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Diamido/diamine cyclam-based zirconium and hafnium complexes: Synthesis and characterization

Rui F. Munhá, Sónia Namorado, Sónia Barroso, M. Teresa Duarte, José R. Ascenso, Alberto R. Dias, Ana M. Martins *

Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais No. 1, 1049-001 Lisboa, Portugal

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Abstract

The synthesis and characterization of amido-amine cyclam based metal complexes is described. A novel tetraazamacrocycle ligand precursor (Li_2[1,8-Bn_2-1,4,8,11-tetraazacyclotetradecane], Li_2Bn_2cyclam, **2**) is reported. Reactions of **2** with $MCl_4(THF)_2$ afforded $M(Bn_2cyclam)Cl_2$ (M = Zr **3**, Hf **4**). The two complexes show trigonal prismatic metal coordination geometries in the solid-state molecular structures. The cross-bridged cyclam 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (CB-H_2cyclam **5**) was used to prepare the lithiated ligand precursor (CB-Li_2cyclam **6**) and (CB-$(Me_3Si)_2$cyclam **7**). M(CB-cyclam)Cl_2 (M = Zr **8**, Hf **9**) were synthesized from reactions of $MCl_4(THF)_2$ with **6**. The structures of **3** and **4** are compared with those of zirconium and hafnium complexes derived from cyclam and unsaturated tetraazamacrocyclic ligands.

Keywords: Zirconium; Hafnium; Cyclam; Tetraazamacrocycles; Amido ligands

1. Introduction

The tuning of electronic and stereochemical properties of metal complexes can be achieved by suitable design of ligand precursors [1], where combinations of donor atoms and frames impart particular kinetic and thermodynamic stability, taking also into account the promotion of new reactivity patterns. The association of neutral and anionic nitrogen donor moieties has proved to be a versatile path to follow as attested by the variety of reactions promoted by its transition metal derivatives. In this context, new classes of Group 4 metal complexes having as ancillary ligands tetraazamacrocycles derived from porphyrins, tetraazaannulenes and tropocoronands have been recently reported [2–9]. Some of these complexes showed unprecedented reactivity and structures [10–14]. In contrast, examples of early-transition metal complexes that incorporate saturated mixed-tetraazamacrocycle ligands are scarce. The first aliphatic azamacrocycle complex of this type, isolated by Power in 1983, was a titanium dimer, [Ti(cyclam)]$_2$, where the tetra-anionic cyclam ligands bridge the two metal centres through two macrocycle amido functions [15]. Since then, only recently other examples of similar tetraazamacrocycle metal complexes have been reported: Floriani used cyclam to prepare a diamido-diamine Zr(IV) dihalide [16] and Berg reported the synthesis of Zr(IV) complexes employing a cross-bridged cyclam [17]. Moreover, suitable synthetic methods for selective functionalisation of cyclic polyamines still represent a challenge [18,19] and therefore, the study of metal derivatives of such compounds is still facing its early years. Following our interest in the reactivity of Group 4 metal centres supported by saturated azamacrocycle ligands [20–24], we turned our attention to cross-bridged and *trans*-disubstituted cyclam ligand precursors. Herein, we present our initial results concerning coordination of zirconium and hafnium to *trans*-*N*,*N*′-dibenzyl cyclam and C_2-cross-bridged cyclam.

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* Corresponding author.
E-mail address: ana.martins@ist.utl.pt (A.M. Martins).

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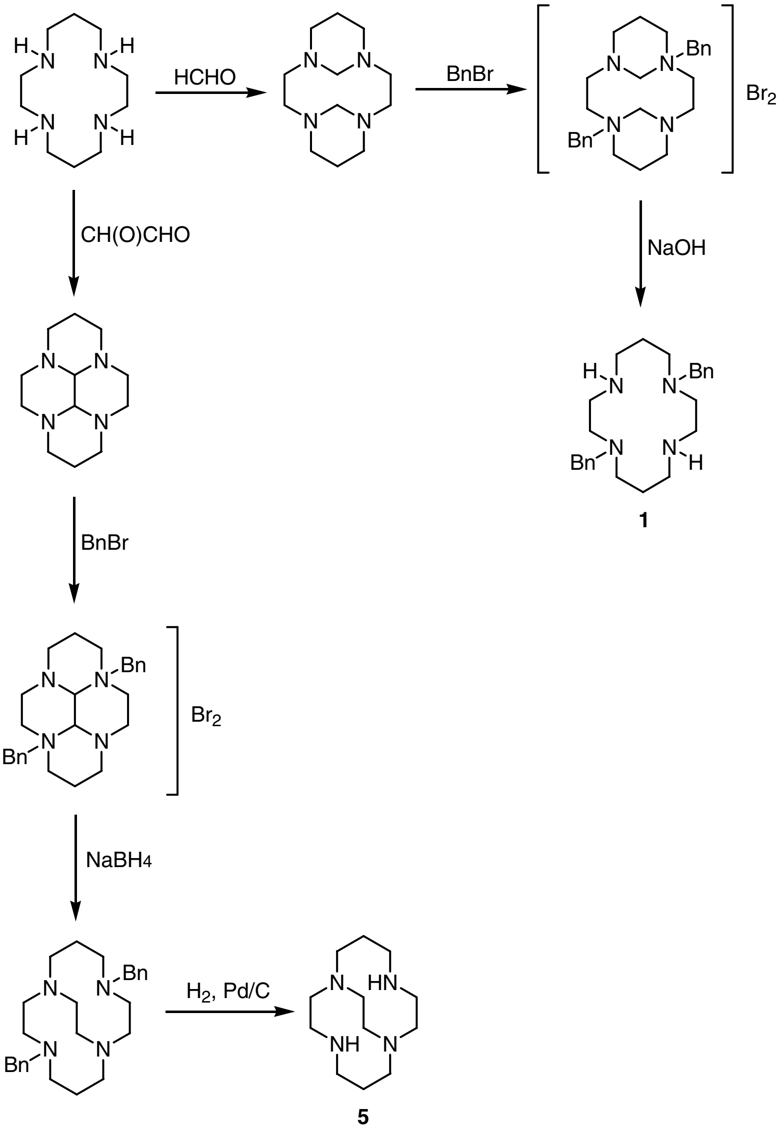
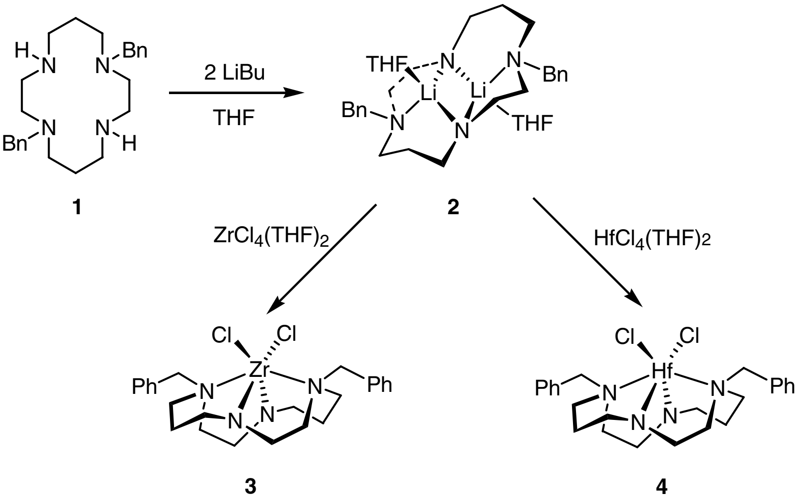
2. Results and discussion

The ligand precursors 1,8-*N*,*N*′-dibenzyl cyclam (H_2Bn_2-cyclam) **1** and cross-bridged cyclam (CB–H_2cyclam) **5** have been prepared according to published procedures, as presented in Scheme 1. The synthetic approach chosen for the synthesis of **1** was reported by Gillard and co-workers [25]. First, cyclam is made to react with formaldehyde producing a bisaminal cyclam allowing the highly-selective *trans*-disubstitution of the macrotricycle, upon addition of benzyl bromide. Basic hydrolysis of the disubstituted macrotricycle results in the formation of the *trans*-disubstituted cyclam **1** in 80% global yield. The product was characterized by NMR spectroscopy and IR, in agreement with the published results. 1,4,8,11-Tetraazabicyclo[6.6.2]hexadecane (**5**) was prepared according to Weisman and co-workers [17]. Similarly to the synthesis of **1**, the first step is a condensation reaction of glyoxal and cyclam to give a tetracyclic bisaminal cyclam, followed by *trans* dibenzylation that leads to the bisquaternary ammonium bromide cyclam salt. Reaction with sodium borohydride produces reductive cleavage to give the double-ring-expanded *N*-*N*′-dibenzyl bicyclic compound, which is finally converted to **5** by Pd/C catalysed reduction with hydrogen. This procedure was accomplished with a global yield of 55%.

Li_2Bn_2cyclam **2** was prepared by reaction of two equivalents of LiBu with **1**, at room temperature, in THF. The ^1H and ^{13}C NMR spectra of Li_2Bn_2cyclam in C_6D_6 reveal the coordination of one THF molecule per lithium. Considering that (i) lithium cations show a structural preference for tetrahedral coordination [26,27], usually maintained in lithium amido solutions [28,29], and (ii) the structure determined by X-ray diffraction of Li_2H_2cyclam [16], it is likely that the two lithium cations of **2** are also located at opposite faces of the macrocycle (Scheme 2). This arrangement would allow the coordination of three macrocycle



Scheme 1.



Scheme 2.

nitrogens and one THF oxygen to each lithium cation, consistent with the pattern displayed by the NMR spectra of Li_2Bn_2cyclam.

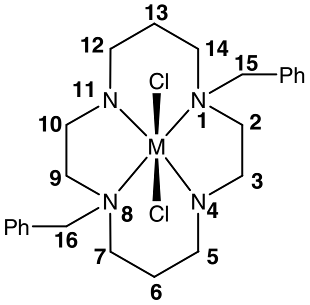
The ^1H NMR spectrum of **2** shows nine multiplets in the range 1.80–3.83 ppm that account for the methylenic macrocyclic and benzylic protons and two multiplets at 1.51 and 3.67 ppm that correspond to the coordinated THF molecules. The methylenic benzyl protons are diastereotopic and appear as an AB system at 3.81 and 3.50 ppm. As a result of lithium coordination, the 20 macrocyclic protons are split in 10 inequivalent resonances that correspond to H_{syn} and H_{anti} protons. The solution structure is consistent with an average C_i symmetry, as six ^{13}C NMR resonances are observed for the ligand core and benzyl methylenic carbons.

Treatment of a THF suspension of $ZrCl_4(THF)_2$ with one equivalent of **2** gave $Zr(Bn_2cyclam)Cl_2$ **3** in 41% yield. The Hf(IV) analogue $Hf(Bn_2cyclam)Cl_2$ **4** was synthesised by the same route in 40% yield, using $HfCl_4(THF)_2$ as starting material (Scheme 2). Despite the addition of Li_2Bn_2cyclam solutions to the metal suspensions resulted in immediate dissolution, the formation of **3** and **4** required reflux. Considering that in general the metathesis of metal halide bonds with lithium amides occurs readily, the higher energy barriers associated with these reactions must result from the structural features of Li_2Bn_2cyclam. This, if consistent with the structure depicted in Scheme 2, has to undergo a structural reorganisation to attain the conformation appropriate to bind the four nitrogen atoms to the same metal centre. Although we do not have been able to grow crystals of Li_2Bn_2cyclam suitable for X-ray diffraction, we tentatively suggest that the disruption of the stable lithium coordination in order to achieve the correct ligand conformation may rule the metal–chloride metathesis reaction.

^1H resonances of **3** and **4** are presented in Table 1. In the ^1H NMR spectra the ligand framework gives rise to a series of multiplets, in the range 1.42–4.22 ppm for **3** and 1.45–4.18 ppm for **4**, corresponding to 10 chemically inequivalent hydrogens. The assignment of the resonances to the C_2 and C_3 chains was possible on the basis of COSY experiments. Either for **3** or **4** the diasteriotopic benzylic protons appear as AB systems. The ^{13}C NMR spectra confirm the average C_2 symmetry in solution, as five ligand core resonances, one benzylic resonance and one set of aromatic signals are observed. The solubility of the complexes in CH_2Cl_2 prevented the assignment of the carbon resonances. As expected, the coordination to the metals has a dramatic effect on the macrocycle and benzyl proton resonances that appear shifted to low field in comparison to the neutral ligand precursor.

Single crystals of **3** were obtained from a dichloromethane solution, by slow evaporation of the solvent. An ORTEP depiction of the molecular structure as determined by single-crystal X-ray diffraction is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. Only half molecule is found in the asymmetric unit, the Zr atom is located along the rotation axis (2) that generates the whole molecule. The zirconium is coordinated to the four nitrogen atoms of the macrocycle and to two chloride ligands in a trigonal prismatic geometry. The prism rectangular face is defined by the four nitrogen atoms of the macrocycle as commonly reported for other tetraazamacrocycle complexes [4,30]. The metal is perched on the macrocycle with a distance of 1.08(15) Å to the plane defined by the four cyclam nitrogen atoms, forcing the chloride ligands to be *cis* to each other. The angle N(1)–Zr(1)–N(2_$1) that belongs to the five member metallocycle defined by the metal and the NC_2N chains, is narrower than the N(1)–Zr(1)–N(2) angle inside the six member metallocycle (72.03(7)° vs. 81.11(7)°). The dihedral angle N–C–C–N, which characterizes the five member metallocycles, is −37.4(7)° and accordingly a λ conformation is assigned to these metallocycles while the six member ones display a chair conformation. The Cl(1)–Zr(1)–Cl(1_$1) angle (84.76(3)°) is comparable with the values reported

Table 1
^{1}H chemical shifts for **3** and **4**

	^{1}H NMR chemical shifts (ppm) H^2/H^9 H^3/H^{10}	 H^5/H^{12} H^7/H^{14}	 H^6/H^{13}	 H^{15}/H^{16}	 Ph
3	3.68	4.22			7.35–7.10
	3.30–3.20	3.47	1.82	4.64	
	3.09–3.03	2.68	1.42	4.26	
	2.38	2.53			
4	3.87	4.18			7.40–7.20
	3.41–3.35	3.52	1.90	4.61	
	3.31–3.23	2.93	1.45	4.28	
	2.48	2.67			

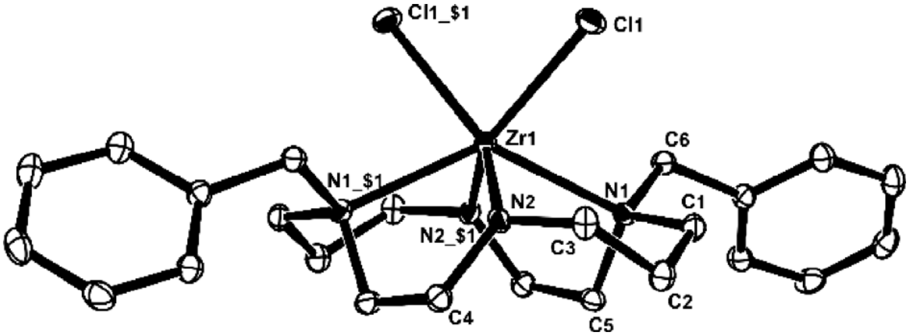


Fig. 1. ORTEP diagram of complex **3** showing thermal ellipsoids at 50% probability level, view along the coordinated N atom plane. Half molecule is generated by symmetry operation $-x + 3/2$, y, $-z + 3/2$. Hydrogens are omitted for clarity.

Table 2
Relevant bond lengths, angles and torsion angles for compounds **3** and **4** [#]

	[M(Bn$_2$cyclam)Cl$_2$][a]	
	3 (M = Zr)	**4** (M = Hf)
Distances (Å)		
M(1)–N(1)	2.437(2)	2.417(11)
M(1)–N(2)	2.062(2)	2.027(11)
M(1)–Cl(1)	2.5107(7)	2.479(3)
M(1)–[N$_4$Plane]	1.08(15)	1.05(75)
Angles (°)		
N(1)–M(1)–N(2)	81.11(7)	72.4(4)
N(1)–M(1)–N(1_$1)	128.85(10)	129.8(5)
N(1)–M(1)–N(2_$1)	72.03(7)	81.5(4)
N(2)–M(1)–N(2_$1)	115.13(15)	116.1(6)
N(1)–M(1)–Cl(1)	80.83(5)	80.7(2)
N(2)–M(1)–Cl(1)	95.28(6)	134.1(3)
N(1)–M(1)–Cl(1_$1)	142.87(5)	142.4(3)
N(2)–M(1)–Cl(1_$1)	134.45(6)	95.2(3)
Cl(1)–M(1)–Cl(1_$1)	84.76(3)	83.86(16)
[N$_4$Plane]–[Phenyl]	48.5(6)	48.4(29)

[#] The numbering scheme used in each complex is not the same due to the half molecule found in the asymmetric unit for each molecule.

[a] $1 symmetry operation $-x + 3/2$, y, $-z + 3/2$.

for other trigonal prismatic zirconium complexes [31]. The Zr(1)–N(1) and Zr(1)–N(2) bond lengths are 2.437(2) Å and 2.062(2) Å, respectively, which are within the ranges of usual values for Zr–amine and Zr–amido bond lengths [30]. The sum of the angles around N(2) (C(3)–N(2)–Zr(1), C(3)–N(2)–C(4) and C(4)–N(2)–Zr(1)) is ~357°, attesting for the sp^2 hybridization of nitrogen and consistent with a zirconium–nitrogen multiple bond. The Cl(1)–Zr(1) bond length is 2.5107(7) Å, which is in the upper range of Zr(IV)–Cl distances reported in the literature [31]. This value is certainly a reflex of the bonding properties of the diamido-diamine donor set that may act as a 12 electron donor to the metal centre when both σ and π bonds are considered. As a consequence, the chloride ligands behave as pure σ donor ligands [32]. Short contact distances between the Cl(1) and H_{syn} atoms located at carbons C(1) and C(3) and one benzylic hydrogen atom, are observed. The dihedral angle between the plane defined by the four nitrogen atoms and the phenyl group is 48.5(6)°.

Single crystals of **4** were obtained by cooling at −20 °C a dichloromethane solution of the compound. The molecular structure of **4**, represented in Fig. 2 and selected bond lengths and angles, given in Table 2, reinforce the similarities between **3** and **4** as already shown by the NMR spectra. The structural features of **4** are the same described for **3** and do not deserve further discussion, as the complexes are isostructural. We should also stress that crystals of compound **4** were of poor quality as described in Section 3.

The addition of two equivalents of LiBu to a toluene solution of cross-bridged cyclam **5** led to the quantitative formation of the dilithiated macrocycle derivative CB-Li_2cyclam, **6** (Scheme 3).

The ^{1}H NMR spectrum of **6** shows a complex pattern of the methylenic macrocyclic resonances between 1.27 and 3.54 ppm. Two multiplets, observed at 1.27 and 1.81 ppm, may be assigned to the CCH_2C protons, but the overlapping of the other resonances prevents further identification. In the ^{13}C NMR spectrum, consistently with an average C_2 symmetry, only six resonances are observed. Full evidence of **6** was obtained through its reaction with Me_3SiCl, which led to the quantitative formation of CB–$(Me_3Si)_2$cyclam **7** as an off-white solid. The ^{1}H and ^{13}C NMR spectra of **7** are consistent with an average C_2 symmetry and the assignment of proton and carbon resonances was established on the basis of additional NMR experiments (HETCOR, COSY and selective NOE irradiation).

The reactions of CB-Li_2cyclam **6** with $ZrCl_4(THF)_2$ and $HfCl_4(THF)_2$ yielded the corresponding zirconium and hafnium cross-bridged cyclam derivatives, Zr(CB-cyclam)Cl_2 **8** and Hf(CB-cyclam)Cl_2 **9** in 30% and 60% yield, respectively (Scheme 3). Complex **8** was previously prepared in high yield through an indirect method that involved the reaction of Zr(CB-cyclam)$(NSiMe_2)_2$ with

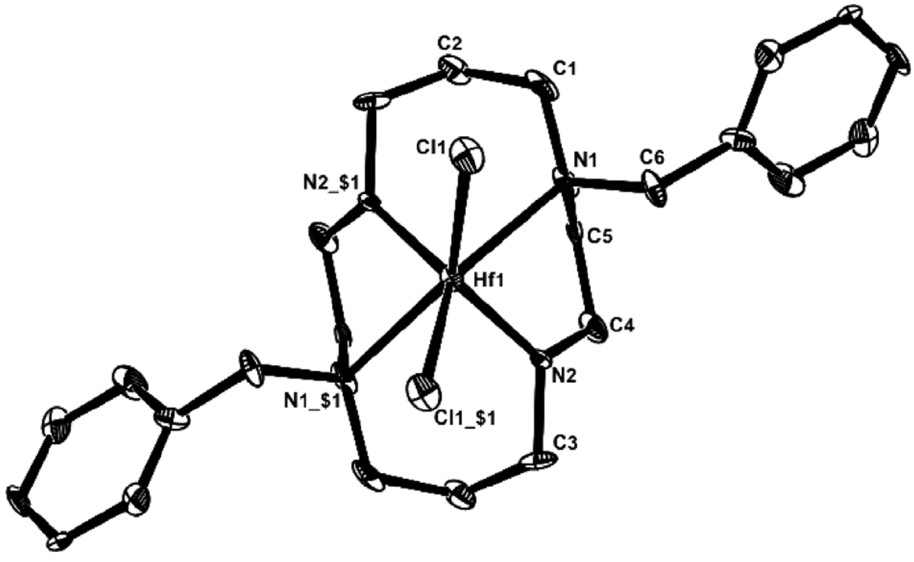
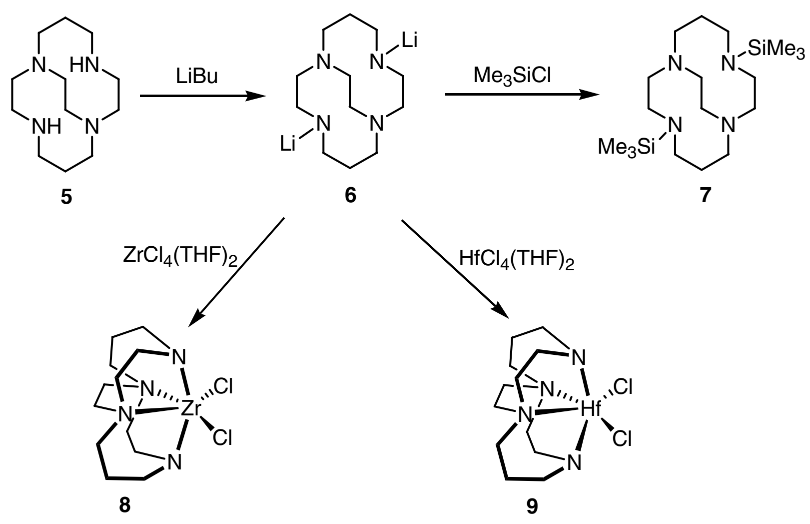


Fig. 2. ORTEP diagram of complex **4** showing thermal ellipsoids at 50% probability level, view perpendicular to the coordinated N atom plane. Half molecule is generated by symmetry operation $-x + 3/2$, y, $-z + 3/2$. Hydrogens are omitted for clarity.



Scheme 3.

Me_3SiCl [17]. Complex **8** proved to be a good starting material for the synthesis of a variety of organometallic compounds [17]. We found that in strictly anhydrous conditions, the deprotonation of CB-cyclam with LiBu proceeds in quantitative yield, allowing the use of metal tetrahalides as convenient starting materials for the syntheses of complexes **8** and **9**. These compounds are extremely reactive and slow decomposition is observed either in solution or in the solid state. The identification of complexes **8** and **9** was established by comparison of its ^1H and ^{13}C NMR spectra with the one reported for **8** [17]. Although the ^1H NMR pattern is complex, the carbon resonances allow unequivocal identification of the compounds.

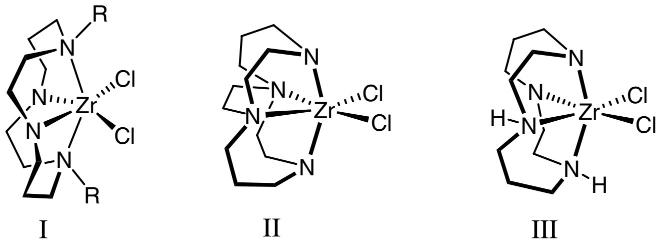
The structural characterization of **3** presented in this work, completes a collection of diamine-diamido cyclam based zirconium compounds for which three different types of structures may be distinguished (Scheme 4).

The comparison of the solid-state structures of **3** and **4** (I in Scheme 4) with those of (CB-cyclam)ZrX_2 [17] (II in Scheme 4) shows that the Bn_2cyclam ligand provides a higher steric hindrance around the metal centres. The R groups in Bn_2cyclam complexes are directed towards the metals, whereas in CB-cyclam complexes the bridge (equivalent to the R groups in **3** and **4**) points back, opposite to the metal. Additionally, the C_2 bridge constrains the ligand coordination in a way that the two amine moieties are *cis* disposed in a distorted octahedral geometry. Thus, the two amido fragments are forced to adopt a *trans* arrangement and it is not possible to define a plane containing the four nitrogen atoms.

In structure III, the metal also displays distorted octahedral coordination geometry but in contrast to II, either the amine or the amide moieties are *cis*. As for II, the metal stereochemical protection is exclusively due to the macrocyclic framework.

The structural differences pointed out are expected to influence the reactivity of these compounds. In type II complexes the Cl ligands are *trans* to the amine nitrogens; in type III compounds one chloride is *trans* to an amine and the other is *trans* to an amido fragment. In complexes **3** and **4** the chloride ligands occupy adjacent positions in the metal trigonal prismatic coordination geometry, as found in tropocoronand, porphirin and annulene metal complexes. Despite the different metal centre coordination geometries in complexes **3** and [Zr(cyclam)Cl_2] reported by Floriani et al. [16], the zirconium-nitrogen and zirconium–chloride bond distances in these compounds are similar. The metal–N_{amido} bond lengths are slightly shorter in **3** (2.062(2) Å vs. 2.073(7) and 2.075(6) Å) whereas, in contrast, the zirconium–N_{amine} distances are longer (2.437(2) Å vs. 2.347(8) and 2.377(6) Å). The Zr–Cl bond length in **3** (2.5107(7) Å) is comprised between the two values reported for [Zr(cyclam)Cl_2] (2.490(2) and 2.523(2) Å). In complexes **3** and **4** the sum of the angles around the anionic nitrogen atoms are close to 360°, as expected for sp^2 hybridized atoms (357° in **3** and 358° in **4**). These data together with the metal–N_{amido} distances reveal that in **3** and **4** the amido fragments coordination have important π donor contributions from the nitrogen, as is currently observed in d^0 metal-amido coordination. In [Zr(cyclam)Cl_2] the sum of the angles around the anionic nitrogen atoms, N(1) and N(4) are 348.5° and 355.2°, respectively. The value for N(1) is noticeably narrower than 360° and close to the values of 342.2° registered for N(3), which is a neutral donor. These features suggest that the alternation of the amine and amido donor fragments occurring in **3** and **4** adapt to the metal coordination requirements readily than the arrangement of consecutive amine and amido donors in [Zr(cyclam)Cl_2]. The dihedral angles N–C–C–N, which characterize the five member metallocycles in [Zr(Bn_2cyclam)Cl_2] (−37.4(7)°) and [Zr(cyclam)Cl_2] (50.30° and 49.30°) determine that the conformations of those metallocycles are also different, namely λ for [Zr(Bn_2cyclam)Cl_2] and δ for [Zr(cyclam)Cl_2], respectively.

The structural characteristics of **3** and **4** pointed out above lead us to anticipate that the fragments M(Bn_2cyclam) (M = Zr, Hf) may be suitable to support an interesting reactivity involving the two additional *cis*-positioned ligands in M(Bn_2cyclam)X_2 complexes. We are currently working in this direction.



Scheme 4.

3. Experimental

3.1. General procedures

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium–benzophenone (toluene, THF) or CaH_2 (*n*-hexane and dichloromethane) under an atmosphere of N_2, and collected by distillation. Deuterated solvents were dried with molecular sieves and freeze-pump-thaw degassed prior to use. Proton (300 MHz) and carbon (75 MHz) NMR spectra were recorded in a Varian Unity 300, at 298 K unless stated otherwise, referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (0 ppm). Elemental analyses were obtained from Laboratório de Análises do IST, Lisbon, Portugal. $SiMe_3Cl$ was purified by removal of residual HCl (by bubbling nitrogen through for ca. 15 min.) and then distilled trap-to-trap. The compounds $ZrCl_4(THF)_2$, 1,8-dibenzyl-1,4,8,11–tetraazacyclotetradecane **1** and 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane **5** were prepared according to described procedures [25,33,34]. All other reagents were commercial grade and used without further purification.

(1,8-Dibenzyl-1,4,8,11–tetraazacyclotetradecane)Li$_2$*-(OC*$_4$*H*$_8$*)*$_2$ *(***2***)*. **1** (1.00 g, 2.63 mmol) was dissolved in 50 mL of THF and two equivalents of a 1.6 M LiBu solution in hexanes (3.28 mL, 5.26 mmol) were added dropwise at room temperature. The white solution turned yellow and it was left stirring for 1 h. The solvent was evaporated and the cream solid was washed with hexanes. The residue was dissolved in THF, filtered and stored at −20 °C. A white crystalline solid was isolated by filtration in 70% yield. NMR (C_6D_6): ^{1}H δ(ppm) 7.30–7.00 (overlapping, 10H, Ph), 3.83–3.67 (overlapping, 6H, NCH_2, NCH_2Ph), 3.67 (m, 8H, OCH_2), 3.40 (d, 2H, $J_{HH} = 13.7$ Hz, NCH_2Ph), 3.30 (m, 2H, NCH_2), 3.04 (m, 2H, NCH_2), 2.91 (m, 2H, NCH_2), 2.72 (m, 2H, NCH_2), 2.44 (m, 4H, NCH_2), 2.05 (m, 2H, CCH_2C), 1.80 (m, 2H, CCH_2C), 1.51 (m, 8H, CH_2); ^{13}C{^{1}H} δ(ppm) 131.0, 130.1 and 127.3 (Ph), 67.9 (OCH$_2$), 59.3, 58.9, 56.8, 56.0 (CH$_2$N) 30.1 (CCH$_2$C), 25.8 (CH$_2$). Elemental analysis was not possible to obtain due to the product instability.

(1,8-Dibenzyl-1,4,8,11–tetraazacyclotetradecane)ZrCl$_2$ *(***3***)*. 1,8-Dibenzyl-1,4,8,11-tetraazacyclotetradecane (1.70 g, 4.46 mmol) was dissolved in 90 mL of THF and a solution of LiBu (5.6 mL, 1.6 M in hexanes) was slowly added. The colourless solution was stirred at room temperature for 1 h and turned yellow. The solution was added to a suspension of $ZrCl_4(THF)_2$ (1.68 g, 4.46 mmol) in 10 mL of THF. During the addition the solid dissolved to give a light orange solution. The reaction mixture was left under mild reflux for 4 h. During this time a yellow precipitate was formed. The mixture was then allowed to cool to room temperature and it was filtered. The yellow solid was extracted with dichloromethane, filtered and taken to dryness (0.98 g, 41%). Crystals were obtained from slow evaporation of dichloromethane. NMR ($CDCl_3$): ^{1}H δ(ppm) 7.35–7.10 (b, 10H, Ph), 4.64 (d, 2H, $J_{HH} = 13.7$ Hz, NCH_2Ph), 4.26 (d, 2H, $J_{HH} = 13.7$ Hz, NCH_2Ph), 4.22 (d, 2H, $J_{HH} = 12.6$ Hz, NCH_2), 3.68 (td, 2H, $J_{HH} =$ 11.7 Hz, $J_{HH} = 4.6$ Hz, NCH_2), 3.47 (td, 2H, $J_{HH} =$ 12.9 Hz, $J_{HH} = 2.6$ Hz, NCH_2), 3.30–3.20 (m, 2H, NCH_2), 3.09–3.03 (m, 2H, NCH_2), 2.68 (m, 2H, NCH_2), 2.53 (m, 2H, NCH_2), 2.38 (m, 2H, NCH_2), 1.82 (m, 2H, CCH_2C), 1.42 (m, 2H, CCH_2C); ^{13}C{^{1}H} δ(ppm) 132.6, 131.1, 128.3, 128.2 (Ph), 56.3, 56.2, 54.9, 53.4, 49.0 (NCH$_2$), 24.7 (CCH$_2$C). Anal. Calc. for $ZrC_{24}H_{34}N_4Cl_2(CH_2Cl_2)$: C, 48.00; H, 5.80; N, 8.96. Found: C, 47.83; H, 5.62; N, 8.71%.

(1,8-Dibenzyl-1,4,8,11-tetraazacyclotetradecane)HfCl$_2$ *(***4***)*. 1,8-Dibenzyl-1,4,8,11-tetraazacyclotetradecane (1.08 g, 2.84 mmol) was dissolved in 40 mL of THF, and a solution of LiBu (3.5 mL, 1.6 M in hexanes) was slowly added. The colourless solution was stirred at room temperature for 1 h and turned yellow. The solution was added to a suspension of $HfCl_4(THF)_2$ (1.31 g, 2.84 mmol) in 5 mL of THF. During the addition the solid dissolved to give a light orange solution. The reaction mixture was left under mild reflux for 4 h. During this time a yellow precipitate was formed. The mixture was then allowed to cool to room temperature and it was filtered. The yellow solid was extracted with dichloromethane, filtered and the concentrated solution was stored at −20°C to give a white-crystalline solid (0.69 g) in 40% yield. NMR (CD_2Cl_2): ^{1}H δ(ppm) 7.40–7.20 (b, 10H, Ph), 4.61 (d, 2H, $J_{HH} = 13.6$ Hz, NCH_2Ph), 4.28 (d, 2H, $J_{HH} = 13.6$ Hz, NCH_2Ph), 4.18 (m, 2H, NCH_2), 3.87 (td, 2H, $J_{HH} = 11.3$ Hz, $J_{HH} =$ 4.5 Hz, N–CH_2), 3.52 (td, 2H, $J_{HH} = 12.7$ Hz, $J_{HH} =$ 2.9 Hz, NCH_2), 3.41–3.35 (m, 2H, NCH_2), 3.31–3.23 (m, 2H, NCH_2), 2.93 (m, 2H, NCH_2), 2.67 (m, 2H, NCH_2), 2.48 (m, 2H, NCH_2), 1.90 (m, 2H, CCH_2C), 1.45 (m, 2H, CCH_2C); ^{13}C{^{1}H} δ(ppm) 133.1, 131.5, 128.7, 128.5 (Ph), 57.0, 56.1, 55.1, 49.4 (NCH$_2$), 25.6 (CCH$_2$C). ^{13}C{^{1}H} ($CDCl_3$) δ(ppm) 132.7, 130.8, 128.4, 128.2 (Ph), 57.2, 56.5, 55.5, 53.4, 49.1 (NCH$_2$), 25.4 (CCH$_2$C). Anal. Calc. for $HfC_{24}H_{34}N_4Cl_2(CH_2Cl_2)$: C, 42.12; H, 5.09; N, 7.86. Found: C, 41.84; H, 5.34; N, 7.58%.

*4,11-Lithium-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (***6***)*. Two equivalents of 1.6 M solution of LiBu in hexanes (1.3 ml; 2.10 mmol) were added dropwise, at −40 °C, to a stirred solution of 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane **5** (0.24 g, 1.05 mmol) in 20 mL of toluene. The solution was allowed to warm up to room temperature and was then evaporated to dryness to give a yellow oil. Further drying afforded a pale yellow solid in quantitative yield. NMR (C_6D_6): ^{1}H δ(ppm) 3.54 (m, 2H, NCH_2), 3.35 (m, 2H, NCH_2), 3.16 (m, 2H, NCH_2), 2.84 (m, 2H, NCH_2), 2.47 (m, 8H, NCH_2), 2.31 (m, 4H, NCH_2), 1.81 (m, 2H, CCH_2C), 1.27 (m, 2H, CCH_2C). ^{13}C{^{1}H} δ(ppm). 60.5, 58.7, 57.7, 55.9, 51.9 (NCH$_2$), 32.2 (CCH$_2$C).

*4,11-Trimethylsilyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (***7***)*. $SiMe_3Cl$ (0.35 mL, 2.71 mmol) was added to a stirred solution of **6** (0.28 g; 1.18 mmol) in 20 mL of toluene at −30 °C. The solution was allowed to warm and was stirred for 2 h at room temperature. The solution was then filtered and the solvent evaporated to dryness leading to an off-white oil that was further dried to give a white solid in quantitative yield. NMR (C_6D_6): ^{1}H δ (ppm) 4.00–3.94 (m, 2H, $H^{7,14}$), 3.02–2.97 (m, 2H, $H^{7,14}$), 2.87–2.82 (m, 2H, $H^{2,9}$ or $H^{3,10}$), 2.66–2.64 (m, 2H, $H^{2,9}$ or $H^{3,10}$), 2.60–2.46 (m, 8H, $H^{15,16}$ and $H^{3,10}$ or $H^{2,9}$), 2.44–2.42 (m, 2H, $H^{5,12}$), 2.33–2.25 (m, 2H, $H^{5,12}$), 1.55 (m, 4H, $H^{6,13}$), 0.12 (s, 18H, CH_3). ^{13}C{^{1}H} δ (ppm) 63.8 ($C^{2,9}$ or $C^{3,10}$ or $C^{15,16}$), 55.2 ($C^{2,9}$ or $C^{3,10}$ or $C^{15,16}$), 54.1 ($C^{5,12}$), 48.7 ($C^{2,9}$ or $C^{3,10}$), 45.5 ($C^{7,14}$), 31.7 ($C^{6,13}$), 0.2 (SiMe_3). Anal. Calc. for $C_{18}H_{42}N_4Si_2$: C, 58.32; H, 11.41; N, 15.11. Found: C, 57.98; H, 12.41; N, 16.21% (see Chart 1)

(1,4,8,11-Tetraazabicyclo[6.6.2]hexadecane)ZrCl$_2$ *(***8***)*. A solution of LiBu in hexanes (1.6 ml; 2.56 mmol) was added dropwise, at −40 °C, to a stirred solution of 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane **6** (0.28 g, 1.23 mmol) in 20 mL of THF. The solution was allowed to

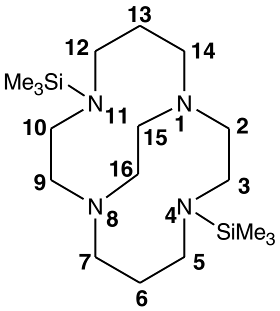


Chart 1.

warm up to room temperature and then added to a suspension of $ZrCl_4(THF)_2$ (0.47 g; 1.24 mmol) in 20 mL of THF. The mixture was refluxed overnight and a precipitate formed. After cooling to room temperature, the solvent was removed under reduced pressure. The solid residue obtained was extracted with toluene (40 mL) and the solution evaporated to give a white solid (0.15 g; 0.38 mmol). Yield: 31%. NMR (CD_2Cl_2): ^{1}H δ(ppm) 3.34–3.04 (m, 4H, NCH_2), 2.97–2.59 (m, 8H, NCH_2), 2.44–2.19 (m, 4H, NCH_2), 2.12–1.90 (m, 4H, NCH_2), 1.61–1.51 (m, 2H, NCH_2), 1.40–1.26 (m, 2H, NCH_2). ^{13}C δ (ppm), 59.5, 59.4, 52.3, 47.9, 43.4 (NCH$_2$), 24.5 (CCH$_2$C).

*(1,4,8,11-Tetraazabicyclo[6.6.2]hexadecane)HfCl$_2$ (**9**).* A stirred solution of 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane **6** (0.23 g, 1.02 mmol) in 20 mL of THF, at −40 °C, was treated with a 1.6 M solution of LiBu in hexanes (1.4 mL; 2.24 mmol). The solution was allowed to raise to room temperature and was then slowly added to a suspension of $HfCl_4(THF)_2$ (0.48 g; 1.03 mmol) in 20 mL of THF. The mixture was refluxed overnight and a precipitate formed. Upon cooling to room temperature the solvent was removed and the solid residue obtained was extracted in toluene (40 mL). The solvent was removed under reduced pressure to give a white solid (0.29 g; 0.61 mmol). Yield: 60%. NMR (CD_2Cl_2): ^{1}H δ(ppm) 3.33–3.04 (m, 4H, NCH_2), 2.94–2.58 (m, 8H, NCH_2), 2.45–2.23 (m, 4H, NCH_2), 2.11–1.85 (m, 4H, NCH_2), 1.65–1.50 (m, 2H, CCH_2C), 1.41–1.26 (m, 2H, CCH_2C). ^{13}C{^{1}H} δ(ppm), 59.5, 59.4, 52.2, 47.9, 43.4 (NCH$_2$), 24.5 (CCH$_2$C).

3.2. X-ray diffraction experimental determination

Crystallographic and experimental details of data collection and crystal structure determinations for the two compounds are given in Table 3. Suitable crystals of complexes **3** and **4** were mounted on a Bruker AXS-KAPPA APEX II diffractometer using graphite monochro-

Table 3
Crystal data and structure refinement for **3** and **4**

Compound	**3**	**4**
Empirical formula	C25 H36 Cl4 N4 Zr1	C25 H36 Cl4 N4 Hf1
Formula weight	625.60	712.87
Temperature (K)	130	130
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	*P*2/*n*	*P*2/*n*
Unit cell dimensions		
a (Å)	13.1498(9)	13.1212(3)
b (Å)	7.5860(5)	7.587(2)
c (Å)	13.7050(10)	13.688(4)
β (°)	100.837(3)	100.928(8)
Volume (Å^3)	1342.75(8)	1337.0(2)
Z	4 (half molecule)	4 (half molecule)
Calculated density (g m^{-3})	1.547	1.769
Absorption coefficient (mm^{-1})	0.83	4.320
F (000)	644	708
Crystal size (mm)	0.1 × 0.1 × 0.2	0.01 × 0.01 × 0.05
Crystal morphology	Parallelepiped	Parallelepiped
Colour	Yellow	White
Theta range for data collection (°)	2.0–32.00	2.0–28.7
Limiting indices	$-19 \leqslant h \leqslant 16$; $-8 \leqslant k \leqslant 11$; $-16 \leqslant l \leqslant 20$	$-17 \leqslant h \leqslant 14$, $-9 \leqslant k \leqslant 10$, $-18 \leqslant l \leqslant 15$
Reflections collected/unique [R_{int}]	13320/4632 [0.0555]	7852/3361 [0.1387]
Completeness to theta (%)	98.7 ($\theta = 27.47$)	99.4 ($\theta = 24.97$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4632/0/156	3361/0/156
Goodness-of-fit on F^2	1.055	0.993
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.108$	$R_1 = 0.0889$, $wR_2 = 0.198$
R indices (all data)	$R_1 = 0.0678$, $wR_2 = 0.1321$	$R_1 = 0.1377$, $wR_2 = 0.2179$
Extinct.coefficient	0.032	None
Absorption correction	Multiscan	Multiscan
Largest difference in peak and hole (e Å^{-3})	1.40 and −0.75	7.68 and −1.72

mated Mo Kα radiation ($\lambda = 0.71069$ Å). Data were collected at 130 K using omega scans of 0.5° per frame and a full sphere of data were collected. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS. Structure solution and refinement were performed using direct methods with program SIR97 [35] and SHELXL [36], both included in the package of programs WINGX-Version 1.70.01 [37]. Non-hydrogen atoms were refined anisotropically. All hydrogens were inserted in idealised positions and allowed to refine riding in the parent carbon atom.

Compound **3** crystallises in the monoclinic space group $P2/n$, with half molecule in the asymmetric unit and one equivalent of co-crystallised dichloromethane.

The poor diffracting power and crystal quality of compound **4** (as seen in the R_{int} value obtained) prevented the final refinement to lower R values. The residual high electron density, localized almost along the rotation axis can be seen as a sign of pseudo-symmetry or probable twinning. Analysing the crystal data, a refinement with two components in a twinning refinement was tried but gave no satisfactory results. Refinement on $P2_1/n$ was also attempted but never gave satisfactory results. With the quality of the data we can conclude that the molecular structure is with no doubt the one presented in the paper. Search for a new batch of crystals are underway to improve the quality of the results.

Torsion angles, mean square planes and other geometrical parameters were calculated using SHELX [36] as well as more experimental details are given in the Supplementary Material. Illustrations of the molecular structures were made with ORTEP3 [38].

4. Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 603066 for complex **3** and 603067 for complex **4**. These may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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