Complexation Studies of Iodides of Trivalent Uranium and Lanthanides (Ce and Nd) with 2,2′-Bipyridine in Anhydrous Pyridine Solutions

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In anhydrous pyridine solution at 294 K, U(III) and Ce(III) triiodides were found to form both 1:1 (ML) and 1:2 (ML$_2$) complexes with bipyridine (*bipy* = L) while Nd(III) triodide formed only a 1:2 complex. The 1:3 (ML$_3$) complexes were identified at low temperature with a large excess of L. Conductometry measurements showed for U(III) a large increase in the conductivity when increasing the molar ratio L:U. The complex UL$_2$ was found to be a 1:1 electrolyte and the species UI$_2{}^+$ was more reactive toward L in comparison with UI$_3$. For Ce(III) and Nd(III), MI$_2{}^+$ and MI$_3$ present about the same affinity for L. The stability of the complexes is limited, and U(III) possesses a slightly higher affinity for *bipy* than the trivalent lanthanides. Interestingly, a preference for the formation of ML$_2$ complex was shown for all the studied M(III) ions. The driving force for complex formation was always the enthalpy, and, surprisingly for a bidentate ligand (*bipy*), no favorable entropy contribution to complex formation was observed. The X-ray crystal structures of [CeI$_3$(bipy)$_2$(py)]$_4$·5py·bipy and UI$_3$(bipy)$_2$(py)·2py were determined. The structures of the molecules MI$_3$(bipy)$_2$(py) are almost identical for U and Ce. The mean M(III)−N(bipy) bond distances are equal to 2.67(3) Å for Ce(III) and 2.65(4) Å for U(III). The slightly smaller M(III)−N(bipy) distances observed for U(III) would reflect a slightly more important covalent character of the U(III)−N(bipy) bonds, in agreement with the slightly better affinity of U(III) than Ce(III) or Nd(III) toward *bipy* observed in solution and with the fact that the enthalpy is the driving force for complex formation.

Introduction

The nuclear vitrified wastes from the reprocessing of spent nuclear fuels contain not only fission products (FPs) but also long-lived α-emitter radionuclides, i.e., nuclides of the elements neptunium (Np), americium (Am), and curium (Cm), known as the minor actinides (MAs). The MAs are responsible for the long-term radiotoxic inventories of these wastes, which will be disposed of in deep geological repositories in the future. New scenarios for the management of these highly active wastes are under worldwide study aiming, in particular, to drastically decrease their long-term radiotoxic inventories. To reach this goal it is envisaged to destroy the long-lived radionuclides by transmutation by neutron bombardment. This implies the prior separation (named partitioning) of the MAs from the complex mixture of nuclear wastes. This scenario is known as the partitioning and transmutation scenario (P&T).[1,2] Among the different partitioning processes under development, those based on liquid−liquid solvent extraction are the most popular. Numerous systems are under study,[1,2] but all of them are faced with a very delicate separation problem: how to separate the trivalent actinides (An(III), with An = Am and Cm) from the trivalent lanthanides (Ln(III)), which represent about one-third of the total mass of the nuclear wastes and which are about

20−30 times more abundant than the trivalent actinides. This An(III)/Ln(III) separation is an old problem which was the subject of numerous studies, reviewed by Nash in 1993 and 1994.[3,4] The difficulty of this problem is reinforced owing to the fact that the aqueous effluents that contain the wastes to be partitioned are highly acidic (nitric acid concentration 3−4 M). As noted by Nash,[3,4] it seems that solutions to this problem can be found if soft nitrogen or sulfur ligands (extractants or aqueous complexing agents) are used within the separation processes. These were, for example, the choices made during the development of a recent European research project.[5]

The trivalent ions of the 4f (Ln(III)) and 5f (An(III)) series are known to be hard acids in the Pearson classification of acids and bases.[6] As a consequence, these ions prefer to bond hard bases such as, for example, oxygen ligands. Consequently, these 4f and 5f trivalent ions are strongly solvated in aqueous solutions;[7,8] eight to nine water molecules are bound to the inner coordination sphere of these trivalent metal ions.[9,10] To compete

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with the water molecules for bonding 4f and 5f trivalent metal ions, soft nitrogen and sulfur ligands should preferably be multidentate. This is why oligopyridines, 2,4,6-tri(pyridin-2-yl)-1,3,5-triazine (TPTZ), 2-amino-4,6-di(pyridin-2-yl)-1,3,5-triazine, 2,6-bis(5,6-di-alkyl-1,2,4-triazin-3-yl)pyridine (BTP), etc.,, and derivatives, are under study.[5] It is thought that the better affinity of the soft nitrogen ligands for 5f vs 4f trivalent ions is due to the fact that the 5f ions are slightly less hard than the 4f ions, leading to the creation of bonds with partially covalent character between the N atoms of the ligand molecules and the 5f ions.[3,4] Nevertheless, little thermodynamic information is available in the literature to support such an interpretation.

The aim of the present study is to put some light onto this important question. As the difference in hardness between the 5f and 4f ions is supposed to be larger at the beginning of the series of elements, trivalent uranium, cerium, and neodymium ions were selected.[11] These ions possess rather similar ionic radii for identical coordination numbers.[12] The ligand chosen for the study was 2,2′-bipyridine (*bipy*), which is the simplest molecule among the oligopyridine family of ligands. Moreover, owing to the fact that the affinity of *bipy* for trivalent 4f and 5f ions is supposed to be limited, thermodynamic data, such as stability constants, enthalpy, and entropy of complexation reactions, were expected to be attainable. This would not be the case for higher oligopyridines, such as terpyridine, or TPTZ, etc. In order to possibly increase the predicted slight differences of affinities between the 4f and 5f ions vs *bipy*, an alternative solvent to water, anhydrous pyridine (*py*), with lower solvation properties, was chosen for the study. Moreover, the binding of *bipy* molecules to the trivalent metal ions will certainly require the removal of *py* molecules from the inner sphere of coordination of the metal ions; this will help to understand the effect of the preorganization of *py* moieties within the *bipy* ligand for M(III) complexation. Finally, the iodide ion was chosen as the counterion for An(III) and Ln(III) because its complexing ability toward these 4f and 5f trivalent ions is known to be low (no complexation is observed, for example, in aqueous solutions), and because Ln(III) and An(III) iodides are salts that are commercially available (Ln(III)) or relatively easy to prepare (U(III)[13]).

NMR spectroscopy, conductometry, and X-ray crystallography were the experimental techniques selected in this work to study the complexation of trivalent uranium, cerium, and neodymium iodides by *bipy* in anhydrous pyridine solutions.

Experimental Section

General Details. All experiments were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Pyridine-d_5 (Eurisotop) was dried over 3 Å molecular sieves. Bipyridine (Aldrich) was sublimated before use; CeI$_3$ and NdI$_3$ (Aldrich) were dried under vacuum, and UI$_3$(py)$_4$ was prepared by a published method.[13a]

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Table 1. ^{1}H NMR Spectra of the *Mono-*, *Bis-*, and *Tris-Bipy* Species of M(III) (δ in Pyridine-d_5)

	H$^{3,3'}$	H$^{4,4'}$	H$^{5,5'}$	H$^{6,6'}$
		At 294 K		
CeL	−2.8	6.7	10.0	14.0
CeL$_2$	3.7	7.1	9.0	11.0
NdL$_2$	6.0	8.6	9.7^a	13.1^b
UL	6.8	c	19.4	19.4
UL$_2$	7.5	6.8	17.7^a	14.3^b
		At 233 K		
CeL	−8.6	6.2	11.2	16.5
CeL$_2$	2.1	8.1	9.6	12.3
CeL$_3$	c	9.5	10.5	14.8
NdL$_2$	3.3	8.8	10.6	15.8
NdL$_3$	c	8.4	11.6	18.2
UL	6.4	c	24.5	23.2
UL$_2$	7.4	6.7	21.0	17.6
UL$_3$	7.7	c	19.0	17.1

^{a} Triplet ($J = 6$ Hz). ^{b} Doublet ($J = 6$ Hz). ^{c} Not detected.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for MI$_3$(bipy)$_2$(py) (M = Ce, U)

	CeI$_3$(bipy)$_2$(py)	UI$_3$(bipy)$_2$(py)
M−N(1)	2.665(4)	2.622(9)
M−N(2)	2.708(4)	2.694(9)
M−N(3)	2.664(4)	2.662(8)
M−N(4)	2.639(4)	2.611(9)
M−N(5)	2.672(4)	2.679(9)
M−I(1)	3.1991(8)	3.2032(8)
M−I(2)	3.2273(6)	3.2071(8)
M−I(3)	3.2588(6)	3.2511(8)
N(1)−M−N(2)	60.74(12)	61.3(3)
N(2)−M−N(3)	66.51(12)	66.5(2)
N(3)−M−N(4)	61.57(12)	62.0(3)
I(1)−M−I(2)	152.115(13)	151.32(2)
I(1)−M−I(3)	79.917(18)	78.65(2)
I(2)−M−I(3)	83.863(19)	84.53(2)

^{1}H NMR spectra were recorded on a Bruker DPX200 spectrometer with its dedicated temperature control unit, using pyridine-d_5 solutions with cyclohexane as internal standard, and were referenced internally using the residual protio solvent resonances relative to TMS ($\delta = 0$). Conductivity measurements were performed at 293 K with a Consort C-832 conductometer; the cell constant was 0.1 cm^{-1}. Elemental analyses were carried out by Analytische Laboratorien, Gummersbach, Germany.

Solution NMR Studies. In a typical experiment, an NMR tube was charged with *bipy* (3.3 mg, 0.021 mmol) and either CeI$_3$ (10.9 mg, 0.021 mmol), NdI$_3$ (11.3 mg, 0.021 mmol), or UI$_3$(py)$_4$ (19.5 mg, 0.021 mmol) in pyridine-d_5 (0.8 mL), and cyclohexane (1 μL) was added via a microsyringe. After stirring for 5 min at room temperature, the spectrum was recorded. Successive additions of *bipy* were performed in the glovebox, and, after each addition, the complexation reactions were monitored by recording the NMR spectra from 294 to 233 K, with intervals of 5 K. In order to reduce the errors resulting from successive weighings of *bipy*, some spectra were recorded after direct addition of *n* equiv of *bipy* to M(III) triodides. The spectra were integrated by using the internal standard, cyclohexane, and thus the stoichiometry of the *bipy* complexes and their concentrations were determined. The spectral data of the *mono-*, *bis-*, and *tris-bipy* species **1**−**3** are reported in Table 1; the values of the corresponding formation constants K_i and β_2 and the values of the corresponding thermodynamic constants ΔH_i and ΔS_i are listed in Tables 3 and 4, respectively.

Conductometry Studies. In a typical experiment, a 10^{-2} M solution of Ce(III) or U(III) in pyridine was prepared in the glovebox by dissolving CeI$_3$ (52.1 mg) or UI$_3$(py)$_4$ (93.5 mg) in pyridine (10 mL). After 5 min at room temperature, the electrode was immersed into the solution and the conductivity measured. The conductivity was also determined after eight successive additions of 1 equiv of *bipy* (15.6 mg) into the solution; the electrode was washed with pyridine between

Table 3. Stability Constants for the M(III)/*Bipy* Systems in Anhydrous Pyridine

M	$K_1{}^a$	$K_2{}^a$	$\beta_2{}^a$	$K_3{}^b$
Ce	4.0 ± 0.5	77 ± 8	308 ± 75	0.8 ± 1
Nd			823 ± 125	0.20 ± 0.05
U	11 ± 2	128 ± 17	1408 ± 390	1.6 ± 0.1

^{a} At 294 K. ^{b} At 233 K.

Table 4. Enthalpy (kJ mol^{-1}) and Entropy (J mol^{-1} K^{-1}) Values for the Formation of the *Mono-*, *Bi*s, and *Tris-Bipy* Species of M(III) in Anhydrous Pyridine^a

| M	ΔH_1	ΔS_1	ΔH_2	ΔS_2	ΔH_3	ΔS_3
Ce	-20	-55	-10	3	-11	-48
Nd			-30^b	-44^b		
U	-21	-52	-9	8	-12	-47

^{a} The uncertainties are within $\pm 10\%$ from the van't Hoff diagrams. ^{b} ΔH_2 and ΔS_2 values are global values for both the first and second complexation reactions.
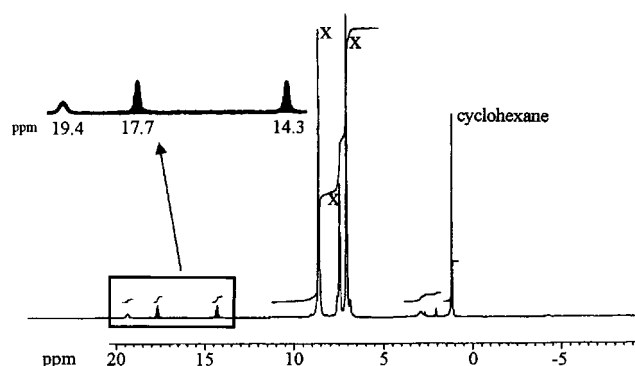
Figure 1. ^{1}H NMR spectrum of a solution of UI$_3$(py)$_4$ (10^{-2} M) and *bipy* (10^{-2} M) in anhydrous pyridine-d_5 at 294 K (x designates the signals of pyridine).
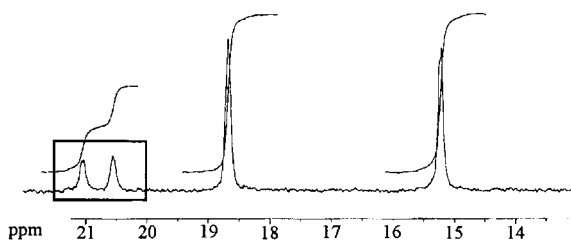
Figure 2. Low-field region of the ^{1}H NMR spectrum of a solution of UI$_3$(py)$_4$ (10^{-2} M) and *bipy* (10^{-2} M) in anhydrous pyridine-d_5 at 233 K.

each measurement. The results are presented in Figure 3. The conductivity of 10^{-2} M solutions of NaI or NR$_4$I (R = *n*-butyl and *n*-pentyl) in pyridine was equal to 120 μS cm^{-1}.

Synthesis of CeI$_3$(bipy)$_2$(py). *Bipy* (1.56 g, 10.0 mmol) was added to a solution of CeI$_3$ (520.8 mg, 1.0 mmol) in pyridine (30 mL). After the resulting mixture was stirred for 2 h at room temperature, the complex precipitated upon addition of diethyl ether (30 mL) and the yellow powder was filtered off, washed with diethyl ether (60 mL), and dried under vacuum (638 mg). Yield: 70%. Anal. Calcd for C$_{25}$H$_{21}$I$_3$N$_5$Ce: C, 32.91; H, 2.32; N, 7.68. Found: C, 32.77; H, 2.35; N, 7.78. The NMR spectrum of this complex in pyridine-d_5 is identical to that obtained after addition of 2 equiv of *bipy* to CeI$_3$.

Synthesis of NdI$_3$(bipy)$_2$(py). *Bipy* (179.0 mg, 1.15 mmol) was added to a solution of NdI$_3$ (86.0 mg, 0.16 mmol) in pyridine (5 mL). After the resulting mixture was stirred for 1 h at room temperature, the complex precipitated upon addition of diethyl ether (5 mL) and the yellow powder was filtered off, washed with diethyl ether (10 mL), and dried under vacuum (88 mg). Yield: 60%. Anal. Calcd for C$_{25}$H$_{21}$I$_3$N$_5$Nd: C, 32.76; H, 2.31; N, 7.64. Found: C, 32.66; H, 2.42;
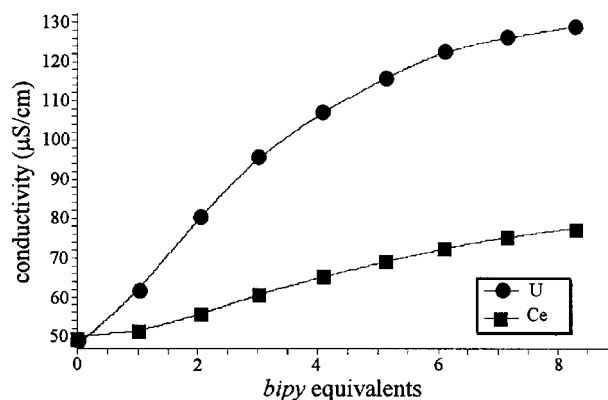
Figure 3. Conductometric titration of UI$_3$(py)$_4$ and CeI$_3$ solutions (10^{-2} M) by *bipy* in anhydrous pyridine at 293 K (the points are experimental data, and the lines are guides for the eyes).

N, 7.79. The NMR spectrum of this complex in pyridine-d_5 is identical to that obtained after addition of 2 equiv of *bipy* to NdI$_3$.

Synthesis of UI$_3$(bipy)$_2$(py)$_{1.5}$. *Bipy* (106.9 mg, 0.7 mmol) was added to a solution of UI$_3$(py)$_4$ (61.4 mg, 0.07 mmol) in pyridine (5 mL). After the resulting mixture was stirred for 1 h at room temperature, the complex precipitated upon addition of diethyl ether (5 mL) and the brown powder was filtered off, washed with diethyl ether (10 mL), and dried under vacuum (44.0 mg). Yield: 60%. The elemental analyses correspond to the formula UI$_3$(bipy)$_2$(py)$_{1.5}$. Anal. Calcd for C$_{27.5}$H$_{23.5}$I$_3$N$_{5.5}$U: C, 31.46; H, 2.26; N, 7.34. Found: C, 31.12; H, 2.37; N, 7.43. The NMR spectrum of this complex in pyridine-d_5 is identical to that obtained after addition of 2 equiv of *bipy* to UI$_3$(py)$_4$.

X-ray Crystallography. Crystals of [CeI$_3$(bipy)$_2$(py)]$_4$·5py·bipy (yellow) and of UI$_3$(bipy)$_2$(py)·2py (black) were obtained by slow diffusion of pentane into a pyridine solution of CeI$_3$ or UI$_3$(py)$_4$ and *bipy* in the molar ratio of 1:10. Selected single crystals were introduced into thin-walled Lindeman glass tubes in the glovebox. Diffraction collection was carried out on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from 10 images recorded with 2° Φ-scans and later refined on all data. The data were recorded at 123 K. A 180° Φ-range was scanned with 2° steps with a crystal to detector distance fixed at 30 mm. Data were corrected for Lorentz−polarization effects. The structure was solved by the heavy atom method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH) times that of the parent atom. For UI$_3$(bipy)$_2$(py)·2py, one pyridine solvent molecule was found disordered on two positions with 0.5 occupation factor and the second pyridine solvent molecule was refined with one fixed thermal parameter. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[14] Selected bond distances and angles are listed in Table 2; crystallographic data are given in Table 5.

Results

Solution ^{1}H NMR Studies. (a) The MI$_3$/*Bipy* Systems (M = Ce, Nd, U). Addition of variable amounts of *bipy* to a 10^{-2} M solution of MI$_3$(py)$_4$ (M = Ce, Nd, U) in pyridine-d_5 leads to the formation of several complexes, as noted by the emergence of low-field-shifted ^{1}H NMR signals ($\delta > 9$) corresponding to *bipy* ligands coordinated to the paramagnetic metal center. The relative intensities of these resonances, measured by comparison with the signal intensity of the internal standard, cyclohexane, is dependent on the metal M, the number n of *bipy* equivalents, and the temperature. At 294 K and for $n \leq 9$, in addition to the peaks corresponding to free *bipy*: (i) two distinct pairs of signals of equal intensities are observed for M = Ce at δ 11.0 and 9.0 and at δ 14.0 and 10.0,

(14) Sheldrick, G. M. SHELXTL; Bruker-AXS: Madison, WI, 1999.

Table 5. X-ray Crystallographic Details for
[CeI$_3$(bipy)$_2$(py)]$_4$·5py·bipy and UI$_3$(bipy)$_2$(py)·2py

	[CeI$_3$(bipy)$_2$(py)]$_4$·5py·bipy	UI$_3$(bipy)$_2$(py)·2py
chem formula	C$_{135}$H$_{117}$I$_{12}$N$_{27}$Ce$_4$	C$_{35}$H$_{31}$I$_3$N$_7$U
fw	4200.84	1168.4
cryst syst	monoclinic	monoclinic
space group	P2$_1$/c	P2$_1$/c
λ (Å)	0.71073	0.71073
d_{calcd} (g cm^{-3})	1.984	2.216
μ (mm^{-1})	3.963	7.314
a (Å)	14.182(3)	13.269(1)
b (Å)	20.779(4)	20.729(1)
c (Å)	23.992(5)	14.168(1)
β (deg)	96.03(3)	115.984(1)
V (Å^3)	7031(2)	3502.9(4)
Z	2	4
indep reflns	43453	13332
obs reflns [$I > 2\sigma(I)$]	9454	2798
R^a	0.032	0.038
$R_w{}^b$	0.063	0.095

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$.

respectively; the intensity of the two latter signals is inferior to that of the two other resonances, passing through a maximum for $n \cong 2$ and being almost negligible for $n = 7$, while the intensity of the other pair of signals increases regularly with n; (ii) for M = U, three signals (cf. Figure 1) corresponding to one pair of equal intensity signals at δ 17.7 and 14.3 and one signal at δ 19.4 are observed; the intensity of the small signal at δ 19.4 passes through a maximum for $n \cong 2$, and this signal vanishes for $n = 9$, while the intensity of the two other signals regularly increases with n; (iii) complexation of Nd(III) with *bipy* at 294 K exhibits some differences since only two signals of equal intensities are visible on the ^{1}H NMR spectra at δ 13.1 and 9.7. With a large excess of *bipy* (10 < n < 20), only the pairs of less-shifted resonances are observed for both Ce(III) and U(III); the intensity of each signal is then constant and represents 4 H of a *bipy* ligand. Also in the case of Nd(III), the intensity of each signal increases with n and reaches the value of 4 H for $n \geq 10$.

New interesting facts emerged from the spectra recorded at lower temperature: (i) the NMR signals of Ce, Nd, and U *bipy* complexes are shifted to lower field, as expected for paramagnetic compounds; (ii) the lowest field single signal observed at room temperature for U is split into two resonances of equal intensity, and two distinct pairs of resonances are thus visible on the spectra when T is lower than 274 K (cf. Figure 2); at 233 K, these pairs of signals are noted at δ 24.5 and 23.2 and at δ 21.0 and 17.6, respectively; (iii) for M = Ce and U, the intensities of each pair of signals vary with the temperature, as well as the ratio of these intensities; for example, this ratio is equal, for M = U and $n = 2$, to 2.8 and 8.1 at 294 and 233 K, respectively; (iv) most notably, new signals of equal intensity appear at $\delta \geq 9$ for M = Ce, Nd, and U; at 233 K, the chemical shifts of these peaks are δ 14.8, 10.5, and 9.5 (M = Ce), δ 18.2 and 11.6 (M = Nd), and δ 19.0 and 17.1 (M = U). These signals are more intense and are visible at higher temperature with increasing values of n. For $n \geq 8$, the NMR spectra show two groups of resonances; one corresponds to the unique pair observed at room temperature, and the other group (three signals for Ce and two signals for Nd and U) appears at ca. 283 K; if an intensity of 4 H is attributed to each signal of the first pair, the integral of each signal of the second group of resonances represents 6 H.

At this stage of the work, it is clear that addition of n equiv of *bipy* to M(III) in pyridine leads to the successive formation of three species **1**, **2**, and **3**, each one characterized by a pair of low-field-shifted NMR signals of equal intensity. At 294 K, species **1** and **2** are observed for $n \leq 7$ while **2** is the only species for $n \geq 8$. Species **3** are detected only at lower temperature. It is interesting to note that all these NMR resonances are broad with half-height widths between 20 and 30 Hz, except those corresponding to species **2** of Nd(III) and U(III). At 294 K, the signals at δ 13.1 (Nd) and 14.3 (U) are doublets while the resonances at δ 9.7 (Nd) and 17.7 (U) are triplets; the coupling constants are equal to 6 Hz. Irradiation experiments showed that, for each of these species **2**, the doublet and triplet signals are coupled to each other but the triplet is also coupled with another resonance which is masked by the solvent and free *bipy* signals. Further information was provided by the two-dimensional homonuclear COSY correlation spectra which showed that (i) there is no coupling between the sets of signals of each species **1**, **2**, and **3** which are distinct; (ii) the signals of each pair of low-field signals corresponding to species **1**, **2**, and **3** are coupled to each other; (iii) for each species **1**, **2**, and **3**, one of the signals of the low-field pair is coupled with a resonance located in the region 10 < δ < 6, but the complexity of this region did not allow us to determine whether this resonance is further coupled with a nearby signal, except in the case of **1** (Ce) and **2** (Ce, Nd, and U). For species **2** of Nd(III), the triplet signal at δ 9.7 is coupled with another resonance at δ 8.6 which is itself coupled with a fourth signal at δ 6.0; coupling is also observed between the signals at δ 13.1 and 8.6, and those at δ 9.7 and 6.0. Finally, each species **1**, **2**, and **3** can be characterized by two to four ^{1}H NMR resonances, at 294 K or at lower temperature, which are listed in Table 1.

(b) The MI$_3$/*Bipy*/NaI Systems (M = Ce, Nd, U). The presence of iodide ions impedes the formation of species **1** and **2** obtained by addition of 2 equiv of *bipy* to U(III) in pyridine, as shown by the decreasing intensities of the low-field NMR resonances associated with these species. The intensities of the **1** and **2** signals are lowered by 17% and 11% in the presence of 0.5 equiv of NaI, and by 42% and 47% in the presence of 1 equiv. In contrast, addition of NaI has practically no influence on the spectra of the Ce(III) or Nd(III)/(2 *bipy*) systems.

(c) The UI$_3$/MI$_3$/*Bipy* Systems (M = Ce, Nd). The ^{1}H NMR spectra of pyridine solutions containing U(III), Ce(III), and *bipy* in the molar ratio of 1:1:1 exhibit signals at the same chemical shifts as those corresponding to species **1** and **2** characterized before for the isolated Ce or U/*bipy* systems. The intensity of each signal is smaller than that observed when individual M(III) is in the presence of 1 equiv of *bipy*. At 294 K, the ratio of species **2** (U:Ce) is equal to 4.5. Similar observations were made with the U(III)/Nd(III)/*bipy* system; in that case, species **2** are in the ratio (U:Nd) = 1.7.

Conductometry Studies. The conductivity of 10^{-2} M solutions of MI$_3$(py)$_4$ (M = Ce, U) in anhydrous pyridine in the presence of increasing quantities of *bipy* (0 $\leq$ n $\leq$ 8) has been measured at 293 K. In this solvent, the conductivity χ of NaI or R$_4$NI (R = Et, n-hexyl) grows in a linear fashion from 10 to 600 μS cm^{-1} when the concentration of the iodide salt varies from 0 to 10^{-1} M; at 10^{-2} M, χ is equal to 120 μS cm^{-1}. The conductivity of solutions of MI$_3$(py)$_4$ (M = Ce, U) in pyridine also increases linearly with the metal concentration, ranging from 15 to 45 μS cm^{-1} for concentrations varying from 10^{-3} to 10^{-2} M. The values χ are greater after addition of *bipy*, and the variations are more important for M = U than for M = Ce (cf. Figure 3). For a concentration of M(III) equal to 10^{-2} M and for $n = 8$, χ is equal to 75 and 130 μS cm^{-1} for M = Ce and U, respectively.

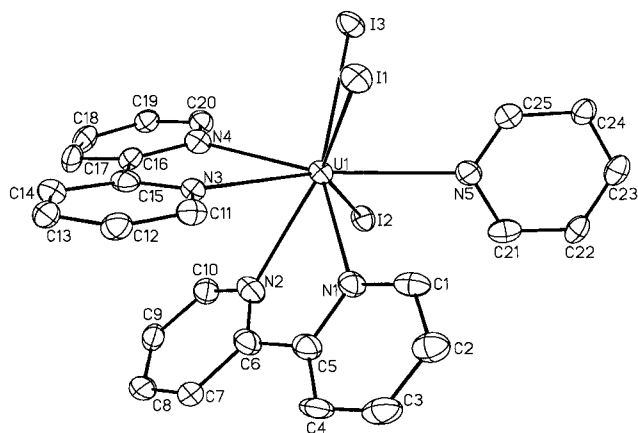**Figure 4.** X-ray crystal structure of UI$_3$(bipy)$_2$(py) with thermal ellipsoids at 30% probability.

Synthesis and Crystal Structure of MI$_3$(bipy)$_2$(py) (M = Ce, U). Yellow (M = Ce, Nd) and brown (M = U) microcrystalline powders of MI$_3$(bipy)$_2$(py) were obtained upon addition of diethyl ether to solutions of MI$_3$(py)$_4$ and 10 equiv of *bipy* in pyridine. The complexes were characterized by their elemental analyses (C, H, N); their ^{1}H NMR spectra in pyridine-d_5 are identical to those of the solutions containing MI$_3$(py)$_4$ and 2 equiv of *bipy*. Crystals of the solvates [CeI$_3$(bipy)$_2$(py)]$_4$· 5py·bipy and UI$_3$(bipy)$_2$(py)·2py were obtained by diffusion of pentane into solutions of CeI$_3$ or UI$_3$(py)$_4$ and excess *bipy* in anhydrous pyridine. The crystal structure of the molecule UI$_3$-(bipy)$_2$(py) is shown in Figure 4, and the crystal structure of CeI$_3$(bipy)$_2$(py) is presented in the Supporting Information; selected bond distances and angles are listed in Table 2. The molecular structures are very similar and cannot be distinguished by any significant feature. In both compounds, the metal center is eight coordinate, being surrounded by five nitrogen atoms of one pyridine and two bidentate bipyridine ligands, and by three iodide ligands. The mean M−N (bipy) bond distances, equal to 2.67(3) Å (M = Ce and for each of the two independent molecules) and 2.65(4) Å (M = U), are unexceptional and can be compared with those of 2.596 and 2.71 Å in Nd(NO$_3$)$_3$-(bipy)$_2$[15] and Nd(TTA)$_3$(bipy) (TTA = thenoyltrifluoroacetonato),[16] respectively. The M−I bond lengths vary from 3.1991(8) to 3.2588(6) Å with a mean value of 3.23(3) Å (M = Ce and for each independent molecule) and 3.22(3) Å (M = U); these values are similar to those of 3.13, 3.28, and 3.157(1) Å found in UI$_3$(THF)$_4$,[13a] polymeric UI$_3$,[17] and CeI$_3$(iPrOH)$_3$,[18] respectively. The M−N(py) bond distances, which are identical in both complexes (2.678(9) Å for M = Ce and 2.679(9) Å for M = U), can be compared with that of 2.684 Å in the tris(indenyl) complex (indenyl)$_3$Ce(py).[19] The *bipy* ligands are not planar; the angles between the two adjacent pyridyl moieties are 6.30° and 13.46° for M = Ce and 9.94° and 11.80° for M = U.

In an attempt to obtain crystals of the neodymium analogue NdI$_3$(bipy)$_2$(py) from solutions of NdI$_3$(py)$_4$ and excess *bipy* in pyridine, crystals of the *μ*-hydroxo complex [Nd(bipy)$_3$(*μ*-OH)]$_2$-[I]$_4$·3py were deposited, the structure of which has already been reported;[20] the formation of this unique example of *tris-bipy*

(15) Bower, J. F.; Cotton, S. A.; Fawcett, J.; Russell, D. R. *Acta Crystallogr.* **2000**, *C56*, e8, e9.
(16) Leipoldt, J. G.; Bok, L. D. C.; Basson, S. S.; Laubscher, E. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1477.
(17) Kanellakopulos, B.; Fischer, E. O.; Dornberger, E.; Baumgartner, F. *J. Organomet. Chem.* **1970**, *24*, 507.
(18) Barnhart, D. M.; Frankcom, T. M.; Gordon, P. L.; Sauer, N. N.; Thompson, J. A.; Watkin, J. G. *Inorg. Chem.* **1995**, *34*, 4862.
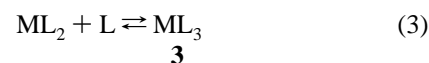(19) Zazzetta, A.; Greco, A. *Acta Crystallogr.* **1979**, *B35*, 457.

lanthanide(III) complex obviously reflects the presence of adventitious traces of water in the solvent.

Discussion

Characterization of the Equilibrating Complexes. The three pairs of low-field-shifted signals which are visible in the ^{1}H NMR spectra clearly indicate that complexation of M(III) with *bipy* in pyridine produces three distinct equilibrating species. One of these, **2**, is always observed, whatever the temperature and the number *n* of equivalents of *bipy*; at 294 K, its concentration increases with *n* to reach a constant value for *n* > 8. Irradiation and COSY experiments revealed that species **2** can be characterized by four resonances, two of those being generally masked by the signals of the solvent and free *bipy* molecules. These resonances can be attributed to the four protons of a C$_5$H$_4$N fragment of the *bipy* ligand, by assuming that all the pyridyl groups of the *bipy* ligands are magnetically equivalent, a situation which would result from the symmetrical structure of the complex or, most probably, from its rapid fluxionality in solution. Such a dynamic behavior of f element compounds is not unusual, being related to the facile intramolecular exchange of the ligands. The other species **1** and **3** should also be characterized by four signals, but the two resonances located in the δ 6−8 region could not be unambiguously detected in every case. The resonances have been attributed from the COSY spectra (cf. Table 1), assuming that the signals of protons 6 and 6′, which are the closest to the paramagnetic metal center, are shifted to low field.

For *n* ≥ 8 at room temperature, M(III) species are completely found in the form of **2** and integration of the NMR signals indicates that two *bipy* molecules are coordinated to the metal center; species **2** can be formulated as M(bipy)$_2$ (in fact MI$_x$-(bipy)$_2$(py)$_y$). Species **1**, which are observed for lower values of *n* and are intermediates in the formation of **2**, should be the 1:1 complexes M(bipy) (in fact MI$_{x'}$(bipy)(py)$_{y'}$). Species **3**, which contain three *bipy* ligands, as shown by the integration of the corresponding resonances, are the 1:3 compounds M(bipy)$_3$ (in fact MI$_{x''}$(bipy)$_3$(py)$_{y''}$), the formation of which is favored at low temperature with large values of *n*.

Therefore, the equilibria which occur in solutions of M(III) iodides and *bipy* (noted L in the equations of reactions below) in pyridine can be described by eqs 1−3 in which all solutes are solvated by the pyridine. Concentrations [**1**], [**2**], and [**3**]

$$M + L \rightleftarrows \underset{\mathbf{1}}{ML} \qquad (1)$$

$$ML + L \rightleftarrows \underset{\mathbf{2}}{ML_2} \qquad (2)$$

$$ML_2 + L \rightleftarrows \underset{\mathbf{3}}{ML_3} \qquad (3)$$

have been measured by integration of the corresponding NMR signals, [M] has been calculated by the difference [M] = [M]$_T$ − [**1**] − [**2**] − [**3**], and [L] = [L]$_T$ − [**1**] − 2[**2**] − 3[**3**], established from mass balance of M and *bipy* species, with [M]$_T$ and [L]$_T$ the total concentrations of M and *bipy*, respectively. Figures 5 and 6 show, in the case of U(III), the relative proportions of free U(III), **1**, **2**, and **3** as a function of *n*, at 298 and 233 K, respectively; similar distributions are observed for M = Ce and Nd, except that for Nd(III) species **1** was not observed.

(20) Rivière, C.; Lance, M.; Ephritikhine, M.; Madic, C.; Nierlich, M. *Z. Kristallogr. NCS* **2000**, *215*, 239.
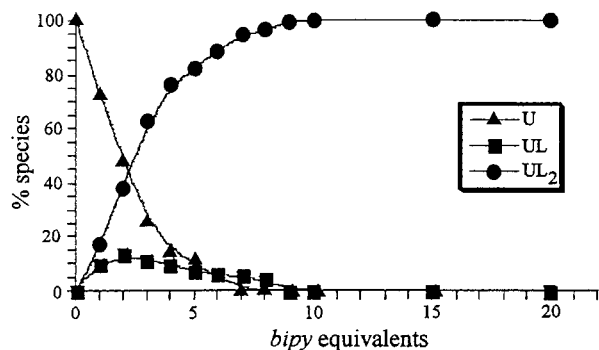
Figure 5. Distribution curves of uranium(III) species during the NMR titration of a 10^{-2} M solution of UI$_3$(py)$_4$ by *bipy* in anhydrous pyridine at 294 K (the points are experimental calculated data, and the lines are guides for the eyes).
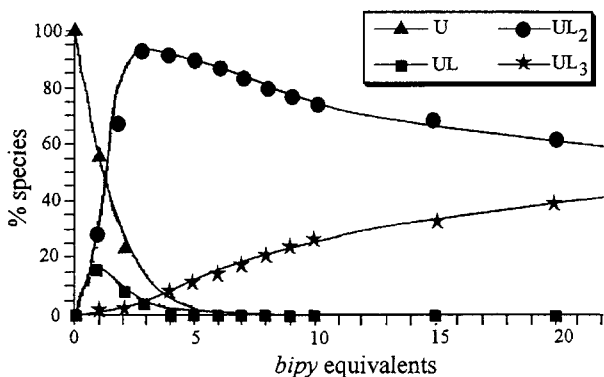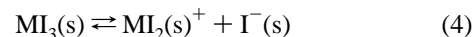

Figure 6. Distribution curves of uranium(III) species during the NMR titration of a 10^{-2} M solution of UI$_3$(py)$_4$ by *bipy* in anhydrous pyridine at 233 K (the points are experimental calculated data, and the lines are guides for the eyes).

Before trying to give a quantitative interpretation, it is worth noting that, whatever the value of *n*, the fraction of complexed M(III) is greater for M = U than for M = Ce or Nd; thus, *bipy* has a greater affinity for the 5f element. It is also clear that at room temperature the most abundant complex in solution is the 1:2 species ML$_2$ which is the major or unique (M = Nd) species even for the lowest studied values of *n*. This strong preference for the formation of the 1:2 complex relative to that of the 1:1 complex remains exceptional in coordination chemistry, and for lanthanides, it has been observed only with tripodal amine ligands.[21] To our knowledge, compounds **3** are the first f element compounds with three coordinated *bipy* ligands which have been observed in solution. In the solid state, the lanthanide nitrate compounds which were formulated as Ln(NO$_3$)$_3$(bipy)$_3$ (Ln = Ce, Pr, Nd, Yb) have been shown to be most likely Ln(NO$_3$)$_3$-(bipy)$_2$·bipy.[16] With the exception of the anionic complex [Li-(THF)$_4$][Yb(bipy)$_3$] in which the *bipy* groups are in the form of one *bipy*$^{2-}$ dianion and two *bipy*$^{-•}$ radical anions,[22] the μ-hydroxo complex [Nd(bipy)$_3$(μ-OH)]$_2$[I]$_4$·3py is the only 1:3 bipy compound of an f element to have been characterized by its crystal structure.[20] The 1:2 complexes ML$_2$ are the only ones which could be isolated pure in the form of MI$_3$(bipy)$_2$(py), from solutions of M(III) iodides and *bipy*; their NMR spectra

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(22) Bochkarev, M. N.; Petrov, B. I.; Fedyushkin, I. L.; Petrovskaya, T. K.; Nevodshikov, V. I.; Patrikeeva, N. B.; Zakharov, L. N.; Struchkov, V. T. *Russ. Chem. Bull.* **1997**, *46* (2), 371.

in pyridine confirm the occurrence of the equilibria 1−3. The cerium and uranium derivatives are rare examples of analogous 4f and 5f complexes, the crystal structures of which can be directly compared. The difference $\Delta \cong 0.02$ Å between the average Ce−N(bipy) and U−N(bipy) bond lengths is exactly the same as that found between the U−N and Ce−N bond distances in (CH$_3$C$_5$H$_4$)$_3$M[N(CH$_2$CH$_2$)$_3$CH][23] and can be considered as not significant considering the experimental errors. It has been pointed out that with nitrogen and oxygen Lewis bases L, which belong to the class of hard donors, the U−L and Ce−L distances are the same and Δ is between 0.01 and 0.02 Å. In contrast, the U−P bond is significantly shorter, by 0.1 Å, than the Ce−P bond in (CH$_3$C$_5$H$_4$)$_3$M(PMe$_3$).[23] This distinctive feature has been explained by a π back-bonding interaction between uranium and the soft ligand which is absent in the lanthanide complex; this difference would indicate that the U−P bond is stronger than the Ce−P bond, in agreement with equilibrium studies. However, in the case of the crystal structures of the MI$_3$(bipy)$_2$(py) compounds (M = Ce and U), which are of the same quality ($R = 0.032$ and 0.038 for M = Ce and U, respectively), we note that (i) the average M−N(bipy) distances are calculated from four M−N bond distances and the values are identical for each of the two independent CeI$_3$-(bipy)$_2$(py) molecules and (ii) the Δ value is positive while the ionic radius of Ce(III) is slightly shorter than that of U(III) (about 0.01 Å).[12] These slightly smaller U−N bond distances than Ce−N ones in these crystalline compounds could possibly be correlated with the slight preference of *bipy* to bond U(III) vs Ce(III) observed in pyridine solutions (vide infra). Since *bipy*, apart from being a σ donor, is capable of π bonding by accepting electron density from filled metal orbitals into π^* orbitals of the ring system, it is possible that its bonding mode to cerium-(III) and uranium(III) within the complexes presents some slight differences owing to the easier access of 5f orbitals of U(III) compared with the 4f orbitals of Ce(III). Interestingly, a difference of 0.03 Å has been found between the mean La−N and U−N bond distances in the complexes M(tpa)I$_3$(py) (M = La or U; tpa = tris[(2-pyridyl)methyl]amine),[21b] while the ionic radii of La(III) and U(III) differ by ca. 0.01 Å,[12] and it was suggested that this difference could reveal the presence of some degree of covalency in the U(III)−tpa interaction. Finally, we note that in the complexes M^{III}{tris[3-(2-pyridyl)pyrazol-1-yl]-borate}$_2^+$ (M = Sm and U), the corresponding M(III)−N bond distances are almost identical,[24] whereas the ionic radius of U(III) is ca. 0.08 Å larger than that of Sm(III).[12] This feature, which was not indicated by the authors, possibly reflects the greater affinity of this ligand for An(III) vs Ln(III) ions, and we think that it would be interesting to evaluate its potential for An(III)/Ln(III) separation.

The Cerium/Uranium Selectivity. A significant difference between the behavior of UL$_2$ and CeL$_2$ complexes in pyridine is revealed by the conductometry studies. By comparison with the conductivity of the 1:1 electrolytes NaI and R$_4$NI (R = Et, *n*-hexyl), it appears that in a 10^{-2} M solution, ca. 40% of solvated M(III) triiodide (noted here MI$_3$(s)) is dissociated, according to eq 4; the dissociation constant K_d (i.e., mass action law constant of eq 4) is thus equal to 2.7×10^{-3}.

$$\text{MI}_3(\text{s}) \rightleftharpoons \text{MI}_2(\text{s})^+ + \text{I}^-(\text{s}) \tag{4}$$

At room temperature, after addition of 8 equiv of *bipy*, the only complex in solution is the 1:2 species and, in the case of

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M = U, the conductivity corresponds to that of a 1:1 electrolyte, indicating that UL_2 would be almost completely dissociated into $UI_2L_2(s)^+$ and $I^-(s)$. In contrast, the conductivity of the solution of the cerium complex increases to a much lesser extent, in relation with a dissociation of CeL_2 equal to 60% (Figure 3). These results indicate that *bipy* exhibits only a slightly greater affinity for $CeI_2(s)^+$ than for $CeI_3(s)$ while it coordinates almost exclusively to the cationic species $UI_2(s)^+$. In agreement with this fact is the influence of iodide ions which, by disfavoring the dissociation of $UI_3(s)$, impedes the formation of *bipy* complexes. These observations emphasize the major competitive role of the counterions in these complexation reactions. The distinct behavior of the cerium and uranium compounds can be tentatively explained by electronic factors, by considering that the uranium iodide, in the low oxidation state +3, is more electron rich than its cerium analogue. As a consequence of the greater important electron density on the U(III) metal center, coordination of the σ donor ligand *bipy* would be more difficult. It has already been demonstrated that coordination of σ donor Lewis bases to U(IV) and U(III) complexes is very sensitive to electronic factors and should not cause the electron richness of the final adduct to exceed an upper limit.[25] A good illustration of these electronic effects is provided by the differences in reactivity and coordination ability of the isosteric trivalent metallocenes $(Me_3SiC_5H_4)_3U$ and $(Me_3CC_5H_4)_3U$, which are respectively less and more electron rich than $(C_5H_5)_3U$; in particular, the adduct $(Me_3SiC_5H_4)_3U(THF)$ is readily formed in benzene while no interaction between the Lewis base and $(Me_3CC_5H_4)_3U$ has been observed.[26] If special attention has been paid to the distinct behavior of $(CH_3C_5H_4)_3U$ and $(CH_3C_5H_4)_3$-Ce toward soft and π accepting ligands (vide infra), comparative studies concerning the coordination of hard Lewis bases like THF seem not to have been considered. It is, however, interesting that, in contrast to $(Me_3CC_5H_4)_3U$,[26] the cerium analogue $(Me_3CC_5H_4)_3Ce$[27] does form a stable adduct with THF which has been observed by NMR. It is also significant that the lanthanum compound $(Me_3CC_5H_4)_3La(THF)$[28] could be isolated by controlled evaporation of a THF solution (the ionic radii of La^{3+}, Ce^{3+}, and U^{3+} are very similar[12]). That THF is more strongly coordinated to Ce(III) or La(III) than to U(III) can be explained by the harder character of the 4f elements.

The overall observations lead us to envisage, to explain the selectivity of *bipy* in its coordination to U(III) and Ce(III), a mechanism which is somewhat different from that usually considered. It is generally accepted that the efficiency of aromatic nitrogen ligands in lanthanide(III)/actinide(III) separations is due to a stronger bonding interaction between the 5f element and the nitrogen atoms, both classified as soft sites. This view is not supported by the results reported here since, on the contrary, it appears that coordination of *bipy* to the U(III) center requires access to a harder site which is obtained after dissociation of an iodide ion from $UI_3(s)$ and formation of the cationic species $UI_2(s)^+$. In addition to this σ bonding, it is conceivable that the uranium *bipy* complexes are also stabilized by π back-donation of the U 5f orbitals into the π^* orbitals of the aromatic ring.

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(25) Baudin, C.; Baudry, D.; Ephritikhine, M.; Lance, M.; Navaza, A.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1991**, *415*, 59.
(26) Berthet, J. C.; Le Maréchal, J. F.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1573.
(27) Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1990**, *9*, 115.
(28) Wayda, A. L. *J. Organomet. Chem.* **1989**, *361*, 73.

The Thermodynamic Constants. The presence of iodide ions in solution resulting from the dissociation of $MI_3(s)$ should be taken into account in the expression of the formation constants K of the various complexes. However, the concentration $[I^-(s)]$ varies at the most by a factor of 2.5, from 0.4×10^{-2} to 10^{-2} M in a 10^{-2} M solution of $MI_3(s)$. This variation is much smaller than that of the other species, in particular *bipy*, the concentration of which varies from 0 to 8×10^{-2} M. As a consequence, the concentration $[I^-(s)]$ will have a limited influence on the values of the constants. The "apparent" formation constants for the ML, ML_2, and ML_3 complexes were calculated from the respective populations of species **1**, **2**, and **3** (Figures 5 and 6). These values were obtained according to eqs 5−8, in which all species are solvated. In these equations, $[M] = [MI_3] + [MI_2^+] = [M]_T − [1] − [2] − [3]$ and $[L] = [L]_T − [1] − 2[2] − 3[3]$.

$$K_1 = [1]/([M][L]) = [1]/(([MI_3] + [MI_2^+])[L]) \quad (5)$$

$$K_2 = [2]/([1][L]) = ([MI_3L_2] + [MI_2L_2^+])/([1][L]) \quad (6)$$

$$\beta_2 = [2]/([M][L]^2) = ([MI_3L_2] + [MI_2L_2]^+)/(([MI_3] + [MI_2^+])[L]^2) \quad (7)$$

$$K_3 = [3]/([2][L]) = [3]/(([MI_3L_2] + [MI_2L_2^+])[L]) \quad (8)$$

Note that, in eqs 5−8, species **1** and **3** are written as a whole without considering their ionic dissociation.

It is possible to evaluate the influence of $[I^-(s)]$ on these constants by considering two extreme cases. If $[I^-(s)]$ does not vary upon addition of *bipy*, i.e., *bipy* coordinates equally to MI_3-(s) and $MI_2(s)^+$, which is the approximate situation for M = Ce, the apparent formation constant β_2 defined by eq 7 is equal to the β'_2 constant corresponding to equilibria 9 and 10.

$$MI_3 + 2L \rightleftharpoons MI_3L_2 \quad (9)$$

$$\beta_2' = \frac{[MI_3L_2]}{[MI_3][L]^2}$$

$$MI_2^+ + 2L \rightleftharpoons MI_2L_2^+ \quad (10)$$
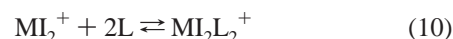
$$\beta_2' = \frac{[MI_2L_2^+]}{[MI_2^+][L]^2}$$

On the other hand, if $MI_3(bipy)_2(s)$ is totally dissociated into $MI_2(bipy)_2(s)^+$, i.e., *bipy* coordinates essentially to $MI_2(s)^+$, which is the case for M = U, the apparent formation constant β_2 is related to β'_2 by eq 11. Under the experimental conditions, the term $1 + [I^-]/K_d$ varies from 2 to 4 and its contribution to log β_2 will not exceed 0.3 unit.

$$\beta'_2 = \beta_2 \{1 + [I^-]/K_d\} \quad (11)$$

The mean values of K_1, K_2, K_3, and β_2 with their corresponding standard deviations, obtained from at least 4 independent values, are listed in Table 3. The trends of these values correspond to the qualitative observations $K_2 > K_1 > K_3$ and $\beta_2(U) > \beta_2(Nd) > \beta_2(Ce)$. As expected for the equilibria, the constants K_1, K_2, and β_2 calculated from the systems Ce(III)/U(III)/*bipy* and Nd(III)/U(III)/*bipy* are equal to those determined from each separate M(III)/*bipy* system. Similar values of K_1

(ca. 10) have been reported[29] for the complexation of lanthanide-(III) ions with *bipy* in 0.5 M aqueous solutions of NaNO$_3$. The value of 2.50(3) for log β_2(Ce) can be compared with that of 5.8(2) determined for the formation of the 1:2 species obtained by the complexation of La(NO$_3$)$_3$ by *o*-phenanthroline in acetonitrile; it is usual for *bipy* complexes to be less stable than those of *o*-phenanthroline.[30] If the better affinity of *bipy* for Nd(III) compared to Ce(III) can be classically interpreted by an electrostatic bonding model,[21c] since the ionic radius of Nd-(III) is smaller than that of Ce(III),[12] this explanation does not hold for the better affinity of *bipy* for U(III) because this ion has the largest ionic radius among the three M(III) ions considered here.

The linear dependence of log K_i versus $1/T$ allowed the determination of the thermodynamic parameters ΔH_i and ΔS_i corresponding to the formation of species **1**–**3**. The values of ΔH_i and ΔS_i with their standard deviations, calculated from ca. 5–13 independent measurements, are presented in Table 4. It is noteworthy that, for M = Ce or U, the values of ΔH_i and ΔS_i are very similar, with ΔH_i and ΔS_i being negative and ΔS_2 slightly positive. Clearly, the driving force for the formation of the complexes is the enthalpy term only and, surprisingly, the chelate effect which is most usually observed in complexation of polydentate amines seems not to be in operation here. Because the exact nature of the M(III)–*bipy* complexes in pyridine solution is uncertain, e.g., we do not know if the coordination numbers of M(III) ions are constant or not in the course of complexation, interpretation of the entropy data related to the 1:1, 1:2, and 1:3 complex formation is difficult.

Conclusions

The main objective of this work was to evaluate the difference in the affinity of a bidendate nitrogen ligand, the *bipy*, toward trivalent 4f and 5f metal ions. The differences in the stability of the U(III)–*bipy* complexes compared with those of Ce(III) and Nd(III) complexes were in fact found to be rather small. This results possibly from the choice of the experimental conditions selected for the study, i.e., use of pyridine solvent and of the iodide counterion, which were perhaps not so ideal. Indeed, even if pyridine is a poorer solvent of 4f and 5f ions in comparison with water, the fact that it corresponds to half the formula of the ligand studied (i.e., the *bipy*), induces a difficulty for *bipy* to remove *py* molecules from the inner coordination sphere of the metal ions. Moreover, this difficulty of *bipy* to bond metal ions is reinforced owing to the presence of iodide counterion in the inner sphere of coordination of M(III). This is due to the poor dissociating properties of the pyridine solvent, which has a dielectric constant equal to 12.3.[31]

Nevertheless, interesting results were obtained, among which one can cite (i) the unusual higher stabilities of M(bipy)$_2$ vs M(bipy); (ii) the slightly, but significantly, higher affinity of *bipy* toward U(III) in comparison with Ce(III) and Nd(III) ions; (iii) the better affinity of *bipy* ligand toward the hard UI$_2^+$ compared with that observed for the less hard UI$_3$ species; (iv) the driving force of the complexation reactions found to be the enthalpy; and (v) the nonexistence of a chelate effect, evidenced by the nonfavorable sign of the entropies of the complexation reactions.

The work was continued with the study of the complexation of U(III), Ce(III), and Nd(III) in similar conditions with the following ligands: *o*-phenanthroline, 2,2′,6′,2″-terpyrine, 2,4,6-tri(pyridin-2-yl)-1,3,5-triazine (TPTZ), and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (BTP), in order to address the effects of (i) ligand preorganization, (ii) ligand denticity, and (iii) ligand basicity on the affinity and selectivity of complexation reactions. This work will be the subject of a forthcoming paper.

Supporting Information Available: COSY ^{1}H NMR spectrum of a solution of NdI$_3$ (10^{-2} M) and *bipy* (10^{-2} M) in anhydrous pyridine-d_5 at 294 K. A view of the X-ray crystal structure of one of the two independent molecules of CeI$_3$(bipy)$_2$(py). Van't Hoff plots for the variation of ln K_1, ln K_2, and ln K_3 stability constants for the U(III)–*bipy* system in anhydrous pyridine. Complete X-ray crystallographic files in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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