Notes

Crystal Structure and Solution Fluxionality of Lanthanide Complexes of 2,4,6,-Tris-2-pyridyl-1,3,5-triazine

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Introduction

The separation of actinides from lanthanides in strongly acidic solutions is a key step to be achieved to perform complete nuclear fuel reprocessing. The similarity of the solution chemistry of these trivalent cations[1] makes it an immensely difficult task. Aromatic nitrogen ligands have revealed some promising properties in this respect. The ligand 2,2′:6′,2″-terpyridine (terpy) is able to extract Am(III) 1 order of magnitude more strongly than Eu(III) from nitric acid solutions of the two metals at pH = 2−3.[2] On the other hand, when used in conjunction with a carboxylate co-extractant, the ligand 2,4,6,-tris(2-pyridyl)-1,3,5 triazine (tptz) allows to extract Am(III) more strongly than Eu(III) at lower pH (pH = 1).[2,3] However the nature of the species involved in the extraction has not been studied. Terpy complexes of lanthanides have been structurally characterized.[4] Nevertheless, while the synthesis of lanthanide complexes of tptz has been described by Hart and co-workers in 1969,[5] no crystallographic report or solution study of these complexes have yet appeared. We report here the crystal structures of the europium chloride and of the praseodymium acetate complexes of tptz and we present NMR evidence for the fluxional behavior of these complexes in solution. In addition, we show that tptz is a better ligand than terpy in acidic media owing to its additional protonation/complexation site.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer using CD_3OD and C_5D_5N solutions with MeOH and C_5H_5N as internal standards. The assignment of the NMR signals for the Pr and Eu complexes in MeOD and for the Eu complex in D_2O has been confirmed by two-dimensional homonuclear COSY correlation spectra. Rate data were obtained from 2D-EXSY spectra using volume integration data treated as a two-site exchange when only the internal rotation exchange occurs and as a three-site exchange when both free/complexed ligand exchange and rotational exchange occur. The 2×2 and the 3×3 matrixes of signal intensities were treated using the program D2DNMR.[6] Mixing time values of 5, 10, and 20 ms were used in the EXSY experiments in MeOD and mixing time values of 5, 20, and 100 ms were used for the EXSY experiments in MeOD/D_2O 50/50. Mass Spectra were measured with a ZAB2-SEQ instrument. Elemental analysis were performed by SCA/CNRS, Vernaison, France. Conductivity measurements were performed with a 712 Metrohm conductimeter. Solvents and starting materials were purchased from Aldrich, Fluka, and Alfa and used without further purification.

Synthesis of [Eu(tptz)Cl$_3$(MeOH)$_2$]·(MeOH) (1). Tptz (71.8 mg, 23.3 mmol) was added to a solution of $EuCl_3 \cdot 6H_2O$ (85.4 mg, 23.3 mmol) in methanol (5 mL). After 1 h of stirring, the complex was precipitated as a beige powder by addition of diethyl ether, filtered, washed with diethyl ether, and dried in vacuo. Yield: 70%. Suitable crystals for X-ray analysis were obtained by slow evaporation of a concentrated solution of the complex in methanol. Anal. Calcd for $[Eu(tptz)Cl_3] \cdot 4H_2O$, $C_{18}H_{20}Cl_3N_6O_4Eu$: C, 33.63; H, 3.14; N, 13.08. Found: C, 33.64; H, 3.29; N, 12.69. ^{1}H NMR (400 MHz, CD_3OD, 298K, δ): 17.82 (s, 2H, H^6); 9.47 (s, 2H, H^5); 8.85 (s, 2H, H^4); 8.53 (s, 1H, H$^{6'}$); 7.95 (s, 1H, H$^{3'}$); 7.86 (s, 1H, H$^{4'}$); 7.36 (s, 1H, H$^{5'}$); 6.51 (s, 2H, H^3). Λ_M at 298 K in methanol: 57 (2) Ω^{-1} cm^2 mol^{-1} at 4.6×10^{-2} M, 136 (10) Ω^{-1} cm^2 mol^{-1} at 10^{-3} M.

The complex $[Eu(tptz)(NO_3)_3]$ was prepared in the NMR tube and was not isolated.

[Eu(tptz)(NO$_3$)$_3$]. ^{1}H NMR (400 MHz, C_5D_5N, 298 K, δ): 25.96 (s, 2H, H^6); 10.74 (s, 2H, H^5); 9.17 (t b, 2H, H^4); 8.46 (s, 1H, H$^{6'}$); 7.49 (d b, 1H, H$^{3'}$); 7.44 (m, 1H, H$^{4'}$); 6.94 (m, 3H, H$^{5'}$, H^3).

Synthesis of [Ln(tptz)(OAc)$_3$]$_2$·2MeOH (Ln = Pr, Eu). $Ln(OAc)_3$ (0.2 mmol) was added to a solution of tptz (0.2 mmol) in methanol (3 mL). After 1 h of stirring, the complex was precipitated as a beige powder by addition of diethyl ether (20 mL), filtered, washed and dried in vacuo. Yield: 65−70%. Suitable crystals for X-ray analysis of $[Pr(tptz)(OAc)_3]_2 \cdot 2MeOH$ (**2**) were obtained by slow evaporation of a concentrated solution (9.6×10^{-2} M) of the complex in methanol.

Eu(tptz)(OAc)$_3$. ^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 31.96 (s b, 2H, H^6); 12.48 (s, 2H, H^5); 10.50 (s, 2H, H^4); 8.69 (s, 3H, H^3 and H$^{3'}$); 8.51 (s, 1H, H$^{6'}$); 8.01 (s, 1H, H$^{4'}$); 7.45 (s, 1H, H$^{5'}$); −3.55 (s b, 9H, $OCOCH_3$). Λ_M at 298 K in methanol: 8.3 (0.2) Ω^{-1} cm^{2}mol^{-1} at 4.6×10^{-2} M, 34 (3) Ω^{-1} cm^{2}mol^{-1} at 10^{-3}M.

Pr(tptz)(OAc)$_3$. ^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 9.38 (s, 1H, H^6); 9.07 (s, 2H, H^5); 8.81 (s b, 10H, H^4, $OCOCH_3$); 8.38 (s, 1H, H$^{6'}$); 8.06 (s, 1H, H$^{3'}$); 7.27 (s, 2H, H$^{4'}$); 4.53 (s, 2H, H$^{5'}$); −0.34 (s, 2H, H^3).

X-ray Crystallography. Crystal parameters and details of data collection and refinement are given in Table 1 (for full details see the Supporting Information). To prevent loss of solvent, a suitable crystal was quickly transferred from the mother liquor to a stream of cold nitrogen at − 130 °C on the diffractometer. The crystal was analyzed using a Siemens SMART CCD area detector three-circle diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å).

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

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Table 1. Crystallographic Data for [Eu(tptz)Cl_3(MeOH)$_2$]·(MeOH) (**1**) and [Pr(tptz)(OAc)$_3$]$_2$·2MeOH (**2**)

	1	**2**
formula	$C_{22}H_{28}N_6O_4Cl_3Eu$	$C_{50}H_{50}N_{12}O_{14}Pr_2$
fw	698.81	1324.84
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	triclinic
space group	*P*1	*P*1
a, Å	7.1306(5)	9.369(4)
b, Å	13.8850(9)	11.168(4)
c, Å	13.9400(9)	12.663(4)
α, deg	96.3090(10)	93.01(3)
β, deg	100.4130(10)	105.53(2)
γ, deg	99.3150(10)	92.57(2)
V, *Z*	1325.7(2) Å^3, 2	1272.4(8) Å^3, 1
D_{calc}, g cm^{-3}	1.751	1.729
μ (Mo Kα), mm^{-1}	2.708	1.972
no. of params refined	325	353
R_1, wR_2[a]	$R_1 = 0.0622$, w$R_2 = 0.1664$	$R_1 = 0.0516$, w$R_2 = 0.1295$

[a] Structure was refined on F_o^2 using all data: wR_2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Eu−O(1)	2.483(4)	Eu−N(5)	2.646(4)
Eu−O(2)	2.488(4)	Eu−Cl(1)	2.6874(14)
Eu−N(1)	2.555(4)	Eu−Cl(2)	2.6967(14)
Eu−N(4)	2.617(4)	Eu−Cl(3)	2.7378(14)
O(1)−Eu−O(2)	67.12(14)	N(5)−Eu−Cl(1)	75.21(11)
O(1)−Eu−N(1)	132.61(13)	O(1)−Eu−Cl(2)	78.49(10)
O(2)−Eu−N(1)	119.90(13)	O(2)−Eu−Cl(2)	87.04(9)
O(1)−Eu−N(4)	78.34(13)	N(1)−Eu−Cl(2)	143.51(9)
O(2)−Eu−N(4)	72.80(13)	N(4)−Eu−Cl(2)	153.82(10)
N(1)−Eu−N(4)	62.67(13)	N(5)−Eu−Cl(2)	80.45(10)
O(1)−Eu−N(5)	141.36(14)	Cl(1)−Eu−Cl(2)	95.92(5)
O(2)−Eu−N(5)	143.28(14)	O(1)−Eu−Cl(3)	75.74(10)
N(1)−Eu−N(5)	63.21(13)	O(2)−Eu−Cl(3)	139.26(10)
N(4)−Eu−N(5)	125.64(14)	N(1)−Eu−Cl(3)	74.55(10)
O(1)−Eu−Cl(1)	138.84(10)	N(4)−Eu−Cl(3)	84.12(11)
O(2)−Eu−Cl(1)	71.92(10)	N(5)−Eu−Cl(3)	77.35(11)
N(1)−Eu−Cl(1)	72.76(10)	Cl(1)−Eu−Cl(3)	144.20(4)
N(4)−Eu−Cl(1)	93.54(11)	Cl(2)−Eu−Cl(3)	101.76(5)

of data was collected. 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[7] 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 reflection with the Siemens SADABS program.[7]

The structures were solved by direct methods using the SHELXTL 5.03 package,[8] and all atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F^2, and hydrogen atoms were included in calculated positions. Selected bond lengths and angles are given in Table 2 for **1** and in Table 3 for **2**.

Results and Discussion

Reaction of tptz with $EuCl_3 \cdot 6H_2O$ in a 1:1 ratio in methanol yields the complex [Eu(tptz)Cl_3(MeOH)$_2$]·MeOH (**1**) which was isolated by adding Et_2O in 70% yield. Single crystals of [Eu(tptz)Cl_3(MeOH)$_2$]·MeOH (**1**) were obtained by slow evaporation of a concentrated methanol solution of the complex. Conductivity measurements show that in methanol at 10^{-3} M the compound behaves as a 1:1 electrolyte. The FAB mass spectra showed a strong peak corresponding to $\{M(tptz)Cl\}^{2+}$ arising from the loss of two coordinated chlorides and two smaller peaks corresponding to $\{M(tptz)\}^{3+}$ and $\{M(tptz)Cl_2\}^+$ arising from the loss respectively of three and one coordinated chlorides. The crystal structure of **1** is shown in Figure 1. It consists of discrete monomeric molecular units. The europium is eight-coordinate with three heterocyclic nitrogens of tptz which acts as a tridentate ligand, three chlorine ions and two methanol molecules. The coordination geometry around the metal is best described as a dodecahedron. The central triazine and two pyridine sidearms of the ligand adopt a cis−cis conformation resulting in a planar coordination of the metal. The torsion angle around the C(2)−C(9) axis relative to C(2)−

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Pr(1)−O(21)#1	2.452(5)	Pr(1)−O(26)	2.574(5)
Pr(1)−O(24)	2.513(5)	Pr(1)−O(21)	2.592(5)
Pr(1)−O(25)	2.535(5)	Pr(1)−N(5)	2.674(6)
Pr(1)−O(23)	2.544(5)	Pr(1)−N(1)	2.687(6)
Pr(1)−O(22)	2.551(5)	Pr(1)−N(4)	2.717(6)
O(21)#1−Pr(1)−O(24)	140.0(2)	N(5)−Pr(1)−N(1)	61.0(2)
O(21)#−Pr(1)−O(25)	81.3(2)	O(21)#1−Pr(1)−N(4)	71.0(2)
O(24)−Pr(1)−O(25)	136.6(2)	O(24)−Pr(1)−N(4)	80.0(2)
O(21)#1−Pr(1)−O(23)	92.2(2)	O(25)−Pr(1)−N(4)	139.8(2)
O(24)−Pr(1)−O(23)	51.6(2)	O(23)−Pr(1)−N(4)	71.0(2)
O(25)−Pr(1)−O(23)	140.2(2)	O(22)−Pr(1)−N(4)	142.9(2)
O(21)#1−Pr(1)−O(22)	115.0(2)	O(26)−Pr(1)−N(4)	93.4(2)
O(24)−Pr(1)−O(22)	73.9(2)	O(21)−Pr(1)−N(4)	118.8(2)
O(25)−Pr(1)−O(22)	75.2(2)	N(5)−Pr(1)−N(4)	119.4(2)
O(23)−Pr(1)−O(22)	72.2(2)	N(1)−Pr(1)−N(4)	59.3(2)
O(21)#1−Pr(1)−O(26)	74.5(2)	O(25)−Pr(1)−O(26)	50.5(2)
O(24)−Pr(1)−O(26)	135.4(2)	O(23)−Pr(1)−O(26)	162.4(2)
O(22)−Pr(1)−O(26)	123.7(2)	O(22)−Pr(1)−N(5)	77.8(2)
O(21)#1−Pr(1)−O(21)	64.7(2)	O(26)−Pr(1)−N(5)	71.8(2)
O(24)−Pr(1)−O(21)	109.6(2)	O(21)−Pr(1)−N(5)	121.2(2)
O(25)−Pr(1)−O(21)	70.8(2)	O(21)#1−Pr(1)−N(1)	112.5(2)
O(23)−Pr(1)−O(21)	70.9(2)	O(24)−Pr(1)−N(1)	72.4(2)
O(22)−Pr(1)−O(21)	50.4(2)	O(25)−Pr(1)−N(1)	109.2(2)
O(26)−Pr(1)−O(21)	112.0(2)	O(23)−Pr(1)−N(1)	109.6(2)
O(21)#1−Pr(1)−N(5)	145.2(2)	O(22)−Pr(1)−N(1)	132.4(2)
O(24)−Pr(1)−N(5)	73.5(2)	O(26)−Pr(1)−N(1)	66.6(2)
O(25)−Pr(1)−N(5)	70.7(2)	O(21)−Pr(1)−N(1)	177.2(2)
O(23)−Pr(1)−N(5)	122.5(2)		

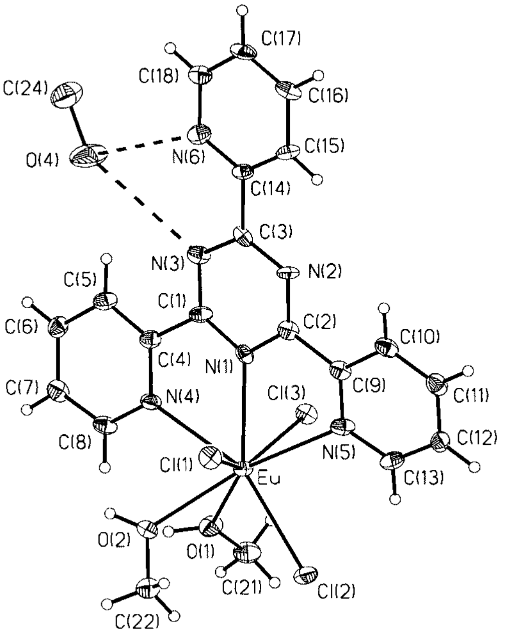

Figure 1. Side view of the crystal structure of the complex [Eu(tptz)Cl_3(MeOH)$_2$]·MeOH **1** with thermal ellipsoids at 30% probability.

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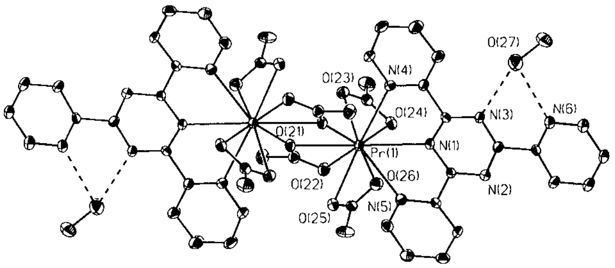

Figure 2. Side view of the crystal structure of the dimeric complex $[Pr(tptz)(OAc)_3]_2$·2MeOH **2** with thermal ellipsoids at 30% probability.

N(1), C(9)−N(5) is 5.7° and the torsion angle around the C(1)−C(4) axis relative to C(1)−N(1), C(4)−N(4) is 4.4°. The metal is 0.25 Å out of the plane of the tptz. The tptz ligand is not strictly planar, the higher deviation values being +0.21 Å for C(8) and − 0.21 Å for C(13). The Eu−N(triazine) distance is shorter (2.555(4) Å) than the Eu−N(pyridine) ones (2.616(4), 2.645(4) Å). This behavior is not shown by the terpy analogue $[Eu(terpy)Cl(H_2O)_5]Cl_2$[4] where the Eu−N distance for the central pyridine is marginally shorter (2.542(5) Å) than those for the pyridine side arms (2.551(4) Å). Therefore it indicates a stronger interaction of the lanthanide ion with the triazine nitrogen than with the pyridine nitrogen. It is noteworthy that a strong hydrogen bond exists between a methanol molecule and the uncoordinated nitrogens of the triazine and a pyridine as shown by the short distances between the oxygen atom O(4) of the uncoordinated methanol molecule present in the cell and the uncoordinated pyridine nitrogen (O(4)−N(6) = 2.921(9) Å) and the uncoordinated triazine nitrogens (O(4)−N(3) = 3.319 (9) Å). The methanol oxygen forms also a strong hydrogen bond with a pyridine C−H (O(4)−H(5) = 2.39(1) Å).

The increased extraction efficiency of tptz in the presence of carboxylato coextractants motivated the structural study of the praseodymium acetato complex of tptz. Single crystals of the complex $[Pr(tptz)(OAc)_3]_2$·2MeOH (**2**) were obtained by slow evaporation of a concentrated methanol solution of the complex. The crystal structure of **2**, which is a dimeric complex, is shown in Figure 2. Each praseodymium ion is ten-coordinate with three heterocyclic nitrogens of tptz which acts as a tridentate ligand, and two bidentate acetates; the remaining three coordination sites are occupied by two oxygens of a bidentate and bridging acetate and one acetato oxygen from the other $[Pr(tptz)(OAc)_3]$ unit. The praseodymium ions are therefore doubly bridged by two (η^2,μ-1,1)-acetates and separated by 4.263 Å. The coordination of the tptz ligand is quite symmetric with a Pr−N(triazine) distance value of 2.687(6) Å and the Pr−N(pyridine) distance values of 2.674(6) and 2.717(6) Å. These values are larger than the values reported for the terpy complex $[Pr(terpy)Cl(H_2O)_5]Cl_2$ (Pr−N = 2.635(4) and 2.625(3) Å).[9] The torsion angle around the C(2)−C(9) axis relative to C(2)−N(1), C(9)−N(5) is 2.2°, and the torsion angle around the C(1)−C(4) axis relative to C(1)−N(1), C(4)−N(4) is 2.0°. The metal is 0.51 Å out of the plane of the tptz. Also in this complex the methanol molecule present in the cell has a strong hydrogen bonding interaction with a triazine nitrogen, a pyridine nitrogen and a pyridine hydrogen (O(27)−N(3) = 3.349(11) Å, O(27)−N(6) = 2.939 (11) Å, and O(27)−H5 = 2.473(11) Å).

The NMR spectra of the complexes **1** and **2** in methanol solution show four signals for the unmetalated pyridine; only four signals of double intensity instead of eight signals of single intensity are observed for the two coordinating pyridines, indicating an equivalence of these pyridines that can only be explained by the presence of an overall 2-fold symmetry in solution which is not present in the crystal structures. This observation suggests that the methanol molecules present in the crystal structure of **1** undergo rapid exchange with solvent molecules and the pyridine non coordinated to the metal rotates rapidly around the C−C bond after breaking of the hydrogen bonds with methanol. In addition conductivity measurements at the NMR concentration indicate the presence of the neutral complex and the monocation. Therefore the bound chloride ions must exchange rapidly on the NMR time scale between the different chloride positions. The symmetry of the NMR spectrum of **2** suggests that the dimeric form of the complex exchanges rapidly in solution with a monomeric form of the complex in which the uncoordinated pyridine rotates rapidly around the C−C bond. The EXSY spectrum of **1** (Figure 3) shows an exchange (slow on the NMR time scale) between all protons indicating that the metal moves around the three coordination sites of the ligand as shown in Scheme 1.

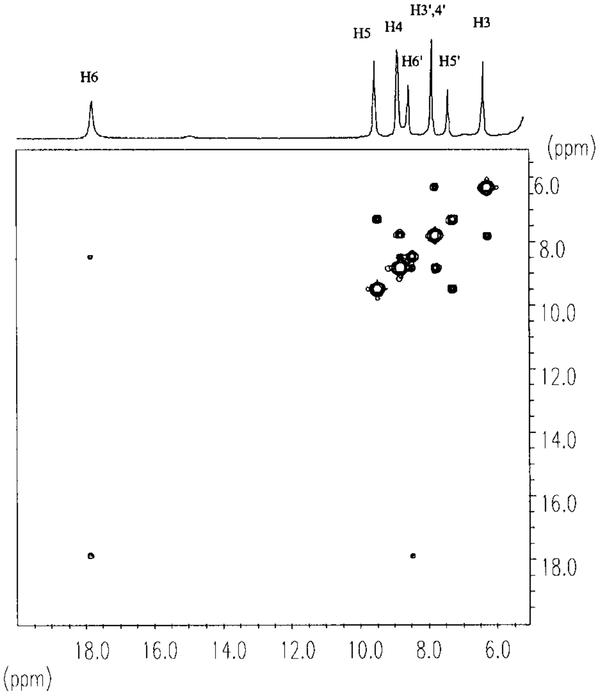

Figure 3. ^1H two-dimensional EXSY spectrum (at 298 K, mixing time 30 ms) of $[Eu(tptz)Cl_3(MeOH)_2]$ in MeOD showing exchanges (H3−H4−H5−H6 ↔ H3′−H4′−H5′−H6′) due to the rotational process.

A similar type of rotational motion has already been observed by Orrell and co-workers[10] in the platinum(II) complex of tptz $[Pt(C_6F_4CF_3\text{-}p)_2(tptz)]$. An intramolecular partially dissociative mechanism was found for the "hurdling" process in the platinum complex. Two mechanisms can be invoked to explain the observed rotation of the europium ion around the ligand: (i) the complete dissociation of the metal followed by reassociation on a different site, and (ii) the partial dissociation of Eu from the triazine and one of the pyridyl nitrogens, followed by rotation of the remaining metal-bound pyridyl group about the pyridyl-triazine bond and metal binding by a different triazine nitrogen and a different pyridyl group. To try and discriminate between these two possibilities, EXSY spectra were recorded on methanol solutions of tptz complexes prepared in situ starting

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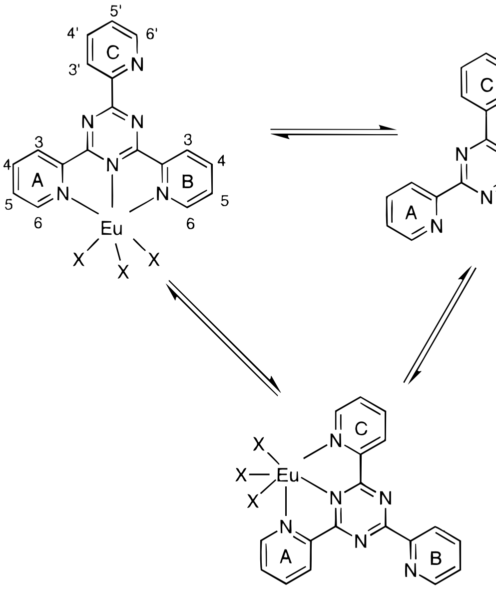
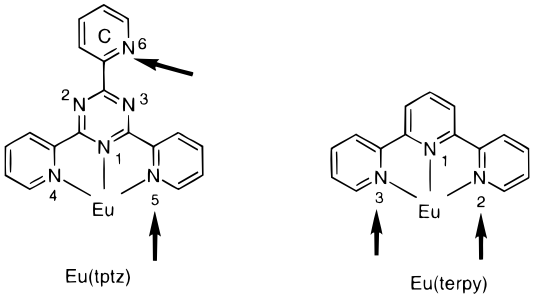
Scheme 1



X = Cl−, NO_3^-, OAc−

Scheme 2



from europium salts $EuX_3 \cdot H_2O$ where the counterions X = NO_3^- and AcO^- are bulkier than Cl^-. Conductivity measurements performed on 10^{-3} M and 4.6×10^{-2} M methanol solutions of the acetate salt of europium gives conductivity values inferior to the one reported for 1:1 electrolytes indicating that only one of the acetate ions is partially dissociated, the remaining acetate ions staying coordinated to the europium. All the corresponding spectra show the same exchange peaks found in the EXSY spectrum of **1** and the first-order rate constants for the rotational process (H3,4,5,6 ↔ H3′,4′,5′,6′) measured from integration of the NMR peaks[11] ($k(s^{-1}) = 7$ for **1** and $k(s^{-1}) = 17$ for $[Eu(tptz)(OAc)_3]_2$) do not indicate any effect of steric hindrance by the ligand X on the rotation of the metal around the tptz. These observations suggest that the rotation mechanism is based on complete metal dissociation. Moreover EXSY spectra were recorded using different mixing time values for a solution of **1** (10 mg) in a solvent mixture CD_3OD/D_2O at a ratio 1/1 (0.7 mL). Under these conditions the 1D ^1H NMR spectrum of the complex shows two sets of signals which were attributed to the complex and to the free ligand with a ratio of complexed to free ligand obtained from signal integration ≅ 3:1. When a mixing time of 5 ms is used to record the EXSY spectrum only the exchange H3*−H4*−H5*−H6* ↔ H3,H3′−H4,H4′−H5,H5′−H6,H6′ between the complex and the free ligand is observed. When a mixing time of 100 ms is used the exchange peaks due to the rotational motion (H3−H4−H6−H5−H6 ↔ H3′−H4′−H5′−H6′) appear in the EXSY spectra (Figure 4) in addition to the peaks (H3*−H4*−H5*−H6*) ↔ (H3,H3′−H4,H4′−H5,H5′−H6,H6′) due to the exchange between free and complexed ligand. The first-order rate constant for the rotational process ($k(s^{-1}) = 0.4$) is an order of magnitude smaller than the one for the exchange between the complex and the free ligand ($k(s^{-1}) = 6$). This experiment indicates that the rate of the rotation process is slower than the rate of tptz dissociation. Again this observation supports a dissociative mechanism.

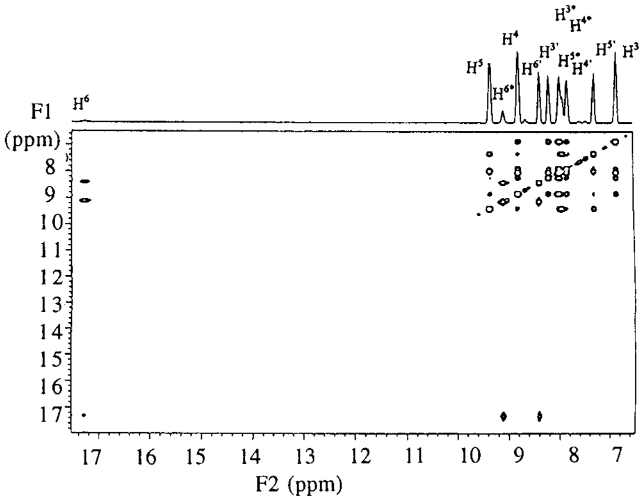


Figure 4. ^1H two-dimensional EXSY spectrum (at 298K, mixing time 100 ms) of $[Eu(tptz)Cl_3(MeOH)_2]$ in $MeOD/D_2O$ 50/50. The cross-peaks result from the rotational process (H3−H4−H6−H5−H6 ↔ H3′−H4′−H5′−H6′) and from the exchange free ligand (*)/complex H3*−H4*−H5*−H6*) ↔ (H3,H3′−H4,H4′−H5,H5′−H6,H6′).

At pH = 1 both ligands, terpy and tptz, are bisprotonated ($pK_{a1} = 4.9$ for terpy and 4.5 for tptz; $pK_{a2} = 4.0$ for terpy and 1.8 for tptz)[2], but while at this pH the terpyridine loses almost completely its extracting efficiency, tptz can still selectively extract actinides. To help understand the different behaviors of terpy and tptz in the extraction in acidic media we studied by NMR spectroscopy the complexation of europium(III) with the mono- and bis-protonated forms of terpy and tptz in methanol solution. Titration of 1:1 solutions of $EuCl_3 \cdot 6H_2O$ and terpy or tptz in CD_3OD (6.1×10^{-2} M) with a solution of trifluoroacetic acid in CD_3OD was followed by NMR. When 1 equiv of acid is added, a ratio of complexed to free protonated ligand of 0.8 was observed for terpy and of 2.0 for tptz. When two equivalents of acid are added this ratio became 0.2 for terpy and 1.2 for tptz indicating a much stronger coordinating ability of tptz at high acid concentration.

We believe that the different behavior of the two ligands is due to the presence in tptz but not in terpy of a protonation site, N6 and N3 (or N2 depending on the pyridine orientation), in addition to the tridentate coordination site N4, N1, N5. Indeed, in the three structurally characterized metal complexes of tptz, the N6, N3(N2) site is either hydrogen bonded (this work) or protonated.[12] Addition of 1 equiv of acid to the tptz complex should result in the protonation of the pyridine nitrogen N6 not bound to the metal. The protonated ligand shows a lower affinity (in methanol solution) for the metal than the non protonated tptz due to the increased electrostatic repulsion occurring upon complexation of $tptzH^+$ with Ln^{3+}. When a second equivalent of acid is added, one of the two pyridine nitrogen bound to the

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(12) Byers, P.; Chan, G. Y. S.; Drew, M. G. B.; Hudson, M. J.; Madic, C. *Polyhedron* **1996**, *15*, 2845.

metal (N4 or N5) should be protonated leaving a bidentate coordination site for the complexation of the metal. Addition of 2 equiv of acid to the terpy complex should result instead in the protonation of two terpy nitrogens leaving only a monodentate coordination site with a very poor affinity for the metal.

The propensity of the site N6, N3(N2) to fix protons leaving the tridentate N4, N1, N5 site available for the metal complexation may be the basis for the superior ability of tptz (vs terpy) to extract Am(III) from nitric acid solutions of Am(III) and Eu(III).

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Supporting Information Available: Tables S1−S19 listing all atomic coordinates, equivalent isotropic and anisotropic displacement parameters and hydrogen coordinates for the structures of **1** and **2**; EXSY spectrum of a solution of 10 mg of **1** in 0.7 mL of a 1/1 mixture CD_3OD/D_2O at 5 ms. X-ray crystallographic files, in CIF format, for the two structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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