ligand (<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup> in the diamagnetic region. When the temperature of the NMR sample was decreased until  $-60 \,^{\circ}$ C, or even at lower temperatures, the spectrum obtained was poorly resolved (see Fig. S11 in ESI), possibly because the exchange process was not completely stopped. However, it is evident that the resonances of the phenolate aromatic protons split into four distinct signals with identical intensity (6.73, 6.67, 6.50 and 6.41 ppm) and two doublets emerged at 4.52 and 4.45 ppm with *J*-coupling of 12 and 12.3 Hz,



Scheme 2. Synthesis of ytterbium complexes 4 and 5.

respectively, that were assigned to two AB spin systems of two different NCH<sub>2</sub>Ar groups. The other two corresponding signals are overlapping with other resonances of 4; nevertheless, it was possible to locate them at 2.26 and 2.32 ppm, respectively, based on a <sup>1</sup>H-<sup>1</sup>H NMR COSY experiment (see Fig. S12 in ESI). Additionally, and in agreement with the presence of two phenolate groups magnetically non-equivalent in solution, it was possible to distinguish four signals at 2.23, 2.09, 2.07 and 2.02 ppm, assignable to four methyl groups of the aromatic rings. The remaining twenty proton resonances of the macrocycle core ranged from 3.40 and 1.28 ppm and the NCH<sub>3</sub> groups were detected at 2.63 and 1.75 ppm (overlapping with the deuterated solvent) (see Fig. S13 in ESI). The <sup>1</sup>H NMR pattern at -60 °C is consistent with two distinct environments of the phenolate groups in solution that could be attributed to the approximate  $C_2$ -symmetry found in the solid state that makes the two  $[Yb{(^{Me2}ArO)_2Me_2-cyclam}]$  units approximately equivalent.

The room-temperature <sup>1</sup>H NMR spectrum of **5** in thf- $d_8$  is wellresolved and indicates a symmetrical arrangement of the ligand (Me2ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup>. Only one phenolate environment is observed, as two singlets for the CH<sub>3</sub> groups of the aromatic substituents (2.47 and 2.13 ppm) and two unique aromatic C-H resonances (6.82 and 6.68 ppm) are present in the spectrum. Moreover, the two *trans*-NCH<sub>2</sub>Ar groups are magnetically equivalent and give rise to one AB spin system at 5.76 and 2.75 ppm with J-coupling of 12 Hz. Large differences in the chemical shifts of the diastereotopic benzyl protons were also observed in the yttrium complex [Y( $\kappa^{5}$ - $\{({}^{tBu2}ArO)_2Me_2-cyclam\})Cl]$  (5.64 and 2.66 ppm and 4.56 and 2.37 ppm), and the high shift observed for the benzyl protons was postulated to result of a combination of a deshielding effect of the phenolate ring current and the polarization induced by the rare earth metal ion on the C–H bond pointing away from it [14]. Also in agreement with a  $C_2$  symmetry in solution for complex 5, the carbon NMR spectrum shows five different methylene carbons assigned to the cyclam frame, one benzyl and one NCH<sub>3</sub> methyl carbon resonances, and one set of signals for the equivalent phenolate groups. Furthermore, the signal assigned to the quaternary carbons bonded to the phenolate oxygens (161.05 ppm) appears shifted to high frequencies relatively to  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (152.8 ppm), attesting the bonding of the phenolate oxygens to the ytterbium ions.

The coordination of labile thf molecules in **5** is confirmed by the observation in the <sup>1</sup>H NMR spectrum in the coordinating deuterated solvent (thf- $d_8$ ) of two resonances at 3.62 and 1.77 ppm assigned to the free solvent. As a whole the NMR data

are consistent with the centrosymmetric dimer obtained in the solid state.

#### 2.4. UV-Vis spectroscopy of the Yb(II) complexes

As expected for Ln(II) complexes [2], the ytterbium compounds 3-5 are intensely colored, and moderate absorptions in the visible region are observed for the orange tetrahydrofuran solutions of the compounds in their UV-Vis/NIR spectra (Fig. S17 in ESI). The absorption spectra of complexes 3-5 show peaks between 471 nm and 290 nm, which are characteristic of divalent Yb complexes (Fig. 2) [15]. The three spectra present different shapes, in agreement with the formation of distinct divalent ytterbium complexes. In the closed-shell Yb<sup>2+</sup> f<sup>14</sup> complexes no f-f transitions are possible and the absorptions observed must be due to ligand-tometal charge transfer and spin-allowed f-d transitions [16]. The absorption bands observed around 453 nm  $(600 \text{ M}^{-1} \text{ cm}^{-1})$  and 467 nm (521  $M^{-1}$  cm<sup>-1</sup>) for **4** and **5**, respectively, could be postulated to correspond to the bis(phenolate) cyclam ligand to ytterbium charge transfer. These absorption bands are absent in the UV-Vis spectrum of the starting material [YbI<sub>2</sub>(THF)<sub>2.5</sub>]. A closer look at the spectra indicates that the shape of the spectrum of **3** resembles more the spectrum of  $[(Yb{(Me2ArO)_2Me_2-cyclam})_2-$ Ybl]I (4), which has the ratio Yb:ligand closer to 1:1, while the dimer [Yb{(<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam}YbI<sub>2</sub>(thf)<sub>2</sub>] (5) presents a maximum of absorption around 390 nm as observed for [YbI<sub>2</sub>(thf)<sub>2.5</sub>].

#### 2.5. Crystallographic studies of the Yb(II) complexes

As mentioned above, both polynuclear Yb(II) complexes, **4** and **5**, crystallized from tetrahydrofuran solutions and were characterized by single-crystal X-ray diffraction analysis. The selected bond lengths and angles are provided in Tables 1 and 2, and the molecular structures of **4** and **5** are shown in Figs. 3 and 4, respectively.

Complex **4** crystallized as orange crystals in the monoclinic centrosymmetric space group P21/n, with a discrete cationic trinuclear structure, with one iodide and four thf molecules in the lattice. The overall monocationic charge of the [(YbL)<sub>2</sub>YbI]<sup>+</sup> unit is consistent with a formal +2 oxidation state for the three ytterbium centers that lead to a +6 charge balanced by two dianionic (<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup> ligands and one iodide ligand.

The molecular structure of **4** features three  $Yb^{2+}$  ions showing a bent arrangement ( $Yb1-Yb2-Yb3 = 158.03(2)^{\circ}$ ) and with an average Yb...Yb distance of 3.661(1) Å. The central Yb2 is five-coordinated by one iodide ligand, which occupies the apical position of



Fig. 2. UV–Vis spectra of 3–5 and of [YbI<sub>2</sub>(thf)<sub>2.5</sub>] in tetrahydrofuran.

 Table 1

 Selected bond lengths (Å) and angles (°) of 4.

	Yb1	Yb2	Yb3
Yb-O	2.268(7), 2.353(7)	2.272(7), 2.298(7) 2.272(7), 2.298(7)	2.298(7), 2.346(7)
Yb-N <sub>benzyl</sub>	2.578(8), 2.529(9)	-	2.585(10), 2.511(10)
Yb-N <sub>CH3</sub>	2.587(9), 2.506(8)	-	2.574(9), 2.522(9)
Yb–I	=	3.0730(14)	-
O-Yb-O	75.4(2)	74.0(2), 74.2(3)	75.7(3)
N <sub>benzvl</sub> -Yb-N <sub>benzvl</sub>	142.8(3)	-	143.1(3)
N <sub>CH3</sub> -Yb-N <sub>CH3</sub>	112.6(3)	-	111.3(3)
O-Yb-N <sub>CH3(trans)</sub>	141.2(3), 137.8(3)	_	145.2(3), 134.3(3)

Table 2

Selected bond lengths (Å) and angles (°) of 5.

	Yb1	Yb2
Yb-O <sub>Ar</sub>	2.340(3)	2.348(3)
Yb-N <sub>benzyl</sub>	2.541(4)	-
Yb-N <sub>CH3</sub>	2.567(3)	-
Yb–I	-	3.1447(3)
Yb-O <sub>thf</sub>	-	2.484(3)
O <sub>Ar</sub> -Yb-O <sub>Ar</sub>	79.54(14)	79.25(14)
N <sub>benzyl</sub> -Yb-N <sub>benzyl</sub>	138.95(18)	-
N <sub>CH3</sub> –Yb–N <sub>CH3</sub>	115.82(19)	-
O-Yb-N <sub>trans</sub>	140.00(11), 131.07(11)	-
O <sub>Ar</sub> -Yb-O <sub>thf</sub>	-	176.89(11)
		98.36(11)
I-Yb-I	-	169.70(2)

a distorted square-based pyramid, and by four bridging phenolate oxygens from two {Yb<sup>II</sup>( $^{Me2}$ ArO)<sub>2</sub>Me<sub>2</sub>-cyclam} moieties, forming the almost planar square base (deviations from the average plane shorter than 0.175 Å). The Yb–I bond length (3.073(1) Å) is similar to those reported in the literature for other five-coordinate Yb(II) complexes with terminal iodides [17].

The two end ytterbium atoms are not symmetrically related in the solid state, however, the coordination environments of Yb1 and Yb3 are very similar. Each ytterbium atom coordinates to two bridging phenolate oxygen atoms and to four amine nitrogen atoms of one  $\{N_4O_2\}^{2-}$  donor ligand in a distorted trigonal prism

coordination environment. One of the quadrangular faces of each ytterbium polyhedron is defined by the nearly coplanar four amine nitrogens of the macrocycle and with the ytterbium ions Yb1 and Yb3 sitting 1.112 Å and 1.120 Å above the plane, respectively. The phenolate groups in the two units are bound in a *cis* fashion with angles of  $75.3(2)^{\circ}$  and  $75.7(3)^{\circ}$  for O1–Yb1–O2 and O3–Yb3–O4, respectively, and with a dihedral angle between the two phenolate rings of each ( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2–</sup> ligand of 63.3° and 59.5°.

All Yb–N bond distances are similar, with mean values of 2.55 (4) Å and 2.54(5) Å for Yb1 and Yb3, respectively. The average Yb–N bond distances compare well with the one found for the divalent samarium complex  $[Sm{(^{tBu2}ArO)_2Me_2-cyclam}]$  (2.71 (6) Å) [10], if the difference in the ionic radii of Sm(II) (1.17 Å) and Yb(II) (1.02 Å) is taken into account [12].

The two YbO<sub>2</sub>Yb cores in **4** show asymmetrical bridging modes with Yb–( $\mu$ -O) ranging from 2.268(7) to 2.421(7) Å (Fig. 3b), with the longer distances corresponding to the *trans* phenolate rings bonding to the central Yb2 ion and with the methyl groups pointing out to the iodide ligand. The longer Yb2–O bond lengths are more characteristic of Yb–O dative bonds, however, the average of all four Yb2–( $\mu$ -O) distances (2.35(8) Å) in the YbO<sub>4</sub>I core is in the range reported for other 5-coordinate bridged bis(phenolate) divalent Yb complexes (2.297(5)–2.371(4) Å) [4a,6,18]. It seems that the bulk of the phenolate rings stabilizes the somewhat low coordination number of the divalent Yb2 ion. As expected, the average Yb1–( $\mu$ -O) (2.31(5) Å) and Yb3–( $\mu$ -O) (2.32(3) Å) bond distances are longer than the terminal Yb–O bonds lengths



**Fig. 3.** (a) Solid-state molecular structure of  $[Yb_3(\mu-\{(^{Me2}ArO)_2Me_2-cyclam\})I]I$  (**4**) with thermal ellipsoids drawn at 40% probability level. Hydrogen atoms are omitted for clarity. (b)  $Yb(\mu-O)_2Yb(\mu-O)_2Yb$  core view and metric parameters from the structure of **4**.

reported for 6-coordinate divalent bis(phenolate) ytterbium complexes [7,8], longer than the ones reported for the 6-coordinate complex Yb(III) [Yb( $\kappa^{5}$ -{(<sup>IBu2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})Cl] (2.062(2) Å) [11], nonetheless, are consistent with the bond distances reported for Yb(II) bridged bis(phenolates) [4a,6,18].

The dinuclear ytterbium complex  $[Yb_2(\mu-\{(^{Me2}ArO)_2Me_2-cyclam\})]I_2(thf)_2]$  (**5**) crystallized in the trigonal space group *P*-3*c*1 with the two ytterbium atoms residing on a twofold rotation axis. The structure of **5** (Fig. 4) shows that the two Yb(II) ions are doubly bridged by the two phenolate oxygens of the bis(phenolate) cyclam ligand, resulting in a Yb...Yb distance of 3.607(4) Å. The two bridging oxygens of the phenolate groups are perfectly in plane with the two ytterbium ions (as required by the crystallographic symmetry), forming a diamond-shaped YbO<sub>2</sub>Yb geometry (Fig. 4b). The structure shows that the two ytterbium(II) ions are six-coordinated, however in different coordination environments.

The connectivity of the  $\{O_2N_2N_2'\}^{2-}$  ligand donor to the Yb1 ion in **5** is analogous to that found for the Yb1 and Yb3 ions in complex **4**. The Yb1 in **5** bonds to the four amine nitrogen atoms of the cyclam ring and to the two oxygen atoms of the phenolate groups in a distorted trigonal prismatic geometry. The four nitrogen atoms of the cyclam define one rectangular face of the prism with a deviation from the plane of 0.237 Å and with the ytterbium center sitting 1.127 Å above the average plane. The Yb2 ion lies in a distorted octahedron defined by the two bridging phenolate oxygens, two iodide atoms and two thf oxygen atoms, with the four oxygen donor atoms in the equatorial plane with O–Yb–O angles ranging between 79.2(1)° and 98.4(1)°. The Yb–O(Ar) bond lengths (2.340 (3) and 2.348(3) Å) and Yb–N (av. 2.554(16) Å) are similar to those found for the terminal ytterbium(II) ions in **4**.

The Yb2–O(thf) bond lengths (2.484(3) Å) are within the values usually reported for other divalent ytterbium thf solvates [5,7,19],



**Fig. 4.** (a) Solid-state molecular structure of  $[Yb_2\{(^{Me2}ArO)_2-cyclam]I_2]$  (5) with thermal ellipsoids drawn at the 50% probability. Hydrogen atoms are omitted for clarity. (b)  $Yb(\mu-O)_2Yb$  core view and metric parameters from the structure of **5**.

but longer than those found in  $[YbI_2(thf)_4]$  (aver. 2.39(2) Å) [20]. The Yb2–I bond distance (3.1447(3) Å) is also consistent with oxidation state +2 for the ytterbium atom and can be compared with 3.146 Å in  $[YbI_2(dme)_3]$  [21], being somewhat longer than the ones in  $[YbI_2(thf)_4]$  (3.103(1) Å), maybe due to the steric demand created by the bis(phenolate) cyclam ligand.

Since the divalent Yb2 ion in 5 has two coordinated iodide ligands, it would be expected longer Yb2-O(Ar) bond distances, nevertheless, the YbO<sub>2</sub>Yb core has symmetrical bridging modes with almost identical Yb-( $\mu$ -O) bond lengths, indicating that the electrons engaged in the bonding are symmetrically shared by the two Yb<sup>2+</sup> cations. Steric reasons may explain these observations, as the coordination of the hexadentate chelate (Me2ArO) Me<sub>2</sub>-cyclam<sup>2-</sup> imparts a greater steric encumbrance for the divalent Yb1 ion that makes the Yb1–O(Ar) bonds elongate. Considering this, the dimer can be described as a combination of a cationic fragment  $[Yb{\kappa^{6}-(^{Me2}ArO)_{2}Me_{2}-cyclam}]^{+}$ , formed by the divalent Yb1 ion and the  $\{O_2N_2N_2'\}$  donor ligand, with an overall charge -1, and an anionic fragment  $[YbI_2(\mu-0)_2O_2]^-$  that is formed by the divalent Yb2 cation bonded to two anionic iodides, two neutral thf oxygen atoms and the two bridging phenolate oxygens with charge -1/2 each.

Apparently the formation of homoleptic dimers with bridging phenolate oxygens of the type [YbL]<sub>2</sub>, as observed with the bis (phenolate) derivatives { $R_2N(CH_2)_2N(CH_2-2-OC_6H_2-3,5-Bu_2^t)_2$ }^2 (R = Me, Et) or { $^{t}Bu_2$ -salan}<sup>2-</sup> [4a,6], is prevented by the constraint imposed by the 14-membered macrocycle of the ( $^{Me2}ArO$ )<sub>2</sub>Me<sub>2</sub>-

Table 3			
Selected crystal data	and data collection	parameters for	complexes 2, 4 and 5.

	2	<b>4</b> (C <sub>4</sub> H <sub>8</sub> O) <sub>4</sub>	5
Empirical formula	$C_{30}H_{48}N_4O_2$	C <sub>76</sub> H <sub>124</sub> N <sub>8</sub> O <sub>8</sub> I <sub>2</sub> Yb <sub>3</sub>	C38H62I2N4O4Yb2
Crystal size (mm)	$0.38 \times 0.18 \times 0.06$	$0.28\times0.18\times0.10$	$0.30 \times 0.08 \times 0.03$
Formula weight	496.72	2050.75	1238.80
Crystal system	monoclinic	monoclinic	trigonal
Space group	C2/c	$P2_1/n$	P-3c1
a (Å)	25.155(3)	9.218(3)	19.6443(6)
b (Å)	7.8454(8)	35.546(6)	19.6443(6)
<i>c</i> (Å)	16.0476(15)	24.468(6)	19.3370(6)
α (°)	90	90	90
β (°)	114.086(4)	92.865(15)	90
γ (°)	90	90	120
$V(Å^3)$	2891.3(5)	8007(4)	6462.4(3)
Ζ	4	4	6
Calculated density $(mg/m^{-3})$	1.141	1.698	1.910
$\mu$ (mm <sup>-1</sup> )	0.072	4.302	5.788
T <sub>minimum</sub> /T <sub>maximum</sub>	0.973/0.996	0.379/0.673	0.2756/0.8455
F(000)	1088.0	4048.0	3936
$\theta_{maximum}$ (°)	25.68	25.03	25.68
Reflections collected	10416	33253	26388
Unique reflections (R <sub>int</sub> )	2738 (0.0520)	14092 (0.0568)	4090 (0.0658)
$R_1[I > 2\sigma(I)]$	0.0448	0.0640	0.0287
wR <sub>2</sub> (all data)	0.1125	0.1347	0.0505
Parameters	167	811	240
Goodness-of-fit (GOF) on $F^2$	1.035	1.131	0.965
Largest diff. peak, hole (e $Å^{-3}$ )	0.217, -0.178	2.620, -1.403	0.730, -0.607

cyclam<sup>2–</sup> chelate. On the other hand, the large divalent ytterbium center seems to require more sterically demanding phenolate rings than the one with methyl substituents to form monomeric Yb(II) complexes. Although it seems that the reaction of the [YbI<sub>2</sub>(thf)<sub>n</sub>] with the sterically bulkier *tert*-butyl ligand, (<sup>tBu2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2–</sup>, leads to the formation of the monomeric complex [Yb {(<sup>tBu2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam}], the facile oxidation of this Yb(II) compound to Yb(III) species cannot be satisfactorily explained at this time.

#### 3. Conclusions

To summarize, a new bis(phenol) cyclam chelate,  $H_2(^{Me2}ArO)_2Me_2$ -cyclam, with methyl groups in the phenolate rings, was synthesized and fully characterized. We have successfully synthesized the first bis(phenolate) cyclam Yb(II) complexes by salt metathesis reaction with ytterbium(II) diiodide. This ligand proved to be efficient in the stabilization of novel dinuclear and trinuclear ytterbium(II) complexes that were structurally characterized. Our studies revealed that the less bulky  $\{O_2N_2N'_2\}^{2-}$  ligand ( $^{Me2}ArO)_2Me_2$ -cylam<sup>2-</sup> can be used as a linker to generate polynuclear lanthanide complexes by taking advantage of the ability of the bis(phenolates) to make bridging oxygen bonds.

#### 4. Experimental

#### 4.1. General procedures

The ytterbium complexes are extremely air- and moisturesensitive, requiring use of both vacuum line and glovebox techniques, with manipulations performed under a nitrogen atmosphere. Tetrahydrofuran and hexane were pre-dried using 4 Å molecular sieves and distilled from sodium-benzophenone under nitrogen and degassed prior to use. Tetrahydrofuran- $d_8$  was dried over sodium-benzophenone. [YbI<sub>2</sub>(thf)<sub>2.5</sub>], 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane and 1,8-bis(2-hydroxy-3,5-di*tert*-butylbenzyl)-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane (H<sub>2</sub>(<sup>tBu2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam) were prepared as previously reported [22,23,11]. All other reagents were of commercial grade and used without further purification. <sup>1</sup>H, <sup>13</sup>C NMR spectra and 2D NMR experiments were recorded using Varian 300 MHz or Bruker AVANCE 300 spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced internally to residual solvents proton or carbon resonances relative to tetramethylsilane (0 ppm). Electrospray ionization mass spectrometry (ESI-MS) was performed using a Bruker HCT quadrupole ion trap instrument. Carbon, hydrogen and nitrogen analyses were performed on a CE Instruments EA1110 automatic analyser. 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.

#### 4.2. Synthesis of $H_2(^{Me2}ArO)_2Me_2$ -cyclam (2)

The bis(phenolate) cyclam pro-ligand was prepared according to the method reported in the literature [11], with the required adaptations. 37% aqueous formaldehyde (1.3 mL) was added to a solution of 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane (1.5 g, 6.57 mmol) in methanol (20 ml). The mixture was refluxed under N<sub>2</sub> for 2 h and a solution of 2,4-di-methylphenol (1.61 g, 13.18 mmol) in methanol (10 mL) was then added and refluxed for additional 16 h. The white precipitate formed was isolated by filtration, washed with methanol and dried under vacuum. Yield: 78% (2.55 g, 5.13 mmol). Colorless crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a tetrahydrofuran solution of **2**. *m*/*z* (ESI-MS):  $[H_2L+H]^+$  497.30 (calc. 497.38). Analysis for C<sub>30</sub>H<sub>48</sub>O<sub>2</sub>N<sub>4</sub>: Calcd. C, 72.54; H, 9.74; N, 11.28; Found C, 72.52; H, 9.85; N, 11.21%.

<sup>1</sup>H NMR (300 MHz, benzene- $d_6$ , 23 °C)  $\delta$ : 10.03 (2H, OH), 6.92 (s, 2H, Ar-*H*), 6.73 (s, 2H, Ar-*H*), 3.88 (br), 3.23 (br), 3.03 (br), 2.44 (s, 6H), 2.25 (s, 6H), 1.91 (s, 6H), 1.71 (br,), 1.33 (br), 0.97 (br).

<sup>1</sup>H NMR (300 MHz, chloroform- $d_1$ , 23 °C)  $\delta$ : 9.92 (br), 6.82 (s, 2H, Ar-*H*), 6.61 (s, 2H, Ar-*H*), 2.32 (br), 2.19 (s, 6H, CH<sub>3</sub>), 2.16 (s, 6H, CH<sub>3</sub>).

<sup>1</sup>H NMR (300 MHz, chloroform- $d_1$ , -40 °C) δ: 10.13 (s, 2H, Ar-OH), 6.82 (s, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 3.93 (d, <sup>1</sup>J<sub>HH</sub> = 12 Hz, 2H, ArCH<sub>2</sub>N), 3.17 (m, 2H, NCH<sub>2</sub>), 2.91 (m, 4H, NCH<sub>2</sub>), 2.60 (d, 2H, <sup>1</sup>J<sub>HH</sub> = 12 Hz, ArCH<sub>2</sub>N), 2.40 (t, 2H, NCH<sub>2</sub>), 2.19 (s, 6H, CH<sub>3</sub>), 2.16 (s, overlapping, 6H + 6H, CH<sub>3</sub> and NCH<sub>3</sub>), 2.15–2.03 (4H, br,

NCH<sub>2</sub>), 1.89 (br, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and NCH<sub>2</sub>), 1.46 (br, 2H, CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>), 1.03 (br, 2H, NCH<sub>2</sub>).

<sup>13</sup>C NMR (75 MHz, chloroform- $d_1$ , 23 °C) δ: 153.40 (ArC-O), 130.44 (ArC-H), 128.70 (ArC-H), 126.37 (ArC), 124.76 (ArC), 123.15 (ArC), 54.98 (NCH<sub>2</sub>Ar), 54.40 (NCH<sub>2</sub>), 51.50 (NCH<sub>2</sub>), 51.02 (NCH<sub>2</sub>), 48.15 (NCH<sub>2</sub>), 43.59 (NCH<sub>3</sub>), 24.33 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.61 (CH<sub>3</sub>), 16.38 (CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, chloroform- $d_1$ , -40 °C) δ: 153.04 (ArC-O), 130.20 (ArC-H), 128.86 (ArC-H), 126.14 (ArC), 124.63 (ArC), 123.24 (ipso-ArC), 54.64 (NCH<sub>2</sub>Ar + NCH<sub>2</sub>), 53.54 (NCH<sub>2</sub>), 50.83 (NCH<sub>2</sub>), 50.57, 47.34 (NCH<sub>2</sub>), 43.63 (NCH<sub>3</sub>), 23.85 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.64 (CH<sub>3</sub>), 16.71 (CH<sub>3</sub>).

## 4.3. Reaction of $[YbI_2(thf)_{2.5}]$ with $K_2(^{tBu2}ArO)_2Me_2$ -cyclam (1-K): compound **3**

Excess of potassium hydride (64 mg, 1.59 mmol) was added to a solution of  $H_2(^{IBu2}ArO)_2Me_2$ -cyclam (300 mg, 0.451 mmol) in thf (15 mL). After stirring for 16 h at room temperature, the resulting colorless solution was separated by centrifugation and added to a solution of 1 equiv. of  $[YbI_2(thf)_{2.5}]$  (274 mg, 0.451 mmol) in thf (15 mL). The solution turned orange and KI precipitated. After stirring over 14 h at room temperature, the reaction mixture was centrifuged, the supernatant was decanted off and the solvent was removed under reduced pressure. The resulting solid was washed with *n*-hexane and after drying in vacuo **3** was isolated as an orange solid (268 mg).

<sup>1</sup>H NMR (300 MHz, thf- $d_8$ , 23 °C) δ: 7.12 (2H, d, Ar-*H*), 6.76 (2H, d, Ar-*H*), 4.30 (2H, br, NCH<sub>2</sub>Ar), 3.06 (2H, t, CH<sub>2</sub>), 2.95–2.41 (10H, CH<sub>2</sub> + NCH<sub>2</sub>), 2.39–2.13 (14H, CH<sub>2</sub>), 2.19 (6H, NCH<sub>3</sub>), 1.66 (2H, CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>), 1.53 (18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.24 (18H, C(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, thf- $d_8$ , 23 °C) δ 166.96 (ArC-O), 136.92 (ArC), 131.86 (ArC), 126.89 (ArC-H), 124.01 (ArC), 123.79 (ArC-H), 62.83 (NCH<sub>2</sub>Ar), 57.43 (CH<sub>2</sub>), 56.27 (CH<sub>2</sub>), 54.22 (CH<sub>2</sub>), 43.17 (NCH<sub>3</sub>), 36.47 (*C*(CH<sub>3</sub>)<sub>3</sub>), 34.50 (*C*(CH<sub>3</sub>)<sub>3</sub>), 32.85 (*C*(CH<sub>3</sub>)<sub>3</sub>), 31.09 (*C*(CH<sub>3</sub>)<sub>3</sub>), 24.16 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

#### 4.4. Synthesis of $[Yb_3(\mu - \{(M^{e_2}ArO)_2Me_2 - cyclam\})_2I]I(4)$

Solid KH (40 mg, 1 mmol) was added to a solution of  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (134 mg, 0.271 mmol) in thf (15 mL). After 16 h of stirring at room temperature, the reaction mixture was centrifuged. The resulting clear solution of **2-K** was added to a yellow solution of [Ybl<sub>2</sub>(thf)<sub>2.5</sub>] (247 mg, 0.406 mmol) in thf (10 mL), and the color changed immediately to a strong orange. After continued stirring overnight, at room temperature, the reaction mixture was centrifuged to separate the KI, and the orange solution was concentrated to a small volume and layered with *n*-hexane. An orange microcrystalline solid precipitated and was collected by centrifugation and dried under vacuum (103 mg, 0.058 mmol, 43% yield).

Analysis for  $C_{60}H_{92}N_8O_4I_2Yb_3$ : Calcd. C, 40.89; H, 5.26; N, 6.36; Found C, 40.97; H, 5.87; N, 6.35%.

<sup>1</sup>H NMR (300 MHz, thf- $d_8$ , 23 °C) δ: 6.71 (Ar-H), 6.47 (Ar-H), 2.55, 2.12 (s), 2.07 (s), 1.50. Not all of the ligand (<sup>Me2</sup>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam<sup>2-</sup> resonances were observed at 23 °C.

<sup>1</sup>H NMR (300 MHz, thf- $d_8$ , -60 °C): δ 6.73 (1H, Ar-*H*), 6.67 (1H, Ar-*H*), 6.49 (1H, Ar-*H*), 6.42 (1H, Ar-*H*), 2.63 (3H, NCH<sub>3</sub>), 2.23 (3H, NCH<sub>3</sub>), 2.09 (3H, CH<sub>3</sub>), 2.07 (3H, CH<sub>3</sub>), 2.02 (3H, CH<sub>3</sub>), 1.75 (3H, NCH<sub>3</sub>, overlapping with solvent), 3.40–1.28 (broad resonances, macrocycle CH<sub>2</sub>). See Figs. S11 and S12 in ESI.

#### 4.5. Synthesis of $[Yb_2(\mu - {(Ar^{Me2}O)_2Me_2 - cyclam})I_2(C_4H_8O)_2]$ (5)

Solid KH (79 mg, 1.98 mmol) was added to a solution of  $H_2(^{Me2}ArO)_2Me_2$ -cyclam (281 mg, 0.567 mmol) in thf (20 mL). A

vigorous reaction took place and after 16 h the reaction mixture was centrifuged. The resulting clear solution of **2-K** was added to a yellow solution of  $[Ybl_2(thf)_{2.5}]$  (689 mg, 1.135 mmol) in thf (15 mL), and the color changed immediately to a strong orange-red. After continued stirring overnight, at room temperature, the reaction mixture was centrifuged to separate the KI, and the orange-red solution was concentrated to a small volume and layered with *n*-hexane. An orange microcrystalline solid precipitated and was collected by centrifugation and dried under vacuum (450 mg, 0.363 mmol, 64% yield). Orange-red crystals of **5** suitable for X-ray diffraction analysis were grown from a concentrated thf solution. Analysis for C<sub>38</sub>H<sub>62</sub>N<sub>8</sub>O<sub>6</sub>I<sub>2</sub>Yb<sub>2</sub>: Calcd. C, 36.84; H, 5.04; N, 4.52; Found C, 36.74; H, 5.15; N, 4.53%.

<sup>1</sup>H NMR (300 MHz, thf- $d_8$ , 23 °C): δ 6.82 (2H, Ar-*H*), 6.68 (2H, Ar-*H*), 5.76 (2H, d, 12 Hz NCH<sub>2</sub>CH<sub>3</sub>), 3.62 (α-thf), 3.30 (t, 2H, CH<sub>2</sub>), 2.83 (t, 2H, CH<sub>2</sub>), 2.75 (2H, d, 12 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 2.47 (6H, CH<sub>3</sub>), 2.60–2.31 (6H, CH<sub>2</sub>), 2.13 (6H, CH<sub>3</sub>), 2.08 (6H, NCH<sub>3</sub>), 2.18–1.98 (6H, CH<sub>2</sub>), 1.77 (β-thf), 0.97 (4H, br, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

<sup>13</sup>C NMR (75 MHz, thf- $d_8$ , 23 °C): δ 161.05 (ArC-O), 132.64 (ArC-H), 130.85 (ArC-H), 129.10 (ArC), 126.16 (ArC), 123.96 (ArC), 68.38 (thf), 66.68 (NCH<sub>2</sub>Ar), 62.71 (CH<sub>2</sub>), 60.12 (CH<sub>2</sub>), 59.85 (CH<sub>2</sub>), 56.62 (CH<sub>2</sub>), 40.50 (NCH<sub>3</sub>), 26.51 (thf), 25.89 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.38 (CH<sub>3</sub>), 20.77 (CH<sub>3</sub>).

#### 4.6. Single crystal X-ray diffraction

Crystallographic and experimental details of data collection and crystal structure determinations for the compounds 2, 4 and 5 are given in Table 3. Suitable crystals of compounds 4 and 5 were selected and coated in FOMBLIN oil under an inert atmosphere. Crystals were then mounted on a loop and the data for compounds 2, 4 and 5 were collected using graphite-monochromated Mo Ka  $(\lambda = 0.71073 \text{ Å})$  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 [24]. The structures were solved by direct methods using either SHELXS-97 [25] or SIR 97 [26] and refined using full-matrix least squares refinement against  $F^2$ using SHELXL-97 [25]. In the former case, all programs are included in the wingx software package [27]. 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 complex 5 some carbons of the ligand are disordered and a constraint model was used (see cif files in ESI).

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#### Appendix A. Supplementary data

CCDC 1487952–1487954 contains the supplementary crystallographic data for **2**, **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2016.09.008. L. Maria et al./Polyhedron 119 (2016) 277-285

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