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# Crystal structure of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene and of the complex of its zwitterionic form with neodymium(III) nitrate

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*p*-Chloro-*N*-benzylhexahomotriazacalix[3]arene reacts with neodymium(III) nitrate to form a 1 : 1 complex in which the cation is bound to the three phenoxide oxygen atoms and to three bidentate nitrate ions. In the uncomplexed ligand, the three phenolic oxygen atoms form hydrogen bonds with the nitrogen atoms, whereas, in the complexed form, the three amine groups are transformed into ammonium cations by intramolecular transfer of protons (zwitterionic form) and form hydrogen bonds with the complexed phenoxide groups. The formation of this complex is peculiar among other lanthanide complexes of calixarenes since it occurs without addition of a basic agent, other than the amine groups included in the ligand molecule itself.

Complexation of trivalent lanthanide ions is widely investigated due to its relevance to some important domains including lanthanide/actinide separation during nuclear fuel reprocessing, catalysis, design of luminescent probes, NMR imaging and other biomedical applications. The presently well-known metal complexing properties of calixarenes led to many developments aimed at complexing lanthanide ions.

The crystal structures of the complexes formed by various rare-earth ions and *p*-*tert*-butylcalix[*n*]arenes ($n = 4, 6, 8$) have been described by Harrowfield and co-workers.[1] In all cases, the complexes are obtained in a basic medium and the calixarene is partly deprotonated (which increases its solubility in common organic solvents). With $n = 8$, both mono- and binuclear complexes can be formed, in which the cations are located inside the oxygen atom array of the calixarene, whereas an 'external' complex is formed for $n = 6$ and a dimeric species for $n = 4$. The photophysical properties and crystal structure of the lanthanide complexes of triply deprotonated *p*-*tert*-butylcalix[5]arene have also been investigated.[2] Europium(III) forms a dimeric complex with *p*-*tert*-butyldihomooxacalix[4]arene, in which both the four phenolic oxygen atoms (three of which are deprotonated) and the ether oxygen atom are coordinated,[3] whereas *p*-*tert*-butylhexahomotrioxacalix[3]arene gives dimeric complexes in which the three ether oxygen atoms are also coordinated in the case of the largest trivalent lanthanide cation, $La^{3+}$.[4] In this case, the metal-binding affinity was inferred from the strength of the base needed for stoichiometric metal binding.

The smaller $Lu^{3+}$ cation is complexed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) whereas $La^{3+}$ complexation is incomplete even with a large excess of $NEt_3$. For these cations, unusual coordination geometries were observed with *p*-*tert*-butylhexahomotrioxacalix[3]arene, as was also observed in the case of the uranyl complex of this ligand.[5] Many calixarene derivatives with grafted complexing arms, either on the upper or lower rim, have also been reported to complex lanthanide ions. In these cases the phenolic oxygen atoms do not bind to the cation.[6]

Recently, we began an investigation of the complexing properties of hexahomotriazacalix[3]arenes, which were first synthesized some years ago.[7] With respect to calixarenes, the azacalixarenes are less rigid, possess two different kinds of potential binding sites bear various substituents on the amine nitrogen atom. The related bifunctional azacalix[4]arene betaine molecule, which possesses a large potential for guest binding, has recently been described.[8] As a first step in this work, we report herein the crystal structures of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene **1** (Scheme 1) and of its mononuclear complex formed in a neutral medium with neodymium nitrate, **2**. Some of us recently reported the crystal structure of a *p*-xylylene-bridged azacalixarene including four phenolic units.[9] To the best of our knowledge, only one other crystal structure has been reported, up to now, in this family of compounds.[10]

## Experimental

### Synthesis

***p*-Chloro-*N*-benzylhexahomotriazacalix[3]arene 1.** A mixture of 2,6-bis(hydroxymethyl)-4-chlorophenol (10.05 g, 53.3 mmol) and benzylamine (5.68 g, 53.0 mmol) in 300 ml of xylene was refluxed for 72 h, and the water generated was removed during the course of the reaction with a Dean–Stark condenser. The xylene was then evaporated and the residual oily material was chromatographed on silica gel with $CH_2Cl_2$ as eluent. Recrystallization of the resulting powder from a mixture of cyclohexane and $CH_2Cl_2$ afforded the desired material as a white powder (4.57 g, yield 33%). Mp 224–226 °C. $^1H$ NMR (270 MHz, $CDCl_3$) in ppm referenced to TMS: $\delta$ 11.2 (bs, 3H, OH), 7.23 (s, 15H, ArH), 6.95 (s, 6H, ArH), 3.64 (s, 12H, $CH_2N$), 3.59 (s, 6H, $CH_2$). FAB-MS: *m*/*z* 778 $(M + H)^+$. Anal., calc. for $C_{45}H_{42}Cl_3N_3O_3$: C, 69.36; H, 5.43; N, 5.39; found: C, 69.37; H, 5.48; N, 5.36%. Slow evaporation of a $CHCl_3$ : $CH_3CN$ (1 : 1) solution gave colourless single crystals of **1** suitable for X-ray crystallography.

**Table 1** Crystal data and structure refinement details

| | 1 | 2 |
|---|---|---|
| Empirical formula | $C_{45}H_{42}Cl_3N_3O_3$ | $NdC_{50}H_{47}Cl_3N_7O_{12}$ |
| $M$/g mol$^{-1}$ | 779.17 | 1188.54 |
| $T$/K | 123(2) | 100(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 11.941(1) | 12.8151(6) |
| $b$/Å | 30.824(3) | 14.1674(9) |
| $c$/Å | 10.4671(4) | 27.891(2) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 94.297(5) | 98.938(3) |
| $\gamma$/° | 90 | 90 |
| $V$/Å$^3$ | 3842(3) | 5002(3) |
| $Z$ | 4 | 4 |
| $\mu$/mm$^{-1}$ | 0.285 | 1.269 |
| Reflections collected | 24486 | 29856 |
| Independent reflections | 6409 | 9210 |
| Observed reflections [$I > 2\sigma(I)$] | 4269 | 6995 |
| $R_{int}$ | 0.107 | 0.094 |
| $R_1$ | 0.067 | 0.059 |
| $wR_2$ | 0.144 | 0.123 |

**Neodymium complex $(Nd^{3+})$1$(NO_3^-)_3{\cdot}C_5H_5N$ 2.** **1** (0.19 g, 0.25 mmol) was dissolved in 40 ml of $CHCl_3:CH_3CN$ (1 : 1) and a solution of $Nd(NO_3)_3{\cdot}6H_2O$ (in excess: 0.3 g, 0.7 mmol) in 15 ml of $CH_3CN$ added dropwise. After stirring for two hours, the solution was allowed to evaporate and the residue was recrystallized several times in pyridine, leading finally, upon slow evaporation, to colourless single crystals of **2** suitable for X-ray crystallography. This complex was characterized using mass spectrometry in electrospray conditions (SPRITE HP apparatus). Three mass peaks were detected: $m/z$ 1047.2, corresponding to $[(C_{45}H_{42}O_3N_3Cl_3)Nd(NO_3)_2 + 4H^+]$; 984.2, corresponding to the loss of a first nitrate ion; 921.2, corresponding to the loss of the second nitrate ion.

### Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer[11] using graphite-monochromated Mo-$K_\alpha$ radiation (0.71073 Å). The crystals were introduced in Lindemann glass capillaries with a protecting 'Paratone' oil (Exxon Chemical Ltd.) coating. The data were processed with the HKL package.[12] The structures were solved by direct methods with SHELXS-97[13] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on $F^2$ with SHELXL-97.[14] No absorption correction was applied for **1**, the product $\mu\langle d\rangle$ being lower than 0.1. Absorption effects in **2** were corrected empirically with the MULABS program from PLATON.[15] Hydroxyl protons in **1** and those of the ammonium groups in **2** were introduced as found on the Fourier difference map, whereas all other hydrogen atoms in both compounds were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. All non-hydrogen atoms were refined anisotropically in both structures. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn using SHELXTL.[16] All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference number 186/1758.

See http://www.rsc.org/suppdata/dt/a9/a908423a/ for crystallographic files in .cif format.

## Results and discussion

The asymmetric unit in **1** is composed of one molecule, which does not assume a regular trigonal symmetry (Fig. 1). The overall shape, when the benzyl substituents are disregarded, is that of a shallow cup, as already observed in the related, crystallographically symmetric (3*m*), compound with *p*-methyl and *N*-methoxycarbonylmethyl substituents (**3**)[10] and also in *p*-*tert*-butylhexahomotrioxacalix[3]arene (**4**),[17] shown in Scheme 1. This shape can be characterized by the dihedral angles between the three phenolic rings and the mean plane defined by atoms O(1), O(2) and O(3). The values of these angles in the present case are 23.6(1), 68.4(1) and 22.2(1)°, indicating that one ring is far more bent than the other two. This conformation is far more irregular than that observed in **3** (26.75° for the three rings) or in **4** [31.6, 39.7, 39.7° {mean value 37(4)°}] and its uranyl ion complex **5** [48.1(3)–57.7(2)° {mean value for the two forms described 52(3)°}; the more pronounced cupping is due to the cation located at the centre of the $O_3$ ring].[5] Two *N*-benzyl substituents are located 'above' the mean plane of the molecule and one 'below', their positions presumably being the result of stacking interactions.

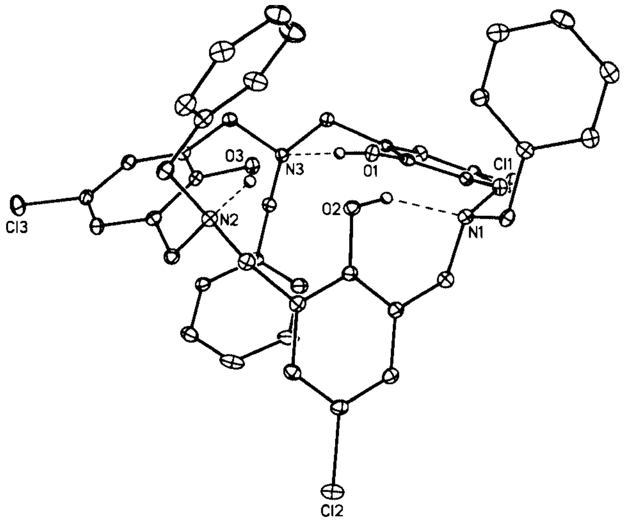
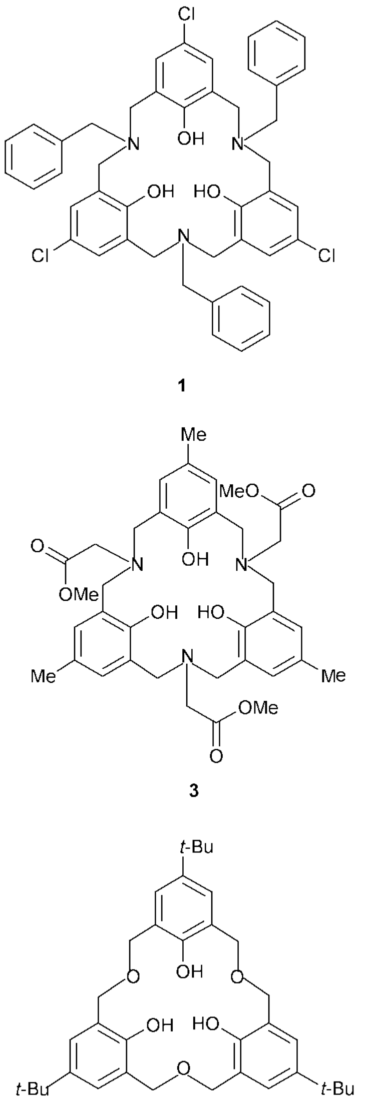


**Fig. 1** View of molecule **1**. Hydrogen bonds in dashed lines. Hydroxyl protons represented as small spheres of arbitrary radii. Other hydrogen atoms omitted for clarity.

As a consequence of the rather flat geometry of the cavity in **1**, no solvent molecule is included, which is an otherwise common trend of calixarenes in *cone* conformation. *Cone* conformations are stabilized by intramolecular hydrogen bonds and this is also the case in **3** and **4**. However, the lengthening of these bond distances in **3** and **4** with respect to those in usual calixarenes was thought to be indicative of a weakening of the OH(phenol) · · · O(phenol) bonds due to alternative OH(phenol) · · · N or OH(phenol) · · · O(ether) bonds. In the present case, both distances and angles involving the phenolic protons indicate that the OH(phenol) · · · N bonds are predominant, with a mean O · · · N distance of 2.7(1) Å and a mean O–H · · · N angle of 151(4)° (Table 2), comparable to those observed in a *p*-xylylene-bridged azacalixarene including four phenolic units.[9] These bonds appear strong (two of them in particular); it may be assumed that they do not result in a molecular rigidity as strong as that observed in calixarenes, since they do not link the phenolic rings between them, which may explain the irregular conformation described above. Conversely, the O · · · O distances [mean value 2.86(9) Å] and especially the low values of the O–H · · · O angles [mean value 121(6)°] do not indicate as strong hydrogen bonding between the phenolic oxygen atoms. The situation is somewhat different in **3**, in which the mean O · · · O and O · · · N distances are more similar (2.900 and 2.912 Å, respectively).

The asymmetric unit in the neodymium complex **2** comprises one complex and one pyridine molecule, giving the formula $(Nd^{3+})$**1**$(NO_3^-)_3{\cdot}C_5H_5N$. As illustrated in Fig. 2, the cation, bound to the three phenolic oxygen atoms and to three bidentate nitrate ions, is located 1.591(2) Å 'above' the plane defined by the three phenolic oxygen atoms. The values of the three



**Scheme 1** *p*-Chloro-*N*-benzylhexahomotriazacalix[3]arene **1**, *p*-methyl-*N*-methoxycarbonylmethylhexahomotriazacalix[3]arene **3** and *p*-*tert*-butylhexahomotrioxacalix[3]arene **4**.

dihedral angles between the phenolic rings and the mean plane defined by the three phenolic oxygen atoms are 20.6(1), 49.3(2) and 2.3(2)°: this conformation is even more irregular than that in **1**, with the aromatic ring bound to O(3) nearly parallel to the mean plane of the coordinating atoms. This is at variance with the conformation modification presented by **4** upon uranyl complexation, which corresponds to an expansion of the oxygen atom array, necessary to accept the cation in its centre. The most interesting feature of the structure of **2** lies with the proton locations. Molecule **1** presents both a proton-donating phenolic group and a proton-accepting tertiary amine group. The crystal structure of **1**, as well as that of **3**, shows that, in the uncomplexed forms of these ligands, the phenolic protons remain on the oxygen atoms. In the neodymium-complexed form **2**, the protons are located on the nitrogen atoms, the O–H···N hydrogen bonds in **1** being replaced by $(N–H)^+\cdots O^-$ bonds in **2**, *i.e.* the coordinating species is the zwitterionic form of **1**, as schematized in the reaction equation (Scheme 2). The hydrogen bond pattern is farther from trigonal symmetry than in **1**, since O(3) is bound to two protons whereas O(2) is not bound. This observation concerning the formation of ammonium groups is particularly interesting in relation to the experimental conditions of complexation. As indicated above, complexation of lanthanide cations (as well as uranyl cations) by calixarenes unsubstituted on their lower rim requires the presence of a basic agent ($NEt_3$,[1] DABCO,[4] imidazole[4] and $K_2CO_3$[1e] have been used) which is also necessary to solubilize the calixarene in organic solvents. **1** and other azacalixarenes present the peculiarity of including the basic agent in their molecular framework itself. Furthermore, in the case of **1**, the acidity of the phenolic proton is enhanced by the chlorine substituent. As a result, no extra basic agent is necessary to promote the complexation, which is accompanied by an intramolecular transfer of three protons, the acid–base equilibrium being displaced towards the phenoxide–ammonium form. Some preliminary results show that uranyl complexation by **1** and other azacalixarenes occurs also without any extra base being added. Hampton *et al.* have previously reported that *p*-chlorooxacalix[3]arene complexes $Na^+$ ions in the absence of base,[18] which suggests that the acid-enhancing effect of chlorine may be sufficient and the amine functions unnecessary for such phenomena to be observed. Conversely, preliminary results

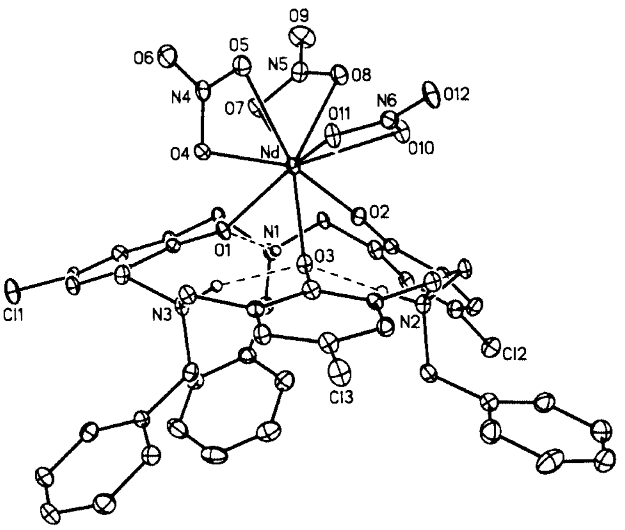
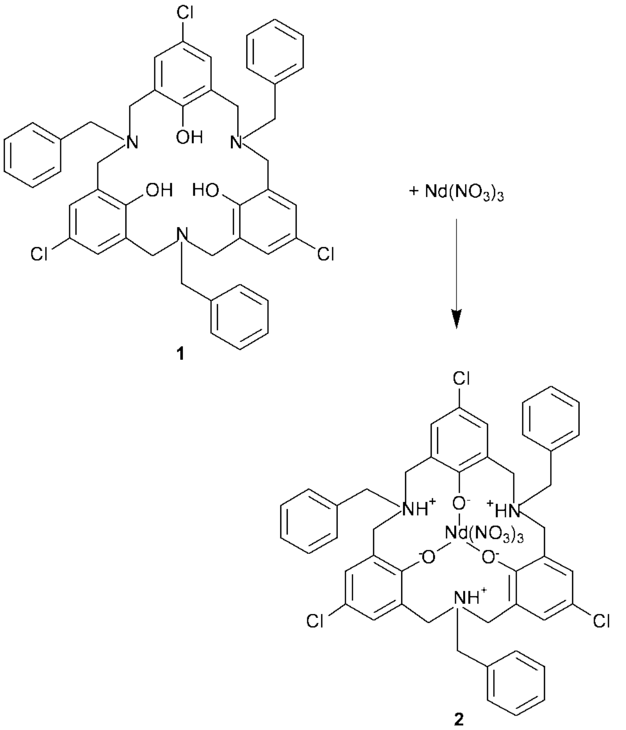


**Fig. 2** View of the complex molecule in **2**. Hydrogen bonds in dashed lines. Protons of the ammonium groups represented as small spheres of arbitrary radii. Other hydrogen atoms and solvent molecule omitted for clarity.



**Scheme 2** Formation of complex **2** from **1** and $Nd(NO_3)_3$.

**Table 2** Selected bond distances (Å) and angles (°)

| | | | | | |
|---|---|---|---|---|---|
| Hydrogen bonds | | | | | |
| **1** | | | | | |
| O(1)···N(3) | 2.834(4) | H···N(3) | 2.125 | O(1)–H···N(3) | 151.4 |
| O(2)···N(1) | 2.652(4) | H···N(1) | 1.807 | O(2)–H···N(1) | 147.1 |
| O(3)···N(2) | 2.674(4) | H···N(2) | 1.784 | O(3)–H···N(2) | 154.7 |
| **2** | | | | | |
| N(1)···O(1) | 2.880(4) | H···O(1) | 2.170 | N(1)–H···O(1) | 137.4 |
| N(2)···O(3) | 2.717(4) | H···O(3) | 1.898 | N(2)–H···O(3) | 144.4 |
| N(3)···O(3) | 2.754(4) | H···O(3) | 1.983 | N(3)–H···O(3) | 139.9 |
| Neodymium environment in **2** | | | | | |
| Nd–O(1) | 2.334(4) | Nd–O(4) | 2.562(4) | Nd–O(8) | 2.595(4) |
| Nd–O(2) | 2.298(4) | Nd–O(5) | 2.540(4) | Nd–O(10) | 2.566(4) |
| Nd–O(3) | 2.399(4) | Nd–O(7) | 2.578(4) | Nd–O(11) | 2.628(4) |
| O(1)–Nd–O(2) | 83.1(1) | O(1)–Nd–O(3) | 74.6(1) | O(7)–Nd–O(8) | 49.4(1) |
| O(2)–Nd–O(3) | 78.3(1) | O(4)–Nd–O(5) | 50.2(1) | O(10)–Nd–O(11) | 48.9(1) |

obtained with a ligand analogous to **1**, having the chloro substituent replaced by a methyl group, indicate that reaction with uranyl ions occurs without a base being added, which suggests that the amine group is also sufficient in itself to promote the reaction. Unfortunately, it has not been possible up to now to grow single crystals of the complex species obtained with **1** in a basic medium (NEt$_3$ or DABCO), for comparison purposes. The absence of positive charges on the macrocycle, as a consequence of ammonium ion deprotonation by such basic agents, is likely to lead to complexes different from **2**. In particular, the absence of electrostatic repulsions between Nd$^{3+}$ and NH$^{+}$ could permit a closer approach of the former.

The three Nd–O(phenoxide) distances in **2** are nearly equal [mean value 2.34(4) Å] with a value in good agreement with other Nd–O$^{-}$ bonds.[19] The coordination sphere of Nd$^{3+}$ is completed by three bidentate nitrate ions, with a mean Nd–O(nitrate) distance of 2.58(3) Å, in good agreement with previously published values.[19] The coordination number of Nd$^{3+}$ in **2** is nine, which is usual for early lanthanoids. Two ideal coordination polyhedron geometries have been described for this coordination number; the capped square antiprism and the tricapped trigonal prism.[20] The coordination polyhedron in **2**, although far from an ideal geometry, can nevertheless be described as a distorted tricapped trigonal prism. The three phenoxide oxygen atoms define the base of the prism, with nearly equal O···O distances ranging from 2.869(6) to 3.072(6) Å; three of the nitrate oxygen atoms [one from each ion: O(5), O(8) and O(11)] define the second base, which is far from regular, with O···O distances ranging from 2.872(6) to 3.914(6) Å and the three remaining nitrate oxygen atoms [O(4), O(7) and O(10)] are the caps. The dihedral angle between the two bases is 26.0(2)° and that between the plane defined by the three capping atoms and the first base is 4.6(1)°. The second base appears particularly distorted, as a result of the small-bite nature of nitrate ions, which also forces the capping atoms to be nearer to the second base than to the first. The coordination geometry of lanthanide ions (La$^{3+}$, Pr$^{3+}$, Eu$^{3+}$, Tm$^{3+}$, Lu$^{3+}$) in their complexes with *p*-*tert*-butylcalix[*n*]arenes ($n = 4$, 6, 8) is very far from the present one, with coordination numbers of 7 or 8. In all those cases, except the mononuclear europium complex of *p*-*tert*-butylcalix[8]arene,[1e] no counter-ion is bound to the cation, the coordination sphere being completed by solvent molecules (DMF, DMSO). The complexes of La$^{3+}$ and Lu$^{3+}$ with *p*-*tert*-butylhexahomotrioxacalix[3]arene obtained by Daitch *et al.*[4] in the presence of excess base, with the general formula [M$^{3+}$(L$^{3-}$)(DMSO)]$_2$ (where L$^{3-}$ is the trianion of the ligand), display a coordination mode and geometry completely different from the present ones, with μ-aryloxide bridges and at least one of the ether oxygen atoms coordinated.

The geometry adopted by the benzyl substituents in **2** is different from that in **1**, which is likely due to the steric hindrance associated with the Nd(NO$_3$)$_3$ group, and also to the conformational change in the calixarene core. In the complex, the three groups are located 'below' the mean plane of the molecule, which implies that, with respect to **1**, two amine groups have undergone an inversion. Such an inversion, which is known to have a low activation barrier, has previously been observed in triazacalixarenes by $^{1}$H NMR spectroscopy at room temperature.[10]

Both the autodeprotonation and the conformational changes evidenced in the present work are indicative of the potential of this and related ligands for cation complexation, the investigation of which is in progress.

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