Selective Complexation of Uranium(III) over Cerium(III) and Neodymium(III) by 2,2′:6′,2′′-Terpyridine − X-ray Crystallographic Evidence for Uranium-to-Ligand π Back-Bonding

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The addition of 2,2′:6′,2′′-terpyridine (terpy) to MI_3 (M = Ce, Nd, U) in anhydrous pyridine led to the quantitative formation of the bis-terpy complexes $[MI_2(terpy)_2]I$ [M = Ce (**1**) and Nd (**2**)] and $[MI_2(terpy)_2L]I$ [M = U and L = pyridine (**3**); M = Ce and L = H_2O (**4**)]. Conductometry measurements indicated that these complexes are 1:1 electrolytes in pyridine solution. ^1H NMR competition experiments showed that the terdentate ligand has a better affinity for U^{III} than for Ce^{III} or Nd^{III}. The X-ray crystal structures of solvates of **1**–**4** have been determined. The average U–N(terpy) bond lengths in **3** are 0.05 Å shorter than the mean Ce–N bond length in **4**; the U–N(central pyridine) distances are shorter than the U–N(distal pyridines) distances in **3**, while the reverse order is found in the early lanthanide compounds. These differences could reflect the presence of a π back-bonding interaction between the uranium atom and the terpy ligand.

Introduction

The separation of trivalent actinides (americium and curium) from trivalent lanthanides represents a challenging goal in the management of spent nuclear fuels. Such a separation process would permit the subsequent destruction of the long-lived americium and curium radionuclides by neutron bombardment, leading to their transmutation into short-lived isotopes; this scenario is called the partitioning and transmutation scenario (P & T).[1] Much attention has been paid to ligands that would favour the selective complexation of trivalent actinides (An^{III}) over trivalent lanthanides (Ln^{III}) in liquid/liquid solvent extraction processes. A generally accepted idea is that such a selectivity could be attainable by using soft nitrogen or sulfur ligands, since these would bind preferentially to the 5f ions as they are slightly less hard than the 4f ions.[2] These ligands should preferably be multidentate in order to compete with the water molecules in their coordination to the 4f and 5f ions. In fact, a number of nitrogen aromatic bases have been shown to selectively extract actinides rather than lanthanides from acidic aqueous effluents into an organic phase. In particular, it has been recently found that the terdentate ligand 2,2′:6′,2′′-terpyridine (terpy), in synergistic combination with 2-bromodecanoic acid, gave an Am^{III}/Eu^{III} separation factor $SF_{Am/Eu}$ of 7 at 0.01 M HNO_3, $SF_{Am/Eu}$ being defined as the ratio of the distribution ratios of Am^{III} and Eu^{III} in the organic and aqueous phases.[3] However, no actinide complex with terpy has been isolated and characterized so far, even though this ligand has been widely used in the coordination chemistry of the d transition metals[4] and 4f elements,[5−14] especially for the synthesis of complexes exhibiting unique luminescence and redox properties.

Following our comparative studies on the coordination of aromatic nitrogen bases to Ln^{III} and An^{III} ions, with the aim of investigating the factors that play a determining role in selectivity, the nature of the metal-ligand bond and the respective involvement of 4f and 5f electrons, we have examined the complexation of CeI_3, NdI_3 and UI_3 with terpy in anhydrous pyridine. As in our previous work on the complexation of these metal triiodides with 2,2′-bipyridine (bipy)[15] and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (btp),[16] U^{III} was used as an actinide analogue of the highly radiotoxic Am^{III} and Cm^{III}, and the similarly sized Ce^{III} and Nd^{III} were chosen as representatives of the lanthanides. The low complexing ability of the iodide counterion and the weaker solvation properties of pyridine relative to water are expected to favour the differentiation of the trivalent 4f and 5f ions. Here we report on the synthesis and characterization of the bis-terpy complexes $[MI_2(terpy)_2]I$ [M = Ce (**1**) and Nd (**2**)] and $[MI_2(terpy)_2L]I$ [M = U and L = pyridine (**3**); M = Ce and L = H_2O (**4**)]. The better affinity of the terdentate ligand for U^{III} vs. Ce^{III} and Nd^{III} was meas-

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ured by ^{1}H NMR competition experiments and the distinct coordination of terpy to the 5f ion was revealed by X-ray crystallography with a comparison of the metal-nitrogen bond lengths in solvates of compounds **1−4**.

Results and Discussion

Formation of the bis-Terpy Complexes

Addition of two equivalents of terpy to a pyridine solution of $[MI_3(py)_4]$ (M = Ce, Nd, U; py = pyridine) led to the formation of the bis-terpy complex $[MI_3(terpy)_2]$ [M = Ce (**1**) or Nd (**2**)] or $[UI_3(terpy)_2(py)]$ (**3**). After evaporation of the solvent, the compound was washed with tetrahydrofuran and isolated as an orange (Ce), yellow (Nd) or dark red powder (U) in good yield. Complexes **1−3** gave satisfactory elemental analyses (C, H, N).

The conductivity of a 10^{-2} M solution of **1** or **3** in anhydrous pyridine at 20 °C has a value of 120 μS cm^{-1} which corresponds to a 1:1 electrolyte. Complexes **1−3** are thus totally dissociated in solution into a cation/anion pair of $[MI_2(terpy)_2(py)_x]^+$ and I^-. This dissociation is also observed in the crystal structures (vide infra). It has previously been found that at the same concentration and temperature, the dissociation of $[MI_3(py)_4]$ (M = Ce, U) and $[CeI_3(bipy)_2(py)]$ is equal to 40 and 60%, respectively, corresponding to a conductivity of 45 and 75 μS cm^{-1}, whereas $[UI_3(bipy)_2(py)]$ is almost completely dissociated into $[UI_2(bipy)_2(py)_x]^+$ and I^-.[15]

The ^{1}H NMR spectra of **1−3** in [D$_5$]pyridine at 20 °C exhibit a set of resonances corresponding to equivalent and symmetrical terpy ligands, thus indicating that the complexes are fluxional in solution, as usually observed with f elements compounds that undergo facile intramolecular exchange of the ligands. Coalescence of the signals occurs at lower temperature, although the slow-limit spectra could not be obtained.

In order to observe a 1:1 complex as a possible intermediate in the formation of **1−3**, a 10^{-2} M solution of $[MI_3(py)_4]$ (M = Ce, Nd, U) in [D$_5$]pyridine was titrated at 20 °C with terpy in the presence of cyclohexane as internal standard. The ^{1}H NMR spectra showed that, whatever the number n of ligand equivalents ($0 \le n \le 2$), only the 1:2 complex **1**, **2** or **3** was formed in an immediate and quantitative manner. For $n > 2$, free terpy was observed in solution, with no exchange with coordinated ligands, and no 1:3 complex was detected. In agreement with the ^{1}H NMR titration, the conductivity of the solution at 20 °C was found to grow in a linear fashion, from 45 to 120 μS cm^{-1}, with increasing quantities of terpy ($0 \le n \le 2$) and was then constant for $n > 2$. Such a preference for the formation of the 1:2 or 1:3 complexes with respect to the 1:1 complex remains very rare in coordination chemistry; for lanthanides, it has been observed with bipy[15] and terdentate nitrogen ligands.[16,17]

The quantitative formation of **1−3** in pyridine contrasts with that of the 1:1 complexes $[LnCl(terpy)(H_2O)_x]Cl_2$ (Ln = Ce − Lu),[5] $[Ln(terpy)(H_2O)_x]Br_3$ (Ln = La, Er, Tm, Yb, Lu),[6] $[Ln(O_2CCCl_3)_3(terpy)(L)]$ (Ln = Yb and L = MeOH; Ln = Lu and L = H_2O),[7] $[Ln(NO_3)_3(terpy)(H_2O)_x]$ (Ln = Nd, Ho, Er, Tm, Yb),[8] $[Er(NO_3)_3(terpy)(EtOH)]$[9] and $[Ln(NO_3)_2(terpy)(H_2O)_x][NO_3]$ (Ln = La, Gd, Tb, Lu)[10] which were synthesized from the corresponding lanthanide salts and one equivalent of terpy in a mixture of water and alcohol or in acetonitrile. Addition of two equivalents of terpy to the halides LnX_3 (X = Cl, Br) in ethanol gave the 1:2 complexes $[LnCl_3(terpy)_2(H_2O)_x]$ in the case of the heavier lanthanides (Eu, Gd, Dy and Er), whereas attempts to prepare the analogues of the early lanthanides Nd and Sm failed.[11] The 1:1.5 complexes $[Ln(NO_3)_2(terpy)_2][Ln(NO_3)_4(terpy)]$ (Ln = La, Nd, Sm, Tb, Dy, Ho) were formed by addition of four equivalents of terpy to a solution of the hydrated lanthanide nitrate in acetonitrile.[8a,10] These results show the difficulty in forming the bis-terpy compounds of the lighter lanthanides by using counterions and/or solvents with strongly coordinating properties. It is only with the weakly coordinating perchlorate anion that the 1:3 species $[Ln(terpy)_3][ClO_4]_3$ (Ln = Ce, Eu, Lu) crystallized from acetonitrile or ethanol solutions.[13] In this context, the formation of the bis-terpy complexes **1−3** as the sole products of the reactions of $[MI_3(py)_4]$ (M = Ce, Nd, U) with terpy in anhydrous pyridine is remarkable.

Not surprisingly, terpy was found to have a better affinity for the trivalent f ions than bipy, since under the same conditions it was necessary to add more than 10 (M = Ce, U) or 20 (M = Nd) equivalents of the bidentate ligand to $[MI_3(py)_4]$ to observe the complete formation of the corresponding 1:2 complexes $[MI_3(bipy)_2(py)]$ or $[MI_2(bipy)_2(py)]I$.[15] By considering only the contribution of the chelate effect,[18] the apparent formation constants $\log\beta_2$ of complexes **1−3** would range between 3.1 and 3.7. However, terpy is a much weaker complexant than the btp molecules which readily give the 1:3 complexes $[M(btp)_3]I_3$ (M = Ce, U) in a quantitative manner.[16]

Selective Complexation of U^{III} over Ce^{III} or Nd^{III}

The competition reactions of Ce^{III} or Nd^{III} and U^{III} with terpy were monitored by ^{1}H NMR spectroscopy. Addition of two mol equivalents of terpy to one mol equivalent of both $[CeI_3(py)_4]$ and $[UI_3(py)_4]$ in [D$_5$]pyridine led to the formation of complexes **1** and **3** with a U^{III}/Ce^{III} separation factor of 3.0. Similar experiments with $[NdI_3(py)_4]$ gave compounds **2** and **3** with a U^{III}/Nd^{III} separation factor of 2.5 (here, the separation factor is expressed as the ratio of the concentrations of **3** and **1**, or **3** and **2**). These results demonstrate that the terdentate ligand has a much better affinity for the 5f ion than for its 4f analogues. The U^{III}/Ce^{III} separation factor of 3.0 observed with terpy is greater than that of 1.3 determined from competition reactions of $[CeI_3(py)_4]$ and $[UI_3(py)_4]$ with bipy in the molar ratio of 1:1:2.

Previous studies on the MI_3/bipy system revealed that the bidentate ligand bipy has a slightly better affinity for $[CeI_2(py)_x]^+$ than for $[CeI_3(py)_4]$ while it coordinates almost exclusively to the cationic species $[UI_2(py)_x]^+$.[15] It was then difficult to determine if the weakly selective complexation of U^{III} over Ce^{III} or Nd^{III} in pyridine solution would result from the stronger complexation of the σ-donor ligand bipy to the hard cation $[UI_2(py)_x]^+$ and/or from the π back-donation of the 5f orbitals into the π* orbitals of the aromatic ring. A more clear-cut situation is encountered with terpy in the competition reactions between Ce^{III} or Nd^{III} and U^{III} since all the 1:2 complexes **1−3** are totally dissociated in solution. The preferred formation of the U^{III} derivative **3** should be related to a more important covalent contribution to the metal-nitrogen bonding.

Moreover, it is remarkable that even though complexes **1−3** have all been prepared and crystallized from pyridine, only the uranium compound **3** retains a solvent molecule in its coordination sphere; this ligand is not labile and could not be eliminated by heating under vacuum. This better affinity of U^{III} vs. Ce^{III} or Nd^{III} for the pyridyl moiety would be an additional indication of the relatively greater softness of the trivalent 5f ion. However, crystallization of the cerium derivative **1** in pyridine in the presence of traces of water gave the addition product $[CeI_2(terpy)_2(H_2O)]I$ (**4**) (vide infra), showing the capacity of the lanthanide ion to coordinate the hard oxygen ligand in preference to the softer aromatic nitrogen base. The synthesis of the uranium compound $[UI_2(terpy)_2(H_2O)]I$ was attempted in order to compare its crystal structure with that of **4**. However, in the presence of traces of water, **3** was oxidized into an U^{IV} oxo complex; this latter will be reported in a forthcoming paper.

The selectivity of terpy for trivalent actinides over trivalent lanthanides, although significant, is much less important than that observed with btp molecules, which is ca. ten times greater.[16,19] The high actinide(III)/lanthanide(III) separation factors obtained with these ligands have been attributed to their weaker basicity and the much softer nature of their nitrogen atoms, which result in the formation of stronger actinide-nitrogen bonds with increased covalent character.

The distinct affinities of bipy, terpy and btp ligands for 5f vs. 4f trivalent ions could also be assessed through the crystal structures of their analogous complexes.

X-ray Crystal Structures of $[MI_2(terpy)_2]I·2py$ (M = Ce, Nd), $[UI_2(terpy)_2(py)]I·2py$ and $[CeI_2(terpy)_2(H_2O)]I·1.5py·0.5Et_2O$

Pyridine solvates of **1**, **2** and **3** crystallized upon slow diffusion of diethyl ether into pyridine solutions of the complexes; crystallization of **1** from solvents containing traces of water gave yellow crystals of $[CeI_2(terpy)_2(H_2O)]I·1.5py·0.5Et_2O$. The crystals are composed of cation/anion pairs and solvent molecules; selected bond lengths and angles for the cations are listed in Table 1.

Compounds **1·2py** and **2·2py** are isostructural; the structure of the cation $[CeI_2(terpy)_2]^+$ is shown in Figure 1. The metal is eight-coordinate in a very distorted square antiprismatic configuration. The two iodide ligands and two distal nitrogen atoms (N_d) of the two terpy ligands [N(3) and N(4)] occupy the opposite corners of the first square base, respectively, whereas the second basis is defined by the two central nitrogen atoms (N_c) [N(2) and N(5)] and the other two distal nitrogen atoms of the terdentate molecule [N(1) and N(6)], which are mutually *trans*. The average Ln−I bond lengths of 3.182(3) Å (Ln = Ce) and 3.153(4) Å (Ln = Nd) are similar to those in $[CeI_3(i\text{PrOH})_3]$ [3.157(1) Å],[20] $[CeI_3(bipy)_2(py)]$ [3.23(3) Å][15] and $[NdI_2(C_5Me_5)(py)_3]$ [3.1603(5) Å].[21] The Ln−N bond lengths are also not exceptional, with mean values of 2.63(2) Å (Ln = Ce) and 2.60(2) Å (Ln = Nd), and are similar to those found in $[LnCl_2(terpy)(H_2O)_5]Cl_2·3H_2O$ [2.64(2) and

Table 1. Selected bond lengths [Å] and angles [°] for the cations $[MI_2(terpy)_2]^+$ (M = Ce and Nd) and $[MI_2(terpy)_2L]^+$ (M = U and L = py; M = Ce and L = H_2O)

	$[CeI_2(terpy)_2]^+$	$[NdI_2(terpy)_2]^+$	$[CeI_2(terpy)_2(H_2O)]^+$	$[UI_2(terpy)_2(py)]^+$
M−I(1)	3.185(1)	3.1560(5)	3.253(1)	3.273(1)
M−I(2)	3.180(1)	3.1502(5)	3.345(1)	3.236(1)
M−N(1)	2.614(3)	2.577(4)	2.686(4)	2.624(9)
M−N(2)	2.641(3)	2.595(4)	2.692(4)	2.618(9)
M−N(3)	2.658(3)	2.626(4)	2.665(4)	2.657(10)
M−N(4)	2.662(3)	2.630(4)	2.652(4)	2.631(10)
M−N(5)	2.636(3)	2.594(4)	2.691(4)	2.602(10)
M−N(6)	2.597(3)	2.570(4)	2.673(4)	2.625(10)
U−N(7)				2.685(12)
Ce−O			2.468(3)	
<M−I>	3.182(3)	3.153(4)	3.30(6)	3.25(2)
<M−N(terpy)>	2.63(2)	2.60(2)	2.68(2)	2.63(2)
I(1)−M−I(2)	119.12(2)	119.07(1)	144.04(2)	147.22(3)
N(1)−M−N(2)	61.4(1)	62.0(1)	61.4(1)	62.1(3)
N(2)−M−N(3)	62.3(1)	63.1(1)	61.1(1)	62.0(3)
N(1)−M−N(3)	122.3(1)	123.7(1)	122.2(1)	124.0(3)
N(4)−M−N(5)	61.9(1)	62.8(1)	61.5(1)	62.4(3)
N(5)−M−N(6)	61.8(1)	62.6(1)	61.8(1)	62.6(3)
N(4)−M−N(6)	121.9(1)	123.6(1)	122.9(1)	125.0(3)
N(2)−M−N(5)	112.4(1)	113.1(1)	112.8(1)	118.7(3)

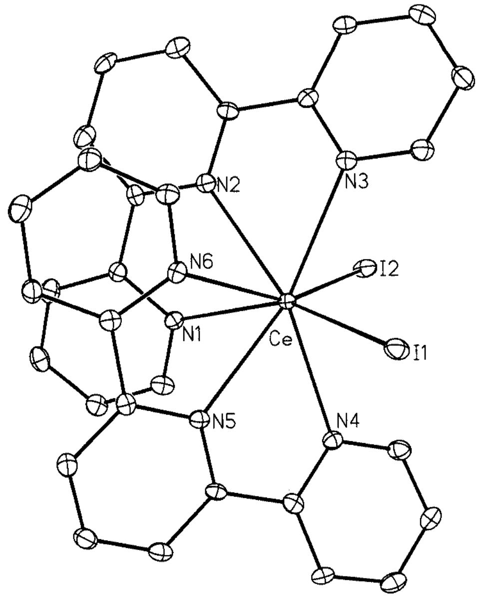

Figure 1. Crystal structure of the cation $[CeI_2(terpy)_2]^+$ in **1·2py** with displacement ellipsoids at the 30% probability level

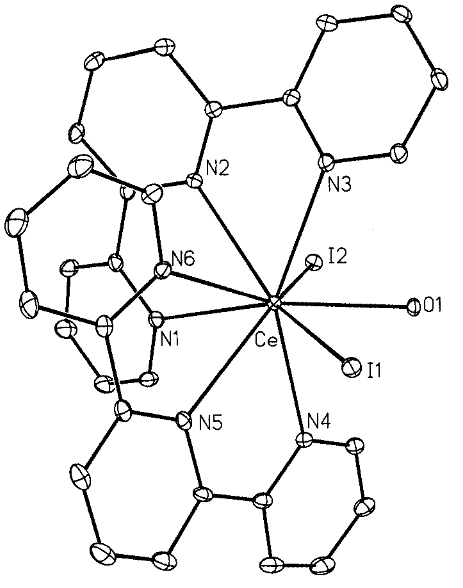

Figure 2. Crystal structure of the cation $[CeI_2(terpy)_2(H_2O)]^+$ in **4·1.5py·0.5Et₂O** with displacement ellipsoids at the 30% probability level

2.61(1) Å for Ln = Ce and Nd, respectively].[5] The Ce−I and Ce−N distances are systematically slightly longer than the Nd−I and Nd−N distances, in agreement with the 0.03 Å difference between the ionic radii of Ce^{III} and Nd^{III}.[22]

A comparison of the X-ray crystal structures of terpy complexes showed that the disparity that is usually observed between the $M-N_c$ and $M-N_d$ bond lengths (i.e. $M-N_c < M-N_d$) diminishes and is eventually reversed as the metal-ligand distance increases.[23] In the series of the lanthanide mono-terpy compounds, the experimental value of 2.58 Å has been found to be the limit for the $Ln-N_c$ distance at which this inversion would occur. Thus, the $Ln-N_c$ distances are generally longer than the $Ln-N_d$ distances for the early lanthanides, as observed in the cation $[Nd(NO_3)_2(terpy)_2]^+$.[8] However, the $Ln-N_c$ distances in **1** and **2** are intermediate between the $Ln-N_d$ distances in both terpy ligands. Such deviations from the general trend, which have also been observed in the other cations $[Ln(NO_3)_2(terpy)_2]^+$ (Ln = La, Sm, Tb),[8,12] have been explained by steric constraints in the coordination sphere.

The structures of the cations $[CeI_2(terpy)_2(H_2O)]^+$ and $[UI_2(terpy)_2(py)]^+$ are shown in Figure 2 and 3, respectively. The configuration of these nine-coordinate complexes can be described as a distorted square antiprism similar to that defined in compounds **1** and **2** which is capped on its I(1)N(3)I(2)N(4) base by a water or pyridine molecule. As a consequence of the coordination of this additional ligand, the I(1)−M−I(2) angles of 147.22(3)° (M = U) and 144.04(2)° (M = Ce) are larger than those found in **1** [119.12(2)°] and **2** [119.07(1)°], and the distortion from planarity of one of the two terdentate ligands [N(1)N(2)N(3)] is more pronounced, the standard deviations of the skeletal atoms from the median planes being ±0.21 Å in **3** and ±0.27 Å in **4**, almost 0.1 Å greater than those found in the other terpy ligands. A similar greater distortion of one of the terpy ligands has been observed in the cations $[Ln(NO_3)_2(terpy)_2]^+$ (Ln = Sm, Dy, Ho).[8] The average Ce−N bond length in **4** is 0.05 Å longer than that found in **1**, a difference which corresponds perfectly to that expected from the increase of the coordination number by one unit.[22] The $Ce-N_c$ distances of 2.691(4) and 2.692(4) Å are then longer than all the $Ce-N_d$ distances, which range between 2.652(4) and 2.686(4) Å. The Ce−I(1) bond length in **4** is 0.07 Å longer than the average Ce−I distance in **1**, although the Ce−I(2) bond length of 3.345(1) Å seems abnormally longer, perhaps reflecting the tendency for the iodide ion to dissociate. The $Ce-O(H_2O)$ bond length of 2.468(3) Å can be compared with the mean distance of 2.53(3) Å in the ten-coordinate complex $[CeCl_2(terpy)(H_2O)_5]Cl_2·3H_2O$.[5]

Because of the coordination of the extra pyridine molecule, the crystal structure of **3** cannot be compared directly with that of its cerium analogue, as was possible with the bipy and btp complexes $[UI_3(bipy)_2(py)]$[15] and $[U(btp)_3]I_3$.[16] However, careful examination of the terpy coordination in compounds **1**, **3** and **4** reveals quite distinct and interesting features. Firstly, the mean value of the U−N(terpy) bond lengths of 2.63(3) Å is exactly the same as the average Ce−N bond length in **1**, even though it would be expected to increase by about 0.05 Å in view of the coordination number of **3**, which is higher by one unit, and the ionic radius of U^{III}, which is about 0.01 Å longer than that of Ce^{III}.[22] It is noteworthy that the mean U−I bond length of 3.25(2) Å is 0.07 Å longer than the average Ce−I distance in **1** and corresponds effectively to the variation of the coordination number. On the other hand, the average U−N(terpy) bond length in **3** is 0.05 Å shorter than the mean Ce−N bond length in **4**, even though the two complexes have the same coordination number and exhibit quite similar geometrical parameters. These observations

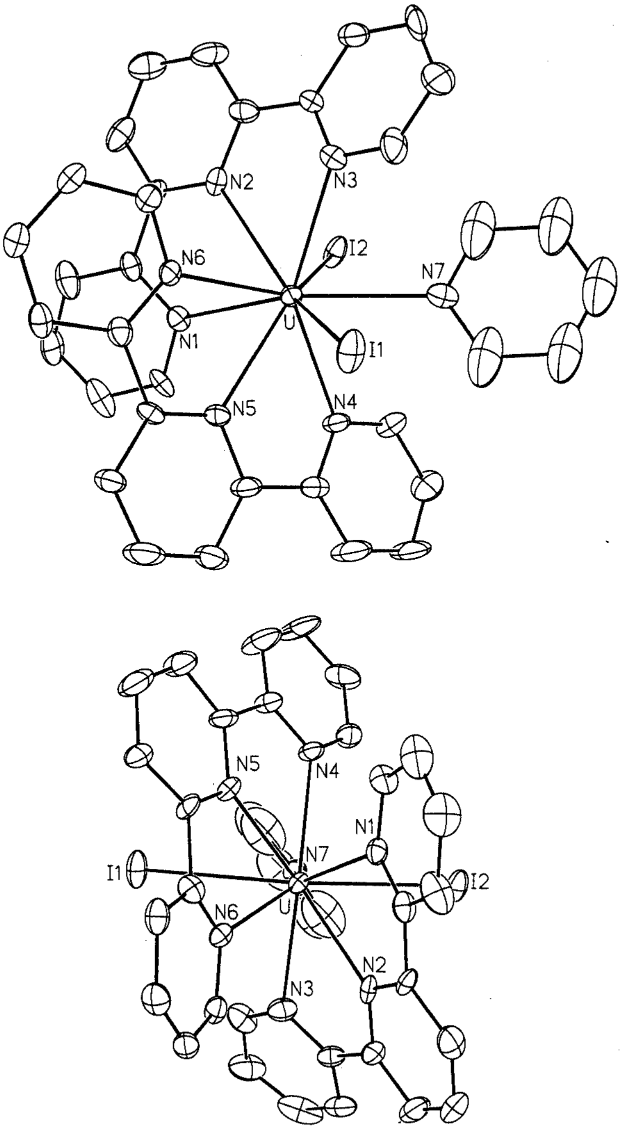

Figure 3. Crystal structure of the cation $[UI_2(terpy)_2(py)]^+$ in **3·2py** with displacement ellipsoids at the 30% probability level; views parallel (top) and perpendicular (bottom) to the bases of the distorted square antiprism

strongly suggest that the terpy ligand is more tightly bond to U^{III} in **3** than to Ce^{III} in **1** and **4**. If the U−N(terpy) bond lengths in **3** are considered to be ca. 0.05 Å shorter than those expected from a purely ionic bonding model, this variation is in the middle of the differences of 0.02 and 0.08 Å that have been measured between the U−N and Ce−N bond lengths in the analogous compounds $[MI_3(bipy)_2(py)]$[15] and $[M(btp)_3]I_3$ [16] (M = Ce, U), respectively. The shortening of the U−N bonds with respect to the Ce−N bonds follows the order bipy < terpy < btp which actually corresponds to the increasing preference of these molecules to bond $[UI_3(py)_4]$ vs. $[CeI_3(py)_4]$ in pyridine solutions. This trend in the interatomic distances indicates that the U−N bonds are stronger than the Ce−N bonds, probably due to a π back-bonding interaction between the uranium atom and the aromatic ligand that is much less likely in the lanthanide complex.[24]

The second striking feature in the structure of **3** concerns the U−N(2) and U−N(5) distances of 2.618(9) and 2.602(10) Å, which are shorter than all the other U−N(terpy) distances which vary from 2.624(9) to 2.657(10) Å. Complex **3** is a unique terpy compound in which the $M-N_c$ bond lengths, while being greater than 2.58 Å, are shorter than the $M-N_d$ bond lengths. As previously noted, the reverse order is generally observed in the terpy complexes of the early lanthanides, especially in **4**, and also in the bismuth compound $[Bi(S_2CNEt_2)I_2(terpy)]$ [$Bi-N_c$ = 2.63(2) Å; $Bi-N_d$ = 2.61(2) Å].[23] It is noteworthy that in these lanthanide and bismuth compounds, metal-to-ligand π back-bonding is unlikely. In the terpy complexes of the d transition metals, the $M-N_c$ distance is always shorter than the average $M-N_d$ bond length, a feature which has been attributed to a more efficient overlap of the metal t_{2g} orbitals with the π^* orbitals of the central pyridyl moiety than with the distal pyridine rings.[25] Spectroscopic studies on terpy complexes of Cu^{II} have also shown that the central pyridine of the terpy ligand is a good π-acceptor.[26] That the $M-N_c$ bond length is the most sensitive to changes in the spin state of the metal ion was demonstrated by the structural studies of the cobalt complexes $[Co(terpy)_2]X_2$ (X = Cl, Br, I, SCN, ClO_4) in which the $Co-N_c$ distances contract by 0.21 Å on passing from a high-spin to low-spin electronic ground state, whereas the $Co-N_d$ distances contract by only 0.07 Å; this variation has been explained by a greater back-bonding from the cobalt to the central pyridine in the low-spin compound.[27] From these considerations, the fact that the $U-N_c$ distances are shorter than the $U-N_d$ distances in **3**, while the reverse situation is found in the aforementioned lanthanide and bismuth compounds, would be a further indication of the presence of a π back-bonding interaction between the metal centre and the terpy ligand in the uranium complex.

Conclusion

Addition of terpy to $[MI_3(py)_4]$ (M = Ce, Nd, U) in anhydrous pyridine gave the complexes $[MI_2(terpy)_2]I$ [M = Ce (**1**) and Nd (**2**)] and $[UI_2(terpy)_2(py)]I$ (**3**) which are unique examples of bis-terpy compounds of the early lanthanides and uranium. Competition experiments showed that terpy has a better affinity for UI_3 than for CeI_3 in pyridine solution, the separation factors being intermediate between those observed with the bipy and btp molecules. This order of selectivities, bipy < terpy < btp, corresponds to the order of the differences between the U−N and Ce−N bond lengths in the crystal structures of analogous U^{III} and Ce^{III} complexes. In the crystal structure of **3**, the first terpy complex of uranium, a further indication of the presence of a π back-bonding interaction between the trivalent 5f ion and the aromatic nitrogen ligand is given by the U−N(central pyridine) distances, which are shorter than the U−N(distal pyridine) distances, while the reverse situation is observed in the early lanthanide terpy complexes.

Experimental Section

General: All experiments were carried out under argon (less than 2 ppm oxygen and water) using standard Schlenk and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. $[D_5]$pyridine was distilled over NaH and stored over 3 Å molecular sieves. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$). Conductivity measurements were performed at 20 °C with a Consort C-832 conductometer; the cell constant was equal to 0.1 cm^{-1}. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). Terpyridine, CeI_3 and NdI_3 (Aldrich) were dried under vacuum, and $[UI_3(py)_4]$ was synthesized as previously reported.[28]

Synthesis of $[CeI_2(terpy)_2]I$ (1): A 25 mL round-bottomed flask was charged with CeI_3 (50 mg, 0.096 mmol) and terpy (45 mg, 0.19 mmol), and pyridine (20 mL) was condensed into it under vacuum at −78 °C. The suspension was heated at 100 °C until a clear solution was obtained. The solvent was evaporated off and the orange powder of **1** was washed with THF (15 mL) and dried under vacuum (90 mg, 94%). ^{1}H NMR (200 MHz, $[D_5]$pyridine): δ = 10.97 (d, J = 7.0 Hz, 2 H), 10.43 (s, 2 H), 10.36 (t, J = 7.0 Hz, 1 H), 8.47 (t, J = 7.0 Hz, 2 H), 6.51 (d, J = 7.0 Hz, 2 H), 3.88 (s, $w_{1/2}$ = 25 Hz, 2 H). $C_{30}H_{22}CeI_3N_6$ (987.4): calcd. C 36.49, H 2.24, N 8.51; found C 36.33, H 2.34, N 8.64.

Synthesis of $[NdI_2(terpy)_2]I$ (2): An NMR tube was charged with NdI_3 (10.0 mg, 0.019 mmol), terpy (9.5 mg, 0.04 mmol) and freshly distilled pyridine (1.0 mL). The reaction mixture was heated at 110 °C for 30 min. After evaporation of the solvent, the yellow powder of **2** was washed with tetrahydrofuran (3 mL) and dried under vacuum (15 mg, 80%). ^{1}H NMR (200 MHz, $[D_5]$pyridine): δ = 11.85 (s,$w_{1/2}$ = 30 Hz, 4 H), 10.36 (s, $w_{1/2}$ = 20 Hz, 1 H), 9.18 (s, $w_{1/2}$ = 20 Hz, 2 H), 8.41 (s, $w_{1/2}$ = 25 Hz, 2 H), 7.7 (masked by the py resonance). $C_{30}H_{22}I_3N_6Nd$ (991.5): calcd. C 36.34, H 2.23, N 8.47; found C 36.57, H 2.34, N 8.53.

Synthesis of $[UI_2(terpy)_2(py)]I$ (3): A 25 mL round-bottomed flask was charged with $[UI_3(py)_4]$ (50 mg, 0.053 mmol) and terpy (25 mg, 0.20 mmol), and pyridine (20 mL) was condensed into it under vacuum at −78 °C. The dark solution was stirred for 30 min at 20 °C. The solvent was evaporated off and the dark red powder of **1** was washed with tetrahydrofuran (15 mL) and dried under vacuum (46 mg, 75%). ^{1}H NMR (200 MHz, $[D_5]$pyridine): δ = 24.61 (t, J = 7.0 Hz, 1 H), 18.20 (t, J = 7.0 Hz, 2 H), 10.49 (s, $w_{1/2}$ = 30 Hz, 4 H), 8.35 (s, $w_{1/2}$ = 20 Hz, 2 H), 7.02 (d, J = 6.0 Hz, 2 H). $C_{35}H_{27}I_3N_7U$ (1164.4): calcd. C 36.10, H 2.33, N 8.42; found C 36.39, H 2.93, N 8.17.

Conductometry Studies: A 10^{-2} M solution of Ce^{III} or U^{III} in anhydrous pyridine was prepared by dissolving CeI_3 (52.1 mg) or

Table 2. Crystal data and structure refinement for the complexes

	1·2py	**2·2py**	**3·2py**	**4·1.5py·0.5Et$_2$O**
Chemical formula	$C_{40}H_{32}CeI_3N_8$	$C_{40}H_{32}I_3N_8Nd$	$C_{45}H_{37}I_3N_9U$	$C_{39.5}H_{36.5}CeI_3N_{7.5}O_{1.5}$
M [g mol^{-1}]	1145.56	1149.68	1322.57	1161.08
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a [Å]	11.081(2)	11.1008(7)	28.865(6)	11.717(2)
b [Å]	13.503(3)	13.4329(6)	12.889(3)	13.534(3)
c [Å]	14.360(3)	14.330(1)	23.840(5)	13.628(3)
α [°]	68.44(3)	68.529(4)	90.0	90.70(3)
β [°]	87.04(3)	87.109(3)	90.73(3)	106.17(3)
γ [°]	78.20(3)	78.252(3)	90.0	94.76(3)
V [Å^3]	1955.5(7)	1946.2(2)	8869(3)	2067.0(7)
Z	2	2	8	2
$\rho_{calcd.}$ [g cm^{-3}]	1.946	1.962	1.981	1.866
μ (Mo-K_{α}) [mm^{-1}]	3.572	3.754	5.792	3.383
Crystal size [mm]	0.60 × 0.20 × 0.20	0.25 × 0.20 × 0.15	0.20 × 0.15 × 0.15	0.20 × 0.15 × 0.10
T_{min}/T_{max}	0.469/0.489	0.380/0.410	0.262/0.369	0.511/0.535
F(000)	1090	1094	4968	1110
2θ range [°]	6−51	10−46	5−49	6−49
T [K]	123(2)	123(2)	123(2)	123(2)
No. of data collected	11717	7621	27690	12840
No. of unique data	6815	5237	7483	6464
Observed data [$I > 2\sigma(I)$]	5752	4191	4895	5690
R_{int}	0.034	0.047	0.088	0.028
No. of parameters	469	469	490	488
R_1 [a]	0.028	0.027	0.057	0.028
wR_2[b]	0.057	0.060	0.113	0.064
S	1.032	0.951	1.062	1.019
$\Delta\rho_{min}$ [e Å^{-3}]	-0.563	-1.457	-1.211	-0.997
$\Delta\rho_{max}$ [e Å^{-3}]	0.495	0.659	0.918	0.776

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ (observed reflections). [b] $wR_2 = [\Sigma w(|F_0^2| - |F_c^2|)^2/\Sigma w|F_0^2|^2]^{1/2}$ (observed reflections).

$[UI_3(py)_4]$ (93.5 mg) in pyridine (10 mL). After 5 min at 20 °C, the electrode was immersed into the solution and the conductivity was equal to 45 $\mu S\ cm^{-1}$. The conductivity was found to grow linearly upon addition of n equivalents of terpy ($0 \leq n < 2$) to reach the maximum value of 120 $\mu S\ cm^{-1}$ for $n \geq 2$. The conductivity of 10^{-2} M solutions of NaI or NR_4I (R = n-butyl or n-pentyl) in pyridine was also equal to 120 $\mu S\ cm^{-1}$.

Competition Experiments: An NMR tube was charged with CeI_3 (2.2 mg, 4.3 10^{-3} mmol) and $[UI_3(py)_4]$ (4.0 mg, 4.3 10^{-3} mmol) in $[D_5]$pyridine (1.0 mL), and cyclohexane (1.0 μL) was added with a microsyringe. Terpy (2.0 mg, 8.6 10^{-3} mmol) was added to the dark violet solution. After 10 min at 20 °C, the spectrum showed the complete complexation of terpy and the formation of **1** and **3** with a U^{III}/Ce^{III} molar ratio of 3.0. A similar experiment with NdI_3 in place of CeI_3 gave a mixture of **2** and **3** with a U^{III}/Ce^{III} molar ratio of 2.5.

An NMR tube was charged with CeI_3 (2.8 mg, 5.4 10^{-3} mmol) and $[UI_3(py)_4]$ (5.1 mg, 5.4 10^{-3} mmol) in $[D_5]$pyridine (1.0 mL), and cyclohexane (1.0 μL) was added with a microsyringe. Bipy (1.7 mg, 10.9 10^{-3} mmol) was added to the dark violet solution. After 10 min at 20 °C, the spectrum showed that 25% of the bipy was complexed, giving a mixture of the 1:1 and 1:2 complexes $[MI_3(bipy)(py)_x]$ and $[MI_3(bipy)_2(py)_x]$ (M = Ce, U)[12] with a U^{III}/Ce^{III} separation factor of 1.3.

X-ray Crystallography Studies: Crystal data and a summary of data collection and refinement parameters are given in Table 2. Diffraction collections were carried out on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 2° Φ scans and later refined on all data. A 180° Φ range was scanned with 2° steps with a crystal-to-detector distance fixed at 28 mm (**1**) or 30 mm (**2**, **3** and **4**). Data were corrected for Lorentz-polarization and absorption[29] effects. The structures were solved by the direct atom method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were introduced at calculated positions and constrained to ride on their parent C atom with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. In compound **3**, all pyridine molecules were constrained to fit a regular hexagon with an equal anisotropic displacement parameter. In compound **4**, one pyridine and one diethyl ether solvent molecule were found on the same position and refined as disordered over two positions with an occupation factor of 0.5 each. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[30]

CCDC-174669 (**1·2py**), -174667 (**2·2py**), -174668 (**3·2py**) and -174666 (**4·1.5py·0.5Et$_2$O**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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