Lanthanide(III) Complexes of Tripodal N-Donor Ligands: Structural Models for the Species Involved in Solvent Extraction of Actinides(III)

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The complexation of lanthanides(III) by the tripodal ligands tpa (tris[(2-pyridyl)methyl]amine) and tpza (tris[(2-pyrazinyl)methyl]amine) has been investigated by solution NMR studies and by X-ray crystallography. The crystallographic studies show that both tpa and the new ligand tpza form complexes with a 1:1 metal:ligand ratio in which the tripodal amine acts as a tetradentate ligand. For the tpa complexes the remaining coordination sites are occupied by chloride counterions to give 7-coordination (Eu, Tb, Lu) or by chloride counterions and a methanol molecule to give 8-coordination (Nd). In $[Nd(tpza)(H_2O)_3(CH_3CN)_3](ClO_4)_3 \cdot 3H_2O$ the remaining coordination sites are occupied by water and acetonitrile molecules to give 10-coordination while the perchlorate counterions remain non coordinating. Tpza complexes have been isolated from acetonitrile solution and dissociate completely in methanol, while the complexes of the more basic tpa can be isolated from methanol and exist in water in equilibrium with the free ligand. Solvent extraction studies of lanthanides(III) and actinides(III) from nitric acid solutions show that the new ligand tpza is, unlike tpa, a selective complexant of actinides(III). Considering their structural analogy, this difference could be explained in terms of the electronic differences between the two ligands resulting in a stronger affinity of actinides(III) for the softer donor tpza.

Introduction

During the last decade there has been a growing interest in the coordination chemistry of lanthanides[1] due to their potential application as luminescent probes in medicine and biology,[2] as contrast agents in magnetic resonance imaging,[3−6] and as mild reagents and catalysts in organic synthesis.[7] These applications require a precise knowledge of the coordination properties of lanthanide ions. Complexes containing macrocyclic hard donor ligands have been the most studied in the past. Nevertheless the number of Ln(III) complexes with non macrocyclic N-donor ligands that are being isolated and studied is rapidly increasing.[8−17] This surge of interest in lanthanide complexes with polydentate aromatic N-donor ligands derives from their photophysical properties and their potential application as supramolecular light-conversion devices.[18,19]

Aromatic nitrogen donor ligands are of interest also in view of their ability to enhance the separation of actinides(III) from lanthanides(III).[20] One possible way to integrate the An(III)/Ln(III) group separation into the process of partitionning Am^{3+} and Cm^{3+} from high-activity raffinate generated through reprocessing of used nuclear fuel is to design a solvent extraction system which can selectively extract An(III) from nitric acid solutions. The An(III)/Ln(III) separation by liquid−liquid extraction is a difficult problem owing to the similarity of the chemical properties of these cations in solution.[21] Extractants containing "soft" donor atoms like N or S have given interesting results in the separation of actinides(III) from lanthanides(III).

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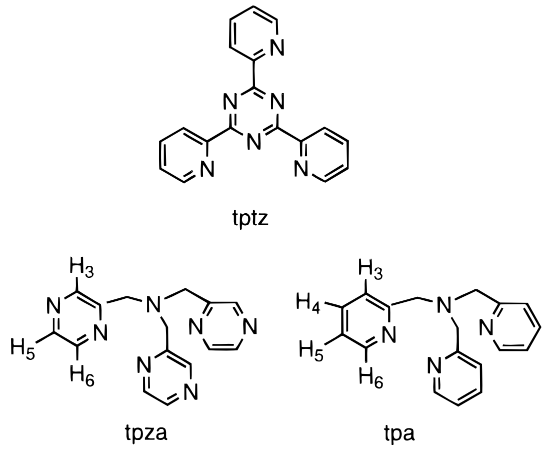
Chart 1



The effectiveness of soft donors has been attributed[22] to the presence of a greater degree of covalency in the actinide bonding[23,24] resulting in a stronger metal−nitrogen interaction. The determination of the nature of the molecular species involved in the extraction, and of the properties of the ligand responsible for the selectivity is essential to design selective complexants for actinides(III). Vitorge[25] has shown that the nitrogen donor ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) (Chart 1) is able to extract americium(III) one order of magnitude more strongly than europium(III) from a nitric acid solution of the two metals, but the structures of the metal complexes involved in the extraction have not been elucidated. To investigate the coordination chemistry of Ln(III) and An(III) with ligands of potential interest in an extraction process we relied on tpa (tris[(2-pyridyl)methyl]amine) and tpza (tris[(2-pyrazinyl)methyl]amine) which contain the same type of N-donor atoms found in tptz, but present a single coordination site. The synthesis of structurally related ligands possessing different hard/soft character is easier for tripodal aromatic amines than for triazine derivatives.

Metal complexes of the tetradentate aromatic N-donor ligand tpa were first described in 1967 by Anderegg and co-workers who also measured its complexation constants with a large number of transition metals.[26−28] The formation of a praseodymium complex of tpa has been observed by UV spectroscopy,[29] but this complex has not been characterized. The crystal structures of La(III) and Tb(III) complexes of the related tetrapodal N-donor ligand (*N*,*N*,*N*′,*N*′-tetrakis[2-pyridyl)methyl]-ethylenediamine) have been recently reported.[30] The synthesis and the photophysical properties of europium complexes of the tripodal aromatic amines tris[(2,2′-bipyridin-6-yl)methyl]amine and tris[(2,2′-bipyrazin-6-yl)methyl]amine have been previously described,[31,32] but, to our knowledge, the crystallographic structure of lanthanide complexes of tripodal aromatic amines has not been reported and structural data on lanthanide complexes of tripodal ligands are only known for polypyrazolylborates[8,14,33,34] and tren derivatives.[35,36]

In this paper we report structural studies in the solid state and in solution of lanthanide complexes with the tripodal N-donor ligand tpa and with the new ligand tpza in which the three pyridine groups of tpa are replaced by softer N-donors (pyrazine groups) in order to study the influence of the electronic configuration of the ligand on the complexation of f elements. This influence is investigated further by assessing the separation efficiency of tpa and tpza in the solvent extraction of Am(III) and Eu(III) from nitric acid solution.

Experimental Section

General Details. ^{1}H NMR spectra were recorded on Bruker AM-400, Bruker AC-200, and Varian U-400 spectrometers using deuterated D_2O, MeOD, and CD_3CN solutions with H_2O, MeOH, and CH_3CN as internal standards. Mass spectra were measured with a ZAB2-SEQ instrument. Elemental analysis were performed by SCA/CNRS, Vernaison, France. Conductivity measurements were performed at 293 K with a 712 Metrohm conductimeter using 10^{-3} M methanol solutions.

Solvents and starting materials were purchased from Aldrich, Fluka, and Alfa and used without further purification unless otherwise stated. TPH diluent (a commercial mixture of branched dodecanes) was purchased from Prochrom. The ligand tris[(2-pyridyl)methyl]amine was prepared according to the literature procedure.[26]

Solvent Extraction Procedure. Aqueous solutions (800 μL) of the radioisotope tracers ^{241}Am and ^{152}Eu containing variable amounts of HNO_3 were placed in 2 mL Nalgen tubes. An 800 μL amount of a TPH solution of the ligands tpa or tpza containing 1 M α-bromodecanoic acid were shaken for 30 mn in a thermostated (22 °C) shaker with the above aqueous solutions. After phase separation by centrifugation, 500 μL samples were analyzed using a gamma counting spectrometer (HPGe detector, Eurysis Mesures). The peaks at 59.54 and 121.78 keV were used for ^{241}Am and ^{152}Eu activity measurements, respectively.

Determination of the pK_a of TPZA. Electronic spectra of aqueous solutions of tpza (2.9×10^{-4} M) with different pH values (from pH = 6.5 to pH = 0.9) were recorded in the range 200−400 nm with a Cary 5E spectrophotometer at 22 °C using quartz cells of 1 mm path length. The pH was adjusted by adding HCl and the value of the ionic strength was maintained constant ($I = 1$) by adding LiCl.

Tpza has one peak around 265−270 nm. The position and intensity of this peak vary with the pH of the solution. Absorbance data ranging from 250 to 300 nm were computed through a partial least-square fitting method, allowing the determination of the molar extinction coefficient and of the aqueous concentration of the neutral and protonated species for each pH value, yielding a pK_a value of 3.0 ± 0.05 at 25 °C.

Synthesis of the Ligand (tpza). 2-Chloromethylpyrazine. To a stirred solution of 2-methylpyrazine (13.7 mL, 150 mmol) in dry CCl_4 (550 mL) were added under nitrogen *N*-chlorosuccinimide (22.03 g, 165 mmol) and 500 mg of catalyst (dibenzoyl peroxide). The suspension was refluxed overnight, cooled in an ice-bath and then filtered to

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eliminate the succinimide. The filtrate was evaporated and the resulting brown oil was chromatographied on silica gel (petroleum ether/diethyl ether 1:1). The first fraction (dichlorinated derivative) and the last fraction (unreacted 2-methyl pyrazine) were discarded. The intermediate fraction was evaporated to give 9.02 g of a light yellow oil. Yield: 46.7%. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.73 (1H, s, H^3); 8.53 (2H, m, H^5/H^6); 4.67 (2H, s, CH_2).

2-Methylaminopyrazine. To a refluxing solution of hexamethylenetetramine (9.87 g, 70.4 mmol) in dichloromethane (100 mL) was slowly added a solution of 2-chloromethylpyrazine (8.23 g, 64 mmol) in chloroform (50 mL) under stirring. The resulting suspension was refluxed for 3 h and allowed to stand overnight at room temperature. The resulting white solid was filtered, dried, and dissolved in EtOH (150 mL). After adding 12 M HCl (25 mL) the mixture was refluxed for 20 h, cooled, and evaporated to dryness. The residue was dissolved in water (70 mL) and dichloromethane (120 mL), and 5 M NaOH was added until the pH was basic. The organic layer was separated and the aqueous layer was extracted three times with 150 mL dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give 1.72 g of a light brown oil. Yield: 22.4%. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.56 (1H, s, H^3); 8.49 (1H, m, H^5); 8.43 (1H, d, $J = 2.4$ Hz, H^6); 4.00 (2H, s, CH_2); 2.13 (2H, s, NH_2).

Tris((2-pyrazinyl)methyl)amine (tpza). To a stirred solution of 2-chloromethylpyrazine (1.6 g, 12.4 mmol) in dry THF (15 mL) were added 2-methylaminopyrazine (0.68 g, 6.2 mmol) and potassium carbonate (1.72 g, 12.4 mmol). The suspension was refluxed for 15 h, cooled to room temperature and then filtered. The resulting solution was evaporated to give a brown oil which was chromatographed on silica gel (CH_2Cl_2/MeOH 9:1). The first eluted fraction was evaporated to give 0.93 g of a light yellow solid. Yield: 50.9%. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm)) 8.74 (1H, d, $J = 1.46$ Hz, H^3); 8.50 (1H, dd, $J = 2.55$, 1.46 Hz, H^5); 8.45 (1H, d, $J = 2.55$ Hz, H^6); 3.97 (2H, s, CH_2). ^{1}H NMR (200 MHz, MeOD): δ (ppm)) 8.96 (1H, d, J=1.46 Hz, H^3); 8.74 (1H, dd, $J = 2.92$, 1.46 Hz, H^5); 8.66 (1H, d, $J = 2.92$ Hz, H^6); 4.26 (2H, s, CH_2). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm)) 8.78 (1H, s, H^3); 8.52 (1H, s, H^5); 8.47 (1H, s, H^6); 4.00 (2H, s, CH_2). Anal. Calcd for $C_{15}H_{15}N_7$: C, 61.41; H, 5.11. Found: C, 61.41; H, 5.24. MS FAB$^+$: (*m/z*) 294 (MH^+).

The instability of 2-chloromethylpyrazine in aqueous basic conditions prevents the use of the standard conditions of tpa synthesis in the preparation of tpza.[26]

Preparation of the Lanthanide Complexes. [Ln(tpa)Cl$_3$ (MeOH)$_n$] ($n = 1$, Ln = La, Nd; $n = 0$, Ln = Eu, Tb, Lu). $LnCl_3 \cdot xH_2O$ (x = 6−7) (0.4 mmol) was added to a solution of tpa (0.4 mmol) in methanol (15 mL). After stirring the resulting mixture for 1 h, a small amount of dichloromethane (5 mL) was added and diethyl ether (15 mL) was allowed to slowly diffuse into the solution at 0°. After 2−4 days white (Ln = La, Eu, Tb, Lu), or light violet (Ln = Nd) crystals were obtained in 65−90% yield. X-ray quality crystals were obtained following the same procedure for Nd, Eu, Tb, and Lu. ^{1}H NMR spectra of all the complexes dissolved in MeOD were recorded and the values of the chemical shifts are given in Table 4. Λ_M at 293 K for 10^{-3} M methanol solutions of [La(tpa)Cl$_3$(MeOH)] = 118 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, [Nd(tpa)Cl$_3$(MeOH)] = 114 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, [Eu(tpa)Cl$_3$] = 105 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, and [Lu(tpa)Cl$_3$] = 125 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. Λ_M at 293 K for a 1.3×10^{-2} M methanol solution of [Eu(tpa)Cl$_3$] = 42 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. FAB$^+$: (*m/z*): 499 ([La(tpa)Cl$_2$]$^+$); 504 ([Nd(tpa)Cl$_2$]$^+$; 513 ([Eu(tpa)Cl$_2$]$^+$; 519 ([Tb(tpa)Cl$_2$]$^+$); 535 ([Lu(tpa)Cl$_2$]$^+$).

Satisfactory elemental analysis were obtained for all tpa complexes.

[Ln(tpza)(H$_2$O)$_x$(CH$_3$CN)$_y$][(ClO$_4$)$_3$](Ln = La, Nd, Eu). A mixture of tpza (0.14 mmol) and $Ln(ClO_4)_3 \cdot xH_2O$ (x = 6−7) (80.3 mg, 0.15 mmol) in 5 mL acetonitrile was stirred at room temperature for 2 h. Addition of diethyl ether (5 mL) resulted in the formation of a white (Ln = La), light yellow (Ln = Eu), or violet (Ln = Nd) solid which was filtered, washed with dichloromethane and dried to give a 60−75% yield. X-ray-quality crystals of [Nd(tpza)(H$_2$O)$_3$(CH$_3$CN)$_3$][(ClO$_4$)$_3$] were obtained from a highly concentrated solution of tpza and $Nd(ClO_4)_3 \cdot 6H_2O$ (0.14 M) in acetonitrile (0.5 mL) left standing overnight at room temperature. ^{1}H NMR (400 MHz, CD_3CN, 297 K) of [La(tpza)(H$_2$O)$_x$(CH$_3$CN)$_y$][(ClO$_4$)$_3$] : δ (ppm)) 8.87 (3H, m, H^3/H^5/H^6); 4.22 (2H, s, CH_2). ^{1}H NMR (400 MHz, CD_3CN, 298 K) of [Nd(tpza)(H$_2$O)$_3$(CH$_3$CN)$_3$][(ClO$_4$)$_3$]: δ (ppm) [proton relaxation time T_1 in s] 10.34 [0.184] (1H, s, H^3 or H^5); 9.24 [0.200] (1H, s, H^5 or H^3); 8.96 [0.0025] (2H, s, CH_2); 8.43 [0.002] (1H, s, H^6). ^{1}H NMR (400 MHz, CD_3CN, 295 K) of [Eu(tpza)(H$_2$O)$_x$(CH$_3$CN)$_y$][(ClO$_4$)$_3$]: δ (ppm) [proton relaxation time T_1 in s] 9.47 [0.034] (1H, s, H^6); 7.63 [0.427] (1H, s, H^5); 5.59 [0.396] (1H, s, H^3); −4.47 [0.059] (2H, s, CH_2,).

The obtention of satisfactory elemental analysis for the Eu complex was prevented by its highly hygroscopic character. Elemental analysis performed on the Nd and La complex are in agreement with the formula [Ln(tpza)(H$_2$O)$_6$][(ClO$_4$)$_3$].

Caution! *Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precaution.*[37]

X-ray Crystallography. All diffraction data were taken using a Siemens SMART CCD area detector three-circle diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å). To prevent loss of solvent, the crystals were coated with a light hydrocarbon oil and quickly transferred to a stream of cold nitrogen at −130 °C on the diffractometer.

The cell parameters were obtained with intensities detected on three batches of 15 frames with a 10 s exposure time for each. The crystal-detector distance was 6 cm. For three settings of Φ and 2Θ, 1200 narrow data frames were collected for 0.3° increments in ω. A full hemisphere of data was collected for each complex. At the end of data collection, the first 50 frames were recollected to establish that crystal decay had not taken place during the collection. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the SAINT program[38] were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the SADABS Siemens program.[38] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (see Table 1). Complete information on crystal data and data collection parameters is given in the Supporting Information.

The structures were solved by direct methods using the SHELXTL 5.03 package,[39] and all atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F^2 and hydrogen atoms were isotropically refined.

Results

Synthesis and Characterization of tpa Complexes. Reaction of $LnCl_3 \cdot 6H_2O$ (Ln = La, Nd, Eu, Tb, Lu) with tpa in a 1:1 ratio in methanol as solvent gives the complexes [LnCl$_3$(tpa)-(MeOH)$_n$] ($n = 0$, for Eu, Tb, Lu; $n = 1$ for La, Nd) in which the lanthanide ions are coordinated by one tetradentate ligand tpa and by three chlorine anions. For lanthanum and neodymium one molecule of methanol completes the 8-coordinate structure, while, in accordance with their smaller size, in the Eu, Tb, and Lu complexes the metal is only 7-coordinate. Reaction of $LnCl_3 \cdot H_2O$ with an excess of tpa (2−6 equiv) yields the 1:1 adduct as only product, probably because of the strong coordinating power of the anionic chlorine ligand.

Crystal Structures of tpa Complexes. The structures of the Nd, Eu, Tb, and Lu complexes were determined by X-ray crystallography.[40] [Eu(tpa)Cl$_3$] (**1**), [Tb(tpa)Cl$_3$] (**2**), and [Lu(tpa)Cl$_3$] (**3**) are isostructural and accordingly only the europium complex is shown in Figure 1. Selected interatomic distances and angles are set out in Table 2. The metal environment for complexes **1**, **2**, and **3** is best described as a capped octahedron

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Table 1. Crystallographic Data for the Five Structures

	[Eu(tpa)Cl$_3$] **1**	[Tb(tpa)Cl$_3$] **2**	[Lu(tpa)Cl$_3$] **3**	[Nd(tpa)(MeOH)Cl$_3$]·(MeOH) **4**	[Nd(tpza)(CH$_3$CN)$_3$(H$_2$O)$_3$](ClO$_4$)$_3$·3H$_2$O **5**
empirical formula	$C_{18}H_{18}N_4Cl_3Eu$	$C_{18}H_{18}N_4Cl_3Tb$	$C_{18}H_{18}N_4Cl_3Lu$	$C_{20}H_{26}N_4O_2Cl_3Nd$	$C_{21}H_{36}N_{10}O_{18}Cl_3$ Nd
fw	548.67	555.63	571.68	605.04	967.19
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	Cc	*P*2(1)
a, Å	8.7149(1)	8.6246(1)	8.5703(2)	10.984(1)	9.9808(4)
b, Å	16.3682(2)	16.2133(2)	16.1226(1)	13.861(1)	12.8914(5)
c, Å	14.7856(1)	14.6368(3)	14.6848(1)	15.831(1)	14.9392(6)
β, Å	104.594(0)	104.511(1)	104.246(1)	97.292(2)	91.733(1)
V, Å^3	2041.07(4)	1981.42(5)	1966.68(5)	2390.6(3)	1921.3(1)
Z	4	4	4	4	2
D_{calc}, g cm^{-3}	1.786	1.863	1.931	1.681	1.672
μ (Mo Kα), mm^{-1}	3.475	3.983	5.437	2.530	1.643
temp, K	153	153	193	153	153
no. of params refined	307	308	308	376	478
R1, wR2[a]	0.0406, 0.0973	0.0229, 0.0559	0.0371, 0.0891	0.0244, 0.595	0.0510, 0.1277

[a] Structure was refined on F_o^2 using all data: $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

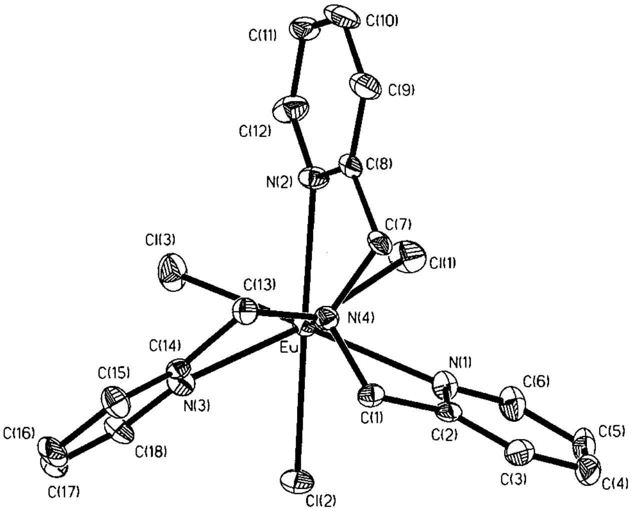

Figure 1. Top view of [Eu(tpa)Cl$_3$] with 50% thermal contours for all atoms.

Table 2. Selected Bond Distances (Å) and Angles (deg) in [Eu(tpa)Cl$_3$], [Tb(tpa)Cl$_3$], and [Lu(tpa)Cl$_3$]

	Eu tpa	Tb tpa	Lu tpa
M−N(1)	2.5849(13)	2.545(3)	2.516(1)
M−N(2)	2.5563(12)	2.513(3)	2.491(1)
M−N(3)	2.5880(11)	2.542(3)	2.519(1)
M−N(4)	2.6120(12)	2.568(3)	2.555(1)
M−Cl(1)	2.6622(4)	2.6212(9)	2.5993(4)
M−Cl(2)	2.6717(4)	2.6284(8)	2.6156(4)
M−Cl(3)	2.6583(5)	2.6165(9)	2.5913(5)
N(1)−M−N(2)	99.10(4)	99.52(9)	100.03(4)
N(1)−M−N(3)	109.09(4)	109.66(9)	111.29(5)
N(1)−M−N(4)	63.63(4)	64.13(8)	65.36(4)
N(1)−M−Cl(1)	81.99(3)	82.23(7)	82.45(3)
N(1)−M−Cl(2)	79.27(3)	78.69(7)	77.96(3)
N(1)−M−Cl(3)	168.37(3)	167.34(7)	165.42(3)
N(2)−M−N(3)	98.93(4)	99.75(9)	101.66(4)
N(2)−M−N(4)	64.42(4)	64.88(8)	66.19(4)
N(2)−M−Cl(1)	81.23(3)	81.08(6)	80.94(3)
N(2)−M−Cl(2)	177.95(3)	178.16(7)	177.57(3)
N(2)−M−Cl(3)	87.54(3)	87.63(7)	87.14(3)
N(3)−M−N(4)	64.67(4)	65.19(9)	66.13(4)
N(3)−M−Cl(1)	168.65(3)	167.62(7)	165.03(4)
N(3)−M−Cl(2)	80.51(3)	80.55(6)	80.42(3)
N(3)−M−Cl(3)	79.01(3)	79.09(7)	79.24(4)
N(4)−M−Cl(1)	124.54(2)	125.24(6)	127.33(3)
N(4)−M−Cl(2)	113.63(3)	113.76(6)	113.85(3)
N(4)−M−Cl(3)	128.00(3)	128.53(6)	129.19(3)
Cl(1)−M−Cl(2)	99.703(12)	99.03(3)	97.375(13)
Cl(1)−M−Cl(3)	89.664(14)	88.63(3)	86.21(2)
Cl(2)−M−Cl(3)	94.274(13)	94.21(3)	94.518(14)

with the tertiary amine nitrogen N(4) lying on the expanded face formed by the three pyridine nitrogen atoms N(1), N(2), N(3) of the tripodal ligand and the chlorine atoms Cl(1), Cl(2), Cl(3) occupying the opposing face. The angle between the two planes is 172° for Eu, 171.7° for Tb, and 171.3° for Lu. The Eu−N distances range from 2.55(1) to 2.61(1) Å, the Tb−N distances from 2.51(3) to 2.57(3) Å with the longer metal-nitrogen distances belonging to the tertiary amine nitrogen. These values are in the range of the Eu−N (2.516(6)−2.976(6) Å)[11,14,30,33,41−43] and Tb−N[30,42,43] (2.509(4)−2.686(7) Å) distances reported in the literature. The Lu−N distances (2.452(4) to 2.514(4) Å) are slightly longer than the values reported in the literature for lutetium complexes with N-donor ligands (2.37(1)−2.479(8) Å).[11,42,44] The decrease in the value of the Ln−N bond lengths from Eu to Lu is ~0.1 Å. This value is in agreement with the expected contraction of 0.09 Å calculated from Shannon ionic radii for 7-coordinated ions.[45] The clear correlation between the Ln−N bond lengths and the metal ionic radii shows that the ligand tpa is sufficiently flexible to accommodate ions of different size. Bite angles for the tetradentate ligand have a mean value of 64° for Eu, 65° for Tb, and 66° for Lu. A view of the complex [Nd(tpa)(MeOH)Cl$_3$]. MeOH (**4**) is shown in Figure 2 and selected bond distances and angles are given in Table 3. The coordination geometry around the neodymium, in complex (**4**) can be seen as a dodecahedron formed by the tetradentate ligand tpa, three chlorine atoms and a methanol molecule. The Nd−N distances range from 2.601(2) to 2.7021(14) Å with the longer distance belonging to one of the pyridine nitrogens. The presence of an additional molecule of methanol in the coordination environment of Nd results in several structural changes relative to the structure of the tpa complexes of Eu, Tb, and Lu. While in the isostructural Eu, Tb, and Lu complexes similar M−N distances are observed for all pyridyl arms, the value of the Nd−N distance is much larger for one of the pyridyl arms (Nd−N1 = 2.7021 Å) than for the others (Nd−N2 = 2.601(2) Å, Nd−N3

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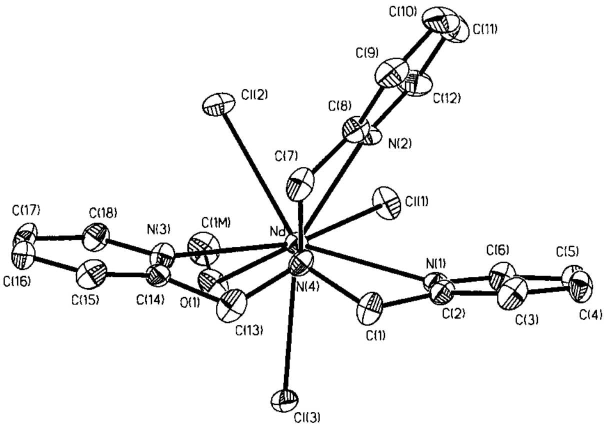

Figure 2. Top view of [Nd(tpa)(MeOH)Cl_3] with 50% thermal contours for all atoms, emphasizing the asymmetric coordination mode.

Table 3. Selected Bond Distances (Å) and Angles (deg) in [Nd(tpa)(MeOH)Cl_3]·(MeOH)

Nd−N(1)	2.7021(14)	Nd−Cl(1)	2.7274(5)
Nd−N(2)	2.601(2)	Nd−Cl(3)	2.7369(5)
Nd−N(3)	2.620(2)	Nd−Cl(2)	2.8159(5)
Nd−N(4)	2.668(2)	Nd−O(1)	2.4933(11)
N(1)−Nd−N(2)	65.06(4)	N(3)−Nd−Cl(1)	152.06(3)
N(1)−Nd−N(3)	127.15(4)	N(3)−Nd−Cl(2)	75.07(3)
N(1)−Nd−N(4)	64.78(4)	N(3)−Nd−Cl(3)	78.92(3)
N(1)−Nd−Cl(1)	80.79(3)	N(3)−Nd−O(1)	78.81(4)
N(1)−Nd−Cl(2)	135.98(3)	N(4)−Nd−Cl(1)	141.93(4)
N(1)−Nd−Cl(3)	77.69(3)	N(4)−Nd−Cl(2)	108.82(3)
N(1)−Nd−O(1)	136.85(4)	N(4)−Nd−Cl(3)	78.35(3)
N(2)−Nd−N(3)	104.46(5)	N(4)−Nd−O(1)	137.79(5)
N(2)−Nd−N(4)	64.76(5)	Cl(1)−Nd−O(1)	78.86(3)
N(2)−Nd−Cl(1)	86.88(4)	Cl(1)−Nd−Cl(2)	84.347(13)
N(2)−Nd−Cl(2)	72.98(3)	Cl(1)−Nd−Cl(3)	110.880(14)
N(2)−Nd−Cl(3)	135.63(3)	Cl(2)−Nd−Cl(3)	145.980(13)
N(2)−Nd−O(1)	149.60(4)	Cl(2)−Nd−O(1)	78.97(3)
N(3)−Nd−N(4)	64.42(4)	Cl(3)−Nd−O(1)	74.76(3)

= 2.620(2) Å). The value of the Nd−N1 bond length is also larger than the other Nd−N distances reported in the literature (2.566(4)−2.622(4) Å).[42,46] The pseudo-C_3 symmetry of the ligand tpa observed in the Eu, Tb, and Lu complexes is disrupted in the Nd complex by the inversion of the orientation of the pyridyl arm containing N1 (relatively to the complexes **1** and **2**). This inversion is a consequence of steric interactions with the neighboring chlorine ion Cl(3). The distances of the chlorine ions from the plane defined by the atoms N(1), N(2), N(3) have values ranging from 2.10 to 2.64 Å for the lutetium complex, from 2.16 to 2.69 Å for the terbium complex and from 2.21 to 2.73 Å for the europium complex, while in the neodymium complex the three distances are quite distinct (0.62 Å for Cl(3) vs 3.28 Å for Cl(1) and 2.00 Å for Cl(2)). The angle between the plane defined by the atoms N(1), N(2), N(3) and the one defined by the atoms Cl(1), Cl(2) Cl(3) is much smaller (39.7°) than in the Eu, Tb and Lu complexes.

Solution NMR Studies. NMR studies have been carried out to investigate the solution structure of the lanthanide complexes, and in particular to assess their stability with respect to tpa dissociation in various solvents and with various counteranions.

In methanol solution, the proton NMR spectra of [Ln(tpa)-Cl_3] complexes show the presence (Table 4) of only one set of signals (down to [Ln(tpa)Cl_3] = 7 × 10^{-3} M) with four resonances for the 12 pyridine protons and a single signal for the six methylene protons. These features are consistent with a threefold symmetry of the solution species in which all chelating arms of the tpa ligand are equivalent. It follows that the small deviation from C_3 symmetry observed for the ligand in the crystal structure of the Eu, Tb, and Lu complexes and the asymmetric coordination of the ligand in the solid state structure of the Nd complex are lost in solution. The dissolution of the Nd complex in methanol probably causes the loss of the coordinated methanol accompanied by rearrangement of the ligand to give a structure similar to the Eu, Tb, and Lu. Such observations, and the chemical shift equivalence of the methylene protons, require a conformational mobility of the ligand branches in solution. Attempts at stopping the rapid exchange between different ligand conformations by lowering the temperature down to −80 °C have been unsuccessful. Moreover conductivity measurements performed on 10^{-3} M methanol solutions showed the presence of 1:1 electrolytes[47] for all complexes in agreement with the presence of only two coordinated chloride ions. At the higher concentration (∼10^{-2} M) used for the NMR experiments, the conductivity is lower than the value reported in the literature for a 1:1 electrolyte, which indicates that a fraction of the complex is undissociated at this concentration. The threefold symmetry observed for all complexes in solution is not consistent with the partial dissociation of the coordinated chloride ions which would result in an asymmetric structure. These contrasting results can be explained by the presence of a rapid (on the NMR time scale) exchange of chloride ions at 298 K between the different chloride positions, resulting in an averaged "symmetric spectra". For [La(tpa)Cl_3] and [Lu(tpa)Cl_3] the pyridine proton H3 is shifted to high field (0.32 ppm for La and 0.38 for Lu, Table 2) and the pyridine proton H6 and the methylene protons are significantly shifted to low field (0.58 ppm for H6 in both complexes and 0.57 and 0.64 ppm for CH_2 respectively in [La(tpa)Cl_3] and in [Lu(tpa)Cl_3]) as similarly observed in other metal complexes[48,49] in which tpa is acting as a tetradentate ligand. A larger shift accompanied by a slight line broadening, as expected for a paramagnetic ion,[50] is observed for [Eu(tpa)-Cl_3] for which the assignment of the NMR signals has been confirmed by a two-dimensional homonuclear COSY correlation spectrum. The proton H6 is shifted at low field while H3 and the methylene protons are both shifted upfield. In the Nd and Tb complexes, the sign of the shift of the resonances of the methylene and pyridine protons is inverted relative to that observed for the Eu complex, in agreement with the different signs of the dipolar contribution to the isotropic hyperfine shift for these ions.[50] Line broadening and spectral range (200 ppm) become very large for the Tb complex. In summary these studies show that while more than one species can exist in solution,

Table 4. Chemical Shifts of Lanthanide Complexes of tpa in MeOD

in MeOD at 298 K	H^6	H^5	H^4	H^3	CH_2
tpa	8.52	7.39	7.88	7.74	3.93
[La(tpa)Cl_3]	9.10	7.42	7.85	7.42	4.50
[Nd(tpa)(MeOD)Cl_3]	5.57	6.87	8.01	9.12	8.68
[Eu(tpa)Cl_3]	11.21	7.10	7.54	4.84	−4.07
[Tb(tpa)Cl_3]	−121.3	−19.10	−3.29	−27.60	78.96
[Lu(tpa)Cl_3]	9.11	7.36	7.83	7.36	4.57

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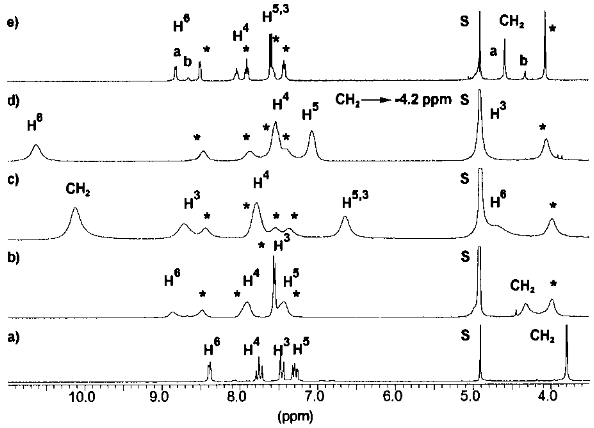

Figure 3. ^{1}H NMR spectra in D_2O at 298K of (a) tpa; (b) [La(tpa)(MeOH)Cl_3]; (c) of [Nd(tpa)(MeOH)Cl_3](MeOH); (d) [Eu(tpa)Cl_3]; and (e) [Lu(tpa)Cl_3] (a and b denote the two forms of the complex when signals do not overlap). Asterisks denote the signals of the free ligand, and S indicates the solvent signal.

depending on the coordination of chloride and methanol, all the tpa ligand is bound to the lanthanide ion.

The reaction of $Eu(ClO_4)_3.H_2O$ with tpa in a 1:1 stoichiometry in methanol was followed by ^{1}H NMR spectroscopy which at low concentrations indicates the presence of the 1:1 complex (H^6, 9.80; H^5, 6.65; H^4, 7.28; H^3, 4.27; CH_2, −4.84) in equilibrium with the free ligand. The value of the conductivity measured on a 10^{-3} M acetonitrile solution of the perchlorate complex ($\Lambda_M = 342\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ at 293 K) indicates the presence in solution of a 3:1 electrolyte and therefore the absence of coordinated perchlorate counterions. It is reasonable to suppose that in methanol, which is more polar, all perchlorate counterions are also dissociated. Therefore the differences in the chemical shifts of the NMR signals of perchlorate complexes relative to the chloride complexes are probably due to the different ligation of the two metals by counterions and solvent molecules.

Proton NMR spectra at 298 K of [Ln(tpa)Cl_3] complexes in D_2O (Figure 3) show for Nd(III) and Eu(III) a partial dissociation of the tpa ligand with distinct signals, which are only slightly broadened, for the complexed and the free form of the ligand. Two dimensional NOESY spectra performed on the Eu and Nd complexes in D_2O confirmed the presence of a slow (on the NMR time scale) exchange between the free tpa and the Eu and Nd complexes, and allowed the confirmation of the assignment of ^{1}H NMR signals of the two complexes. The formation constants of these tpa complexes in D_2O at 298 K were determined by integration of the ^{1}H NMR signals corresponding to the complex and to the free tpa. Rather similar stability constants were found for Nd ($K_f = 250 \pm 20$ mole^{-1} L) and for Eu ($K_f = 260 \pm 20$ mole^{-1} L). The proton spectrum of [La(tpa)Cl_3] in D_2O solution shows broad but distinct signals for the complex and the free tpa only in the case of the methylene groups and the H6 proton of the pyridine, while the other signals have already coalesced at 298 K. Finally, the ^{1}H NMR spectra at 298 K of [Lu(tpa)Cl_3] in D_2O solution presents, in addition to the signals of the free ligand, two other sets of similar narrow signals which where assigned to two different lutetium complexes which do not exchange rapidly and where the tpa ligand appears coordinated to Lu(III) in a symmetric manner. The exchange between free tpa and its complexed forms appears slower for Lu than for La. The two forms (a) and (b) of the Lu(III) complex are present in a 3:1 (a:b) ratio with a K_f at 298 K calculated for the totality of the complexed form of 130 ± 10 mole^{-1} L. A two-dimensional homonuclear COSY correlation spectrum has allowed the assignment of the signals, and has unambiguously confirmed the presence of two different forms of the complex. Addition of 1 equiv of acid results in removal of the NMR signals of the complexed species (b). Addition of an excess of NaOD (~10 equiv) results in the increase of the relative intensity of the signals of the complexed species (b) at the expense of the signals of species (a) (*a*:*b* = 1:1). On the basis of these observations it is proposed that the form (b) is a binuclear hydroxocomplex of tpa of the type $[Lu(tpa)(OH)]_2^{4+}$. The fact that the formation of a hydroxocomplex is not observed in water for the other lanthanides studied is a result of the higher acidity of the water molecules bound to the lutetium ion. The formation of binuclear hydroxoderivatives has been reported[51] for several lanthanide complexes and has also been observed when $Eu(ClO_4)_3{\cdot}6H_2O$ is reacted with an excess of tpa in methanol solution.[52]

When different lanthanide salts $LnX_3{\cdot}6H_2O$ (Ln = Eu, Nd, Lu; X = Cl^-, NO_3^-, ClO_4^-) are reacted with tpa in D_2O, the proton spectra of the resulting solutions are not affected by the presence of a different type of counterion. This observation may be explained by the fact that in water solution all counterions are not coordinated whatever their type.

Synthesis and Characterization of tpza Complexes. Investigation of the reaction of the ligand tpza with $LnCl_3{\cdot}6H_2O$ in deuterated methanol using ^{1}H NMR spectroscopy showed the presence of an equilibrium at room temperature between the free ligand and its complexed form. This prevents isolation of the 1:1 chloride complex from methanol solution, while the use of non protic solvents was prevented by the poor solubility of $LnCl_3{\cdot}H_2O$. The ^{1}H NMR spectra at 298 K of a 1:1 mixture of $LnCl_3{\cdot}6H_2O$ (Ln = Eu, Lu) and tpza in methanol solution shows, in addition to the signals of free tpza, 3 signals in the aromatic region (for Eu(III), H3, 6.86; H6, 8.06; H5, 7.79 ppm; for Lu(III), H3, 6.8; H6, 8.1; H5, 7.8 ppm) and one signal for the methylene protons (for Eu, −1.28; for Lu, 4.67 ppm) indicating the presence of a complex with a threefold symmetry exchanging slowly on the NMR scale time with the free ligand. The assignment of the NMR signals has been achieved by two-dimensional NOESY spectra. Proton spectra of 1:1 mixtures of $LaCl_3$ or $NdCl_3$ and tpza in methanol solution present broadened signals only slightly shifted from the chemical shift values of the ligand, indicating a faster exchange between tpza and its complexed form than for the heavier lanthanides. Proton spectra of these mixtures cooled at 243 K show separate signals for the free and the complexed forms of the ligand. While more detailed NMR studies are under way to investigate further the thermodynamic and kinetic parameters of the equilibrium involving lanthanide complexes of tpa and tpza, from our preliminary study we found that these complexes are kinetically more labile for the lighter than for the heavier metals, as expected for an essentially electrostatic interaction between the metal and the ligand.

In order to increase the solubility in organic solvents of the lanthanide salts on the one hand, and to study how the complexation is affected by the nature of the counterion on the other hand, we investigated the reaction of the tripodal ligand

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(53) Density functional calculations show the presence of a smaller electron density on the pyrazine nitrogen than on the pyridine nitrogen. They also indicate that tpza has a stronger π-acceptor character than tpa (Maldivi, P., unpublished results).

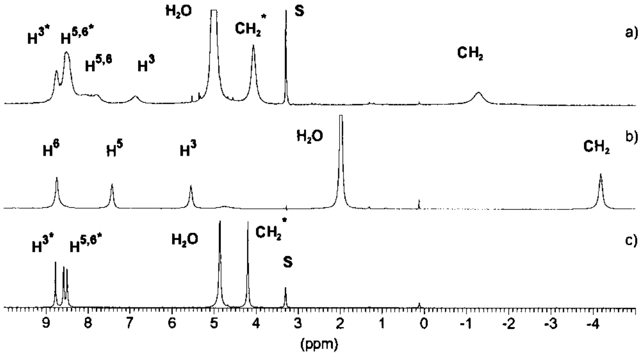

Figure 4. ^{1}H NMR spectra at 298K of (a) a 1:1 mixture of tpza ([tpza] = 1.3×10^{-1} M) and $EuCl_3{\cdot}6H_2O$ in MeOD; (b) a 1:1 mixture of tpza ([tpza] = 7.1×10^{-2} M) and $Eu(ClO_4)_3{\cdot}6H_2O$ in CD_3CN; (c) a 1:1 mixture of tpza ([tpza] = 7.1×10^{-2} M) and $Eu(ClO_4)_3{\cdot}6H_2O$ in MeOD (* = free ligand; S = solvent).

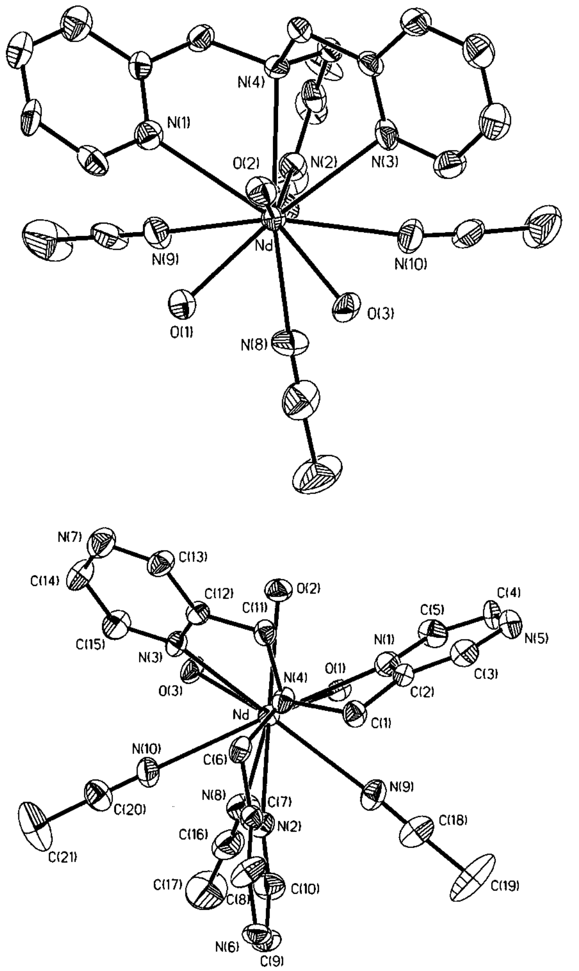

Figure 5. Side and top views of $[Nd(tpza)(H_2O)_3(CH_3CN)_3]^{3+}$ with 50% thermal contours for all atoms.

tpza with $Ln(ClO_4)_3{\cdot}6H_2O$. The reaction of tpza with $Nd(ClO_4)_3{\cdot}6H_2O$ in a 1:1 ratio in acetonitrile as solvent gives the complex $[Nd(tpza)(CH_3CN)_3(H_2O)_3](ClO_4)_3{\cdot}3H_2O$ (**5**) which slowly precipitates out of the solution as light violet crystals. An analogue perchlorate complex of La(III) was isolated in a similar way, while the Eu(III) complexes show a very high solubility in acetonitrile which makes crystallization difficult and results in a low yield. The proton NMR spectra of lanthanide complexes of tpza show that tpza dissociates completely in MeOD. On the other hand the dissociation of the ligand is not observed in acetonitrile over a long period of time in absence of moisture.

Table 5. Selected Bond Distances (Å) and Angles (deg) in $[Nd(tpza)(H_2O)_3(CH_3CN)_3](ClO_4)_3{\cdot}3H_2O$

Nd−N(1)	2.770(8)	Nd−N(9)	2.641(8)
Nd−N(2)	2.719(7)	Nd−N(10)	2.698(8)
Nd−N(3)	2.753(7)	Nd−O(1)	2.424(6)
Nd−N(4)	2.734(7)	Nd−O(2)	2.543(6)
Nd−N(8)	2.620(9)	Nd−O(3)	2.467(6)

N(1)−Nd−N(2)	98.4(2)	N(3)−Nd−N(10)	64.2(2)
N(1)−Nd−N(3)	101.4(2)	N(4)−Nd−N(8)	139.9(3)
N(1)−Nd−N(4)	61.2(2)	N(4)−Nd−N(9)	91.7(2)
N(1)−Nd−N(8)	132.3(2)	N(4)−Nd−N(10)	92.3(2)
N(1)−Nd−N(9)	64.4(2)	N(4)−Nd−O(1)	134.0(2)
N(1)−Nd−N(10)	153.3(3)	N(4)−Nd−O(2)	87.1(2)
N(1)−Nd−O(1)	72.9(2)	N(4)−Nd−O(3)	134.7(2)
N(1)−Nd−O(2)	65.6(2)	N(8)−Nd−N(9)	71.8(3)
N(1)−Nd−O(3)	129.5(2)	N(8)−Nd−N(10)	65.7(3)
N(2)−Nd−N(3)	95.6(2)	N(8)−Nd−O(1)	74.5(2)
N(2)−Nd−N(4)	61.9(2)	N(8)−Nd−O(2)	132.7(3)
N(2)−Nd−N(8)	78.0(3)	N(8)−Nd−O(3)	71.5(3)
N(2)−Nd−N(9)	64.3(2)	N(10)−Nd−N(9)	117.0(3)
N(2)−Nd−N(10)	63.1(2)	N(9)−Nd−O(1)	68.6(2)
N(2)−Nd−O(1)	130.8(2)	N(9)−Nd−O(2)	122.9(2)
N(2)−Nd−O(2)	148.9(2)	N(9)−Nd−O(3)	133.5(2)
N(2)−Nd−O(3)	132.0(2)	N(10)−Nd−O(1)	133.6(2)
N(3)−Nd−N(4)	59.9(2)	N(10)−Nd−O(3)	70.8(2)
N(3)−Nd−O(1)	133.6(2)	N(10)−Nd−O(2)	120.0(2)
N(3)−Nd−O(2)	64.2(2)	O(1)−Nd−O(2)	72.1(2)
N(3)−Nd−O(3)	75.0(2)	O(1)−Nd−O(3)	74.9(2)
N(3)−Nd−N(8)	126.3(3)	O(2)−Nd−O(3)	68.1(2)
N(3)−Nd−N(9)	151.3(2)		

The ^{1}H NMR spectra of lanthanide complexes of tpza in CD_3CN solution show the presence of only one set of signals with three resonances for the pyrazine protons and only one signal for the methylene protons. These features are consistent with a threefold symmetry of the solution species. Also in this case the chemical shift equivalence of the methylene protons requires the presence of a fast exchange between different ligand conformations. The ^{1}H NMR spectrum of the La(III) complex shows that the signals of all protons of tpza are slightly shifted to low field, as a consequence of the mutual shielding of the pyrazine rings. The ^{1}H NMR spectrum of the Nd(III) complex shows a strong upfield shift of the methylene protons (4.43 ppm) relative to the free ligand, while the protons of the pyrazine show a smaller shift. In the Eu complex the proton H6 of tpza is shifted at low field (0.81 ppm) while the methylene protons are shifted upfield (8.73 ppm for CH_2), as already observed for the tpa complexes of Eu(III). Figure 4, which illustrates the ^{1}H NMR spectra of the tpza complex of Eu in presence of chloride in methanol and in presence of perchlorate as counterion in methanol and acetonitrile, underscores the stabilizing effect of the coordinating counterion on the metal-tpza interaction.

Crystal Structure of $[Nd(tpza)(CH_3CN)_3(H_2O)_3](ClO_4)_3{\cdot}3(H_2O)$. Confirmation of the formulation of the neodymium complex was provided crystallographically. Two views of the complex $[Nd(tpza)(CH_3CN)_3(H_2O)_3](ClO_4)_3{\cdot}3H_2O$ are shown in Figure 5 and selected bond distances and angles are given in Table 5. In complex **5** the neodymium is 10-coordinate with the tetradentate tpza, with three molecules of water and three molecules of acetonitrile, while the perchlorate anions remain non coordinating. The Nd-N distances range from 2.719(7) to 2.770(8) Å for the ligand tpza and from 2.620(9) to 2.698(8) Å for the coordinated acetonitrile and have larger values than the ones reported for the nine coordinate complex of 2,2′:6′,2″-terpyridine, $[(C_{15}H_{11}N_3)NdCl(H_2O)_5]$, (2.613(4)−2.622(4) Å)[42]. The Nd−N distances for the tripodal ligand tpza in **5** are considerably longer than the Nd−N distances for tpa in **4** and the bite angles of the tripodal ligand (average value of 61°) are smaller than for the tpa complex. The difference in coordination

Table 6. Distribution Ratios and Separation Factors of tpa and tpza

ligand	concentration (mol/L)	$[HNO_3]_{eq}$ (mol/L)	$D_{Am(III)}$[a]	$D_{Eu(III)}$	$SF_{Am/Eu}$[b]
tpa	0.001	0.012	0.25	0.13	1.9
	0.001	0.014	0.22	0.12	1.8
	0.001	0.015	0.22	0.13	1.6
tpza	0.02	0.009	4.60	0.43	10.8
	0.02	0.06	0.004	0.0004	10.0
	0.001	0.011	0.46	0.13	3.5
	0.001	0.013	0.44	0.16	2.7

[a] The distribution ratio D_M for a metallic cation M is defined as the ratio of the concentration of the metallic species in organic phase (1 M TPH) over the concentration in aqueous phase. The error of the measure of D_M was estimated to be 5%. [b] The separation factor $SF_{M1/M2}$ for two metallic cations M_1 and M_2 is defined as the ratio of their distribution ratios. The error of the measure of SF was estimated to be 10%.

number between the two complexes affects the value of the bond distances, but not to such an extent as to justify the differences observed in the values of the Nd−N distances. The significant lengthening of the Nd−N in the tpza complex is explained by a lessened affinity of this ligand, relative to tpa, for the lanthanide ions resulting from the reduced donating power of tpza.

Once we established the ability of the ligands tpa and tpza to complex Ln(III) we then studied the potential application of these ligands in the selective extraction of Am(III) from aqueous acid solutions of Eu(III) and Am(III).

Metal Extraction. The synergistic extraction system tptz/α-bromodecanoic acid (HA) reported by Vitorge[25] yields a value of $SF_{Am/Eu} = 10$ up to pH = 2 in the extraction of americium(III) and europium(III). Equation 1 (where the upper bar denotes the organic phase and M = An, Ln) has been proposed to describe the extraction process,

$$M^{3+} + 3\overline{HA} + \overline{tptz} \rightleftarrows \overline{M\ tptzA_3} + 3H^+ \qquad (1)$$

We have studied the synergistic extraction of americium(III) and europium(III) using α-bromodecanoic acid as cationic exchanger in the presence of the tetradentate soft donor ligands tpa and tpza. The low solubility of the ligands tpa and tpza in the organic diluent used, TPH, is the limiting factor for the concentration conditions of the experiment. Addition of α-bromodecanoic acid (synergist) is necessary to enhance metal extraction efficiency. Replacement of nitrate by α-bromodecanoate results in a decreased hydrophilicity of Am(III) complexes of tpa and tpza. The pH of the aqueous nitric acid solutions of Am(III) and Eu(III) has been measured at equilibrium conditions after separation of the aqueous and organic phase. The results of these experiments, summarized in Table 6, show that for $[tpza] = 10^{-2}$ M the separation factor reaches, at pH $\cong$ 2, a value of 10.8 ± 1.1. It has not been possible to determine the separation factor for $[tpa] = 10^{-2}$ M because of the lower solubility of tpa in the organic phase. However, while the separation factor for tpa ($SF_{Am/Eu} = 1.8 \pm 0.2$) at $[tpa] = 10^{-3}$ M at pH $\cong$ 2 is almost equal to that of the α-bromodecanoic acid alone ($SF_{Am/Eu} \cong 1.5$), at the same concentration of 10^{-3} M the separation factor for tpza is significantly larger ($SF_{Am/Eu} = 3.5 \pm 0.4$ at pH $\cong$ 2). The distribution coefficients of Am and Eu in the extraction experiment with tpza decrease dramatically when the pH is decreased from 2 to 1. In fact, at low pH the ligand tpza ($pK_a = 3.00$) is protonated and loses its coordination capacity toward the metal.

Discussion

The complexation of lanthanides(III) with the tripodal amines tpa and tpza has been studied in order to investigate the complexation abilities of the two ligands in view of their potential use as selective extracting agents in lanthanides/actinides separation.

NMR studies have shown in tpa complexes of lanthanide(III) chlorides that tpa is not dissociated in methanol even at low concentration. In water, on the other hand, free and complexed tpa are in equilibrium. The latter behavior is observed also for tpa in the presence of europium(III) perchlorate in methanol. In the case of tpza, ligand binding is found in methanol for lanthanide chlorides but not for lanthanide perchlorates, and in acetonitrile for the latter salts. These results show that tpa binds lanthanides more strongly than tpza. This is in agreement with the higher electron-donating ability[53] of tpa relative to tpza.

Moreover, the NMR data reveal an additional interesting feature: the binding of both tripodal ligands is enhanced by the coordinating chloride with respect to the non or poorly coordinating perchlorate. This observation seems at odds with the widely accepted view that the bonding in lanthanide complexes is essentially electrostatic, since a reduction of the positive charge of the metal by anion complexation is not likely to enhance the binding of other coligands. Two explanations can be advanced to rationalize this behavior: (i) an interaction between the chloride(s) and the tripodal ligand within the complex, and (ii) the destabilization of solvent bonding which therefore becomes a weaker competitor of the tripodal ligand. The former would imply a rather large covalency of the lanthanide−ligand bonding which is not expected.

The metal extraction experiments show a low separation factor for tpa, while the ligand tpza extracts Am(III) more strongly than Eu(III). This behavior could be explained by the softer character of tpza which is expected to give rise to a stronger interaction with the actinides. It must be kept in mind that at the low pH where these experiments are conducted the competition between the proton and the metal ion for the ligand may play an important role. Examination of the pK_a of the two ligands ($pK_{a_1} = 6.17$, $pK_{a_2} = 4.35$, $pK_{a_3} = 2.55$ for tpa[26]; $pK_a = 3.00$ for tpza) shows that the protonation is certainly minimized for tpza in comparison to tpa over the range of aqueous nitric concentrations investigated.

Both features are likely to contribute to a stronger complexation of Am(III) by tpza but the second should influence only the complexing abilities of the ligands and not their selectivity. It is interesting to note that the behaviors of these ligands follow the expectation derived from tptz studies, and that the performance of tpza in terms of separation is close to that of tptz.[22,25]

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Supporting Information Available: Tables S1−S25 listing X-ray experimental details and crystallographic data, all atomic coordinates, equivalent isotropic and anisotropic displacement parameters and hydrogen coordinates for the five structures (25 pages). Ordering information is given on any current masthead page.

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