Reactions of *t*Bu-Calix[6]arene with Lanthanide Triflates: Synthesis and Crystal Structure Determination of Novel Bimetallic Calixarene Complexes of La, Sm and Yb

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The reactions of *t*Bu-calix[6]arene (H_6L) with $Ln(O_3SCF_3)_3$ (Ln = La, Sm, Yb) were used to isolate $[\{La(O_3SCF_3)(pyridine)_7\}_2H_2L]$ (**1**), $[\{Sm(O_3SCF_3)(pyridine)_4\}_2H_2L]$ (**2**) and $[\{Yb(O_3SCF_3)(terpyridine)(pyridine)\}_2H_2L]$ (**3**), three novel bimetallic calixarene complexes of the lanthanides. The solid state structures of **2** and **3** were determined by X-ray crystallography revealing compounds where the two metal cations are anchored on both sides of the macrocycle in the 1,2,3-alternate conformation. Compounds **1–3** are the first bis-alkoxy triflate species $\{M(OR)_2(O_3SCF_3)\}$ to be characterized in lanthanide coordination chemistry.

Introduction

Calixarenes consist of phenolic units linked by methylene bridges into a macrocyclic arrangement. These molecules, and their various substituted derivatives, make up one of the most important families of supramolecular chemistry.[1] From a coordination chemistry point of view, the parent unsubstituted calixarenes can be considered as large, flexible polyalkoxide ligands whose size and flexibility vary with the number of their phenolic units.[2] The interest and fascinating potential of this class of molecules for the design of new metal complexes is well illustrated by calix[6]arene, which has already been used for the synthesis of compounds containing one,[3] two,[4] three,[5] and even five[6] metal cations. Moreover, like all calix[$n > 5$]arenes, it has a tendency to act as a "cluster keeper"[2c,7] and has been used to stabilise polymetallic species of uranium,[2c] titanium[8] and potassium.[9]

Although the donor properties of the calixarenes have long prompted the interest of coordination chemists in their search for new ligands well-suited for the large and hard cations of the f-elements,[2d] it seems that the coordination chemistry of calix[6]arene as a ligand for the lanthanide family has not yet been investigated in detail. In fact the europium complex $[Eu(H_4L)(OH)(dmf)_6]$ (H_6L = *t*Bu-calix[6]arene) is the only 4f-metal complex of a calix[6]arene derivative whose crystal structure has been solved.[3a] This is all the more surprising, as the supposed most usual 1,2,3-alternate conformation of this macrocycle suggests that it should be an ideal platform for the complexation of two trivalent cations on both sides of the inverted cone (Figure 1). The only example of a calix[6]arene derivative complexing two metal cations is the dimeric $[UO_2(H_2L)]_2$,[4] where the uranyl units (UO_2^{2+}) are sandwiched between the two organic macrocycles in a distorted pinched-cone conformation.

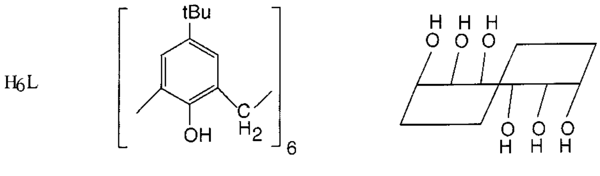

Figure 1. Schematic representation of the 1,2,3-alternate conformation of H_6L

In order to improve the knowledge of the use of H_6L as a ligand towards the lanthanides and to test the possibility of complexing two metal cations on both its coordination sites, we set out to study the reactions of H_6L with lanthanide triflates. We report herein the synthesis of $[\{La(O_3SCF_3)(pyridine)_7\}_2H_2L]$ (**1**), $[\{Sm(O_3SCF_3)(pyridine)_4\}_2H_2L]$ (**2**) and $[\{Yb(O_3SCF_3)(terpyridine)(pyridine)\}_2H_2L]$ (**3**). The solid state structures of **2** and **3** have been determined by X-ray crystallography. Compounds **1−3** are the first bis-alkoxy triflate species $\{M(OR)_2(O_3SCF_3)\}$ to be characterized in lanthanide coordination chemistry.

Results and Discussion

Treatment of $Ln(O_3SCF_3)_3$ with H_6L in pyridine led to the formation of a pale-yellow solution of $[\{Ln(O_3SCF_3)(pyridine)_n\}_2H_2L]$ [Scheme 1; Ln = La (**1**), Sm (**2**)]. In the case of ytterbium, an insoluble yellow powder, probably closely related to **1** and **2**, was instantly formed by the reaction. This precipitate was insoluble in hot pyridine and had a tendency to decompose in the other organic solvents.[10] However, it could be successfully dissolved in a mixture of terpyridine and pyridine to afford a bright orange solution of the complex $[\{Yb(O_3SCF_3)(terpyridine)(pyridine)\}_2H_2L]$ (**3**). The synthesis of **3** can

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easily be achieved from the addition of stoichiometric amounts of the three reagents in pyridine.

$$2\ \mathrm{Ln(O_3SCF_3)_3} + \mathrm{H_6L} \xrightarrow{\text{pyridine}}$$

$$[\{\mathrm{Ln(O_3SCF_3)(pyridine)}_x\}_2\mathrm{H_2L}] + 4\ [\mathrm{HNC_5H_5}][\mathrm{O_3SCF_3}]$$

(Ln = La, Sm, x = 7, 4)

$$2\ \mathrm{Yb(O_3SCF_3)_3} + \mathrm{H_6L} + \text{terpyridine} \xrightarrow{\text{pyridine}}$$

$$[\{\mathrm{Yb(O_3SCF_3)(pyridine)(terpyridine)}\}_2\mathrm{H_2L}] + 4\ [\mathrm{HNC_5H_5}][\mathrm{O_3SCF_3}]$$

Scheme 1

One difficulty we had to circumvent in order to fully characterise complexes **1**−**3** was their rapid decomposition when isolated as solids. Although the solutions of the complexes in pyridine can be kept long enough to proceed with crystallisation experiments and analyses, in the form of microcrystalline powders they invariably turned to dark green after a few hours under argon or N_2,[11] even when the samples were kept in the dark to prevent light-induced reactions. No further complexes could be isolated from this stage. This transformation, which has not yet been understood, affects **2** and **3** completely within a few hours, but is slower for **1**. This somewhat puzzling behaviour (air-sensitive complexes are usually less sensitive in the solid state than in solution) could be due to the displacement of coordinated pyridine molecules under vacuum, leading to an increased reactivity with even traces of water or air, or to a redox process leading to the degradation of the calixarene, possibly into its quinone form. As a result, all elemental analysis had to be performed on freshly isolated samples. Compared to its Sm and Yb counterparts, **1** is highly soluble in pyridine thus we did not manage to grow single crystals suitable for an X-ray analysis.[12] The exact stoichiometry of complex **1** had to be determined by mass spectrometry. The solubility of **1** in pyridine, combined with its decomposition in the other usual organic solvents, was a hindrance to its complete purification.[10] In the end, we did not manage to synthesize **1** in its elementally pure form, but only as a triflic acid containing mixture. Solutions of **2** and **3** were allowed to stand and, after a few days, crystals suitable for X-ray crystallography could be recovered. The crystal structures were solved and revealed that in both **2** and **3**, *t*Bu-calix[6]arene acts as a double-bidentate ligand that is able to bind a metal cation on its two symmetry-related coordination sites (Figure 2 and 3).

The molecular structures of **2** and **3** present similarities in the way the trivalent cations are bound to the macrocycle. The metal centres are coordinated by seven donor atoms, the coordination geometry being a distorted, capped trigonal prism.[13] Two σ-bonds are made with phenolate groups of the calixarene. The mean M−O distances are equal to 2.179(5) Å in **2** and 2.07(2) Å in **3**, in good agreement with similar bond lengths found in the literature.[14] The crystal structures of samarium and ytterbium complexes of calixarene derivatives containing an aryloxide bond have only been reported on two occasions but never yet for the parent calixarenes.[15] One unchanged triflate group makes the last σ-bond to the metal. The M−O(triflate) bonds are significantly longer than the alkoxide one and equal to 2.449(4) Å in **2** and to 2.30(1) Å in **3**. Although only a few triflate complexes of Sm and Yb have been characterized crystallographically,[16] bond lengths of that order of magnitude are to be expected from this fairly labile ligand. The rest of the coordination sphere is occupied by nitrogen ligands coming from four pyridine molecule in **2** and from one pyridine molecule and one ter-

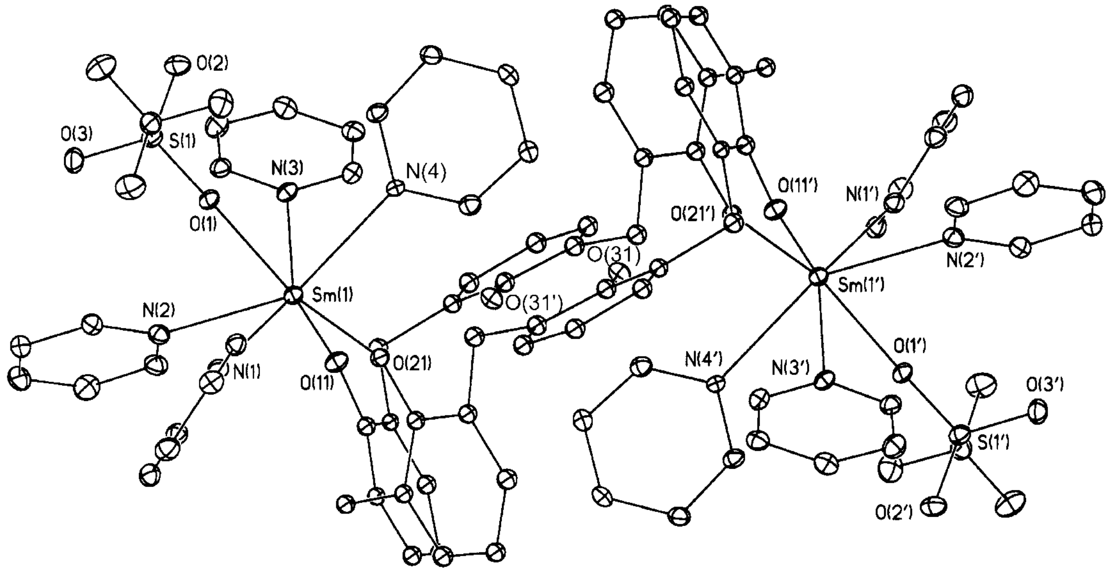

Figure 2. X-ray structure of complex **2** showing partial atom labelling; all *t*Bu groups and hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Sm(1)−O(1) 2.449(4), Sm(1)−O(11) 2.184(5), Sm(1)−O(21) 2.174(4), Sm(1)−N(1) 2.610(5), Sm(1)−N(2) 2.629(6), Sm(1)−N(3) 2.672(5), Sm(1)−N(4) 2.604(5)

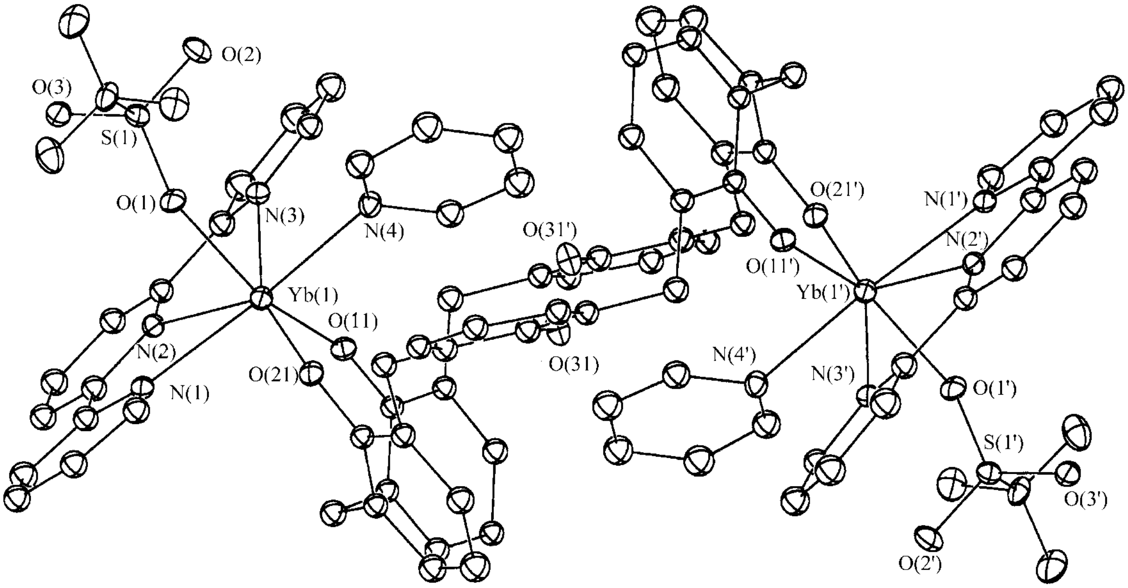

Figure 3. X-ray structure of complex **3** showing partial atom labelling; all *t*Bu groups and hydrogen atoms have been omitted for clarity; selected mean bond lengths [Å] and angles [°]: Yb(1)−O(1) 2.301(4), Yb(1)−O(11) 2.071(6), Yb(1)−O(21) 2.081(9), Yb(1)−N(1) 2.48(2), Yb(1)−N(2) 2.49(2), Yb(1)−N(3) 2.508(5), Yb(1)−N(4) 2.472(4)

pyridine ligand in **3**. The mean M−N bond lengths for the pyridine ligand are 2.63(3) Å in **2** and 2.472(4) Å in **3**, and 2.49(2) Å for the terpyridine ligand in **3**. All M−N distances are unremarkable when compared to literature data.[17] Along the series **1−3**, the number and type of N donor ligands adapt to the decreasing size of the lanthanide cation: whereas seven pyridine molecules are bound to the large La cation in **1**, only four remain on the Sm complex **2** and one in the Yb complex **3,** where the coordination sphere of the cation is completed by a terpyridine molecule. Interestingly, the replacement of three pyridine ligands in **2** by a terpyridine molecule in **3** does not lead to major differences in the coordination geometry of the two complexes, probably because the smaller bite angle imposed by the chelating ligand is balanced by the ionic radius of the smaller cation [N(1)−M−N(3) angles are equal to 147.0(1)° and 126.3(4)° in **2** and **3**, respectively]. The main crystallographic difference between **2** and **3** is the presence of two independent molecules in the asymmetric unit of **3**, both sitting on an inversion centre, thus resulting in a larger cell volume.

The organic macrocycles in **2** and **3** are deprotonated four times and both adopt the same distorted 1,2,3-alternate conformation. The presence of a hydrogen bond between O(31) and O(11′) in **2**, which is absent in **3** [O(31)−O(11′) bond lengths equal to 2.976(5) Å and 3.85(2) Å in **2** and **3**, respectively], could be one reason for the differences that can be observed in the torsion angles φ and χ[1a] of the two complexes.[18] Interestingly, the pyridine ligand bearing N(4) is located within the macrocycle in a niche that is delimited by the aromatic faces bearing O(11′) and O(21′), their methylene bridge and *t*Bu groups.[19] In this respect, the calixarene is both a first- and a second-sphere ligand of the lanthanide cation.[20]

As far as we are aware, such bis-alkoxy triflate species $\{M(OR)_2(\text{triflate})\}$ as **1−3** have not yet been encountered in the coordination chemistry of terminal lanthanide alkoxides. This new combination of ligands, where a metal is anchored by two strong alkoxide bonds to an organic platform but retains a reactive site, could be of interest especially in the field of catalysis in which f-metal alkoxides have long been renowned for their activity.[21] In this respect, calix[4]arene complexes were successfully used as models of d-metal oxide surfaces.[22] The synthesis of **1−3** further reinforces the ideas that large polyalkoxide ligands, such as calixarenes, are appropriate for the design of new metal-complex architectures, and that a rich chemistry can be built at the boundary between macrocyclic, supramolecular and coordination chemistries.

Experimental Section

General: All NMR spectra were performed on a Bruker DPX-200. ^{19}F NMR spectra were referenced internally by addition of $CFCl_3$. Elemental analyses were performed at Service de Microanalyse, I.C.S.N., C.N.R.S., 91198 Gif sur Yvette, France. All reactions were performed in a glove box under a dry N_2 atmosphere. All chemicals were purchased by Aldrich and used without further purification. H_6L was dried under vacuum for 12 hours at 323 K. Pyridine was dried on Na (CAUTION!) and distilled prior use. The mass spectrum of **1** was recorded on a ZAB HF VG-analytical F.A.B. mass spectrometer.

Synthesis of 1: $[La(O_3SCF_3)_3]$ (0.150 g, 0.256 mmol) was treated with $H_6L[6]$ (0.125 g, 0.128 mmol) in pyridine (20 mL) at 293 K for 2 hours. The colourless solution obtained was filtered, concentrated under vacuum to 5 mL and toluene was then added (5 mL). After 45 days at 253 K, the yellow powder that had deposited was separated by filtration, washed with toluene and dried under vacuum to afford $[\{La(NC_5H_5)_2(O_3SCF_3)\}_2(H_2L)]\cdot 2.7(HO_3SCF_3)$ (0.172 g, 0.076 mmol, 30%). − ^{1}H NMR: $\delta = 0.74$ (s, 18 H, *t*Bu), 1.29 (s, 36 H, *t*Bu), 2.82 (d, $J = 11$ Hz, 2 H, $Ar-CH_2-Ar$), 4.27 (d, $J = 13$ Hz, 4 H, $Ar-CH_2-Ar$), 4.28 (d, $J = 13$ Hz, 4 H, $Ar-CH_2-Ar$), 4.36 (d, $J = 11$ Hz, 2 H, $Ar-CH_2-Ar$), 7.12 (s, 12 H, ArH), 15.35 (br., 2 H, OH). − ^{19}F NMR: $\delta = -6.56$ ($CFCl_3$) − $C_{90.7}H_{102.7}F_{14.1}La_2N_4O_{20.1}S_{4.7}$ (2267.02): calcd. C 48.05, H 4.57, 2.47; found C 48.09, H 4.76, N 2.49.[23] During the course of the reaction an aliquot of the pyridine solution was taken and sent to the mass analysis: *m*/*z* = 2653.94 ($[\{La(O_3SCF_3)(pyridine)_7\}_2H_2L]$).

Synthesis of 2: $[Sm(O_3SCF_3)_3]$ (0.150 g, 0.251 mmol) was treated with $H_6L[6]$ (0.122 g, 0.125 mmol) in pyridine (20 mL) at 293 K for 2 hours. The pale-yellow solution obtained was filtered and concentrated under vacuum to 10 mL. It was then left standing for two days to afford a colourless microcrystalline powder that was filtered off, washed with cold pyridine and dried in vacuo to afford $[\{Sm(NC_5H_5)_6(O_3SCF_3)\}_2(H_2L)]\cdot 0.5(HO_3SCF_3)$ (0.204 g, 0.096 mmol, 77%). − $C_{98.5}H_{110.5}F_{7.5}N_6O_{13.5}S_{2.5}Sm_2$ (2117.87): calcd. C 55.86, H 5.26, N 3.97; found C 55.78, H 4.83, N 3.95. Several recrystallizations from pyridine enabled us to separate $[\{Sm(NC_5H_5)_3(O_3SCF_3)\}_2(H_2L)]$ from residual triflic acid (0.062 g, 0.030 mmol, 24%) − $C_{98}H_{110}F_6N_6O_{12}S_2Sm_2$ (2042.83): calcd. C 57.62, H 5.43, N 4.11; found C 58.17, H 5.62, N 3.88.[23]

Synthesis of 3: $[Yb(O_3SCF_3)_3]$ (0.150 g, 0.242 mmol) was treated with $H_6L[6]$ (0.118 g, 0.121 mmol) and terpyridine (0.057 g, 0.244 mmol) in pyridine (20 mL) at 293 K for 2 hours. The orange microcrystalline powder that formed was filtered off, washed with pyridine and dried in vacuo to afford $[\{Yb(N_3C_{15}H_{11})(O_3SCF_3)\}_2(H_2L)]\cdot(NC_5H_5)$ (0.171 g, 0.079 mmol, 65%). − $C_{103}H_{107}F_6N_7O_{12}S_2Yb_2$ (2159.23): calcd. C 57.30, H 5.00, N 4.54; found C 56.98, H 5.01, N 4.68.[23]

X-ray Crystallographic Studies: Crystal data collection was performed on a Nonius Kappa-CCD diffractometer equipped with a fibre glass collimator.

Crystal Data of 2·4(NC$_5$H$_5$): $C_{128}H_{140}F_6N_{12}O_{12}S_2Sm_2$ (2517.34), $0.14 \times 0.12 \times 0.10$ mm^3, triclinic, $P\bar{1}$, $Z = 1$, $a = 14.852(3)$, $b = 15.160(3)$, $c = 15.364(4)$ Å, $\alpha = 91.17(3)°$, $\beta = 118.85(3)$, $\gamma = 92.55(3)°$, $V = 3023(2)$ Å^3, $\rho_{calcd.} = 1.382$ g·cm^{-3}, $F(000) = 1298$, $2\theta_{max} = 51.42°$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), $\mu M_o = 1.070$ cm^{-1}, $T = 100$ K. The structure was solved by direct methods[24] and refined on F^2.[25] Of the 20805 reflections measured, 10577 were found to be independent ($R_{int} = 0.113$), 6735 of which were considered as observed [$I > 2\sigma(I)$]. All reflections were used in the refinement of the 611 parameters, leading to a final R_1 of 0.0625 and an R_{all} of 0.1205. wR_{obs} and wR_2 were equal to 0.1134 and 0.1343, respectively. All atoms were considered anisotropic with the exception of the carbon atoms of the calixarene core, which were kept isotropic in order to keep a reasonable data/parameter ratio. Hydrogen atoms were introduced in the calculation as riding on their parent atom. The goodness-of-fit parameter S was 0.983 and the maximum residual density 0.620 eÅ^{-3}. Two other cells corresponding to different solvates were found for the monocrystals of **1** recrystallised from pyridine: **1**·3(NC$_5$H$_5$): $a = 14.84(1)$, $b = 15.15(1)$, $c = 15.34(1)$ Å, $\alpha = 86.45(3)°$, $\beta = 61.15(3)$, $\gamma = 87.53(3)°$, $V = 3014(7)$ Å^3; **1**: $a = 14.929(3)$, $b = 13.799(3)$, $c = 28.128(5)$ Å, $\beta = 94.62(3)$, $V = 5776(4)$ Å^3.

Crystal Data of 3·4.5(NC$_5$H$_5$): $C_{130.5}H_{134.5}F_6N_{12.5}O_{12}S_2Yb_2$ (2594.21), $0.14 \times 0.12 \times 0.12$ mm^3, triclinic, $P\bar{1}$, $Z = 2$, $a = 15.679(3)$, $b = 15.917(3)$, $c = 26.833(4)$ Å, $\alpha = 102.52(3)°$, $\beta = 93.12(3)$, $\gamma = 107.18(3)°$, $V = 6195(2)$ Å^3, $\rho_{calcd.} = 1.391$ g.cm^{-3}, $F(000) = 2654$, $2\theta_{max} = 51.56°$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), $\mu M_o = 1.607$ cm^{-1}, $T = 100$ K. The structure was solved by direct methods[24] and refined on F^2.[25] Of the 32794 reflections measured, 19393 were found to be independent ($R_{int} = 0.124$), 8349 of which were considered as observed [$I > 2\sigma(I)$]. All reflections were used in the refinement of the 864 parameters, leading to a final R_1 of 0.0884 and an R_{all} of 0.2199. wR_{obs} and wR_2 were equal to 0.1830 and 0.2444, respectively. Solvent pyridine molecules were constrained to regular hexagons. All non-carbon atoms were considered anisotropic, with the exception of the nitrogen atoms of the solvated pyridine molecules. Hydrogen atoms were introduced in the calculation as riding on their parent atoms. The goodness-of-fit parameter S was 0.970 and the maximum residual density 0.943 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150779 [**2·4(NC$_5$H$_5$)**] and -150780 [**3·4.5(NC$_5$H$_5$)**]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[10] With the exception of pyridine and for **1** of the 1:1 mixture of toluene/pyridine, compounds **1−3** decompose in more or less all the solvents or mixtures of solvents we tried to dissolve them in. They were too reactive to survive in solution containing anhydrous pentane, diethyl ether, tetrahydrofuran or toluene for a long time.

[11] The change of colour from pale-yellow or orange to a dark green was observed for the microcrystalline powders of **1−3** even when kept in closed tubes in N_2 or argon atmosphere glove boxes ($O_2 < 1$ ppm). In the end, the complexes had to be kept in glass tubes sealed under vacuum to prevent decomposition.

[12] Concentrated solutions of **1** (0.5 g, 2−5 mL) in pyridine and in mixtures of pyridine and toluene were left standing at room temperature and in the fridge (253 K) for several months but never grew any single crystal suitable for an X-ray analysis.

[13] The geometry around the metal centre is a distorted, capped trigonal prism in both **2** and **3**. O(11)−O(21)−N(1) and N(4)−N(3)−O(1) define the faces of the prism and N(2) caps the O(11)−N(3)−O(1)−N(1) face.

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[18] Listing of the pairs of torsion angles φ and χ in **1**: +81.6 −89.6, +10.7 −86.0, −127.2 +69.2, and in the two molecules of **2**: +86.7 −76.9, +14.4 −123.9, −103.2 +40.9 and +96.6 −71.9, +32.5 −130.4, −95.7 +38.7. This succession of angles designates the conformation as C_i + −, + −, − +, − +, − +, + −, expect for the distorted 1,2,3-alternate conformation.[1a]

[19] The six atoms of the pyridine molecule bearing N(4), the lanthanide cation and the methylene bridge between the aromatic faces bearing O(11′) and O(21′) are found within a plane (standard deviation ±0.12 Å in **2** and ±0.27 Å in **3**). In both molecular structures, the carbon atom in the *para* position on the pyridine molecule is located at a distance inferior to 3.60 Å to the centroid of the aromatic face bearing O(11′) and also at a distance inferior to 4.00 Å to the carbon atoms of the *t*Bu groups and to at least two carbon atoms belonging to each of the aromatic rings bearing O(11′) and O(21′).

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