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FULL PAPER

Solution and solid state structures of uranium(III) and lanthanum(III) iodide complexes of tetradentate tripodal neutral N-donor ligands†

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The solid state structure of the isostructural complexes [M(tpa)I_3(py)] (M = La^{III} or U^{III}) containing the tripodal ligand tris[(2-pyridyl)methyl]amine (tpa) has been determined. The metal ions are eight-co-ordinated by the tetradentate tpa, three iodide ions and a pyridine molecule. The $[U(Mentb)_2]I_3$ complex was prepared by treating $[UI_3(thf)_4]$ with two equivalents of tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb). Crystallographic studies show that the U^{III} is eight-co-ordinated by two tetradentate Mentb with the ligand arms wrapped around the metal in a pseudo-D_3 symmetric arrangement. Solution NMR studies in pyridine show a large difference in the behaviour of ntb and tpa towards complexation, and a greater stability of the bis(ligand) complexes for ntb than for tpa. At a ntb : metal ratio of 0.5 : 1 the bis(ligand) complex is already present in solution in greater quantity than the mono(ligand) complex for both La and U and at a ratio of 2 : 1 only the bis(ligand) species exists in solution. On the other hand the bis(tpa) complexes of La and U appear in pyridine solution only at tpa : metal ratios larger than 1 : 1, and even at ratios larger than 3 : 1 both the bis(tpa) and the mono(tpa) species are still present in solution. The preferential formation of the bis(ntb) complexes with respect to the mono(ntb) complexes ($K_2/K_1 = 8 \pm 1$ for U and $=35 \pm 4$ for La) has been related to the presence in solution, as well as in the solid state, of strong π–π interaction between benzimidazole rings. The absence of such interactions in the bis(tpa) complexes can explain their lower stability with respect to the bis(ntb) complexes.

Introduction

During the last two decades an increasing number of organometallic derivatives of uranium(III) have been isolated and characterised.[1] However the co-ordination chemistry of U^{III} remains poorly developed,[2] in spite of the convenient synthetic route to useful uranium(III) starting materials reported by Clark and co-workers.[3] A few complexes of tripodal anionic N-donor ligands have been crystallographically characterised in the past few years.[4–6] Among these a complex containing a tripodal amido ligand was shown to have an interesting reactivity with molecular nitrogen.[6] Furthermore, the co-ordination chemistry of f elements with neutral nitrogen-containing aromatic heterocycles is of interest owing to their potential application in actinide(III)/lanthanide(III) separation, a difficult problem in nuclear waste disposal. Indeed, ligands containing sulfur or nitrogen donor atoms have been reported to complex actinides(III) more strongly than lanthanides(III), and this property has been attributed to a greater covalent contribution to the metal–ligand bonding for the actinides.[7] In particular we have shown that tetradentate oligoamines such as tris[(2-pyridyl)methyl]amine (tpa) and tris[(2-pyrazinyl)methyl]amine (tpza)[8] extract selectively actinides in preference to lanthanides from nitric acid solutions into an organic phase with the ligand tpza displaying a higher selectivity than tpa. This behaviour could be explained by the softer character of tpza, which is expected to give rise to a stronger interaction with the actinides. A correlation has been found for organo-lanthanide and actinide complexes between the structural (bond lengths) and the physicochemical properties of these systems and the covalent character of the metal–ligand bond.[9–14] However, similar structural and physicochemical studies have not been reported for non organometallic derivatives containing N- or S-donor ligands, although very recently computational investigations of the electronic structure of the dinitrogen complex $[\{U(NH_2)_3(NH_3)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)]$ have shown evidence for U–N_2 back bonding.[15] In order to assess possible differences in bonding of An^{III} *vs.* Ln^{III} to aromatic nitrogen donors we are studying the complexation of uranium(III) and lanthanum(III) with tripodal amines.

In a preliminary communication we have recently reported the structure of the iodide complexes of U^{III} and La^{III} with a heptadentate tripodal ligand containing bipyridyl arms,[16] showing that tripodal ligands containing neutral aromatic heterocyclic binding units can displace iodide ligands and yield stable uranium(III) complexes. In order to relate possible structural differences between complexes of La^{III} and U^{III} with the presence of a larger degree of covalency in the U^{III}–ligand interaction it is necessary to compare isostructural complexes of La and U containing the same iodide counter ion. However, while a large number of lanthanide(III) complexes of neutral N-donor ligands have been characterised in the past few years, in very few cases these contain the iodide anion as a ligand or counter ion.[17] Additionally, besides the need to obtain the

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† Electronic supplementary information (ESI) available: ^1H NMR chemical shifts at 298 K of tpa and ntb complexes, crystallographic experimental details. See http://www.rsc.org/suppdata/dt/b0/b004179n/

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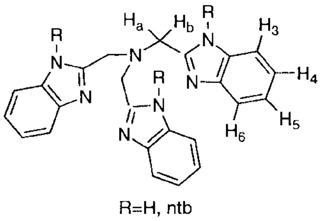
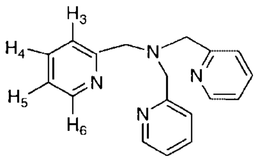
lanthanide analogues of the uranium(III) iodide complexes of nitrogen-containing aromatic heterocycles, it is of interest to study how the soft iodide ions affect the co-ordination properties of the hard lanthanide(III) ions.

Here we report the synthesis and structure in solution and in the solid state of 1:1 and 1:2 uranium(III) and lanthanum(III) complexes of tpa and ntb in presence of iodide as counter ion. The ligands ntb and tpa are able to displace all the iodide ions of $[UI_3(thf)_4]$ to form the first uranium(III) complexes containing only neutral N-donor ligands.



R=H, ntb

R=Me, Mentb



tpa

Experimental

General details

^{1}H NMR spectra were recorded on Bruker AM-400, AC-200 and Varian U-400 spectrometers using deuteriated C_5D_5N and CD_3CN solvents with C_5H_5N and CH_3CN as internal standards vacuum distilled from K or CaH_2. Elemental analyses were performed under argon by SCA/CNRS, Vernaison, France.

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and a Braun glovebox equipped with a purifier unit. The water and oxygen levels were always maintained at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous form, conditioned under argon, and vacuum distilled from K (pyridine, tetrahydrofuran, hexane) or CaH_2 (acetonitrile). Depleted uranium turnings were purchased from the "Societé Industrielle Combustible Nucleaire" of Annecy (France). Solid or solution samples of the uranium complexes were stored in the glovebox in glass vessels sealed with silicon greased stoppers. Starting materials were purchased from Aldrich, Fluka, and Alfa and used without further purification unless otherwise stated. The ligand tris(2-benzimidazolylmethyl)amine (ntb) was purchased from Aldrich, recrystallised from hot ethanol and vacuum dried for 24 h. LaI_3 anhydrous beads were purchased from Aldrich. The ligands tris[(2-pyridyl)methyl]amine (tpa)[18] and tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb)[19] were prepared according to the literature procedures. $[UI_3(thf)_4]$ and $[UI_3(py)_4]$ were prepared as described by Clark and co-workers.[3]

$[LaI_3(py)_4]$ and $[LaI_3(thf)_4]$ were prepared by stirring overnight anhydrous beads of LaI_3 in pyridine or thf. The white powders obtained after filtration were purified by extraction in hot pyridine or hot thf.

Preparations

$[U(Mentb)_2]I_3$ 1. A blue solution of $[UI_3(thf)_4]$ (33.5 mg, 0.037 mmol) in pyridine (2 mL) was added to a stirred white suspension of Mentb (33.2 mg 0.074 mmol) in pyridine (2 mL). The reaction mixture, which became dark green after a few minutes, was stirred for 2 h at room temperature. The resulting green solid was then collected (40 mg, yield: 70%). X-Ray quality crystals were obtained by recrystallisation from a mixture acetonitrile–pyridine. Calc. for $[U(Mentb)I_3]$, $C_{54}H_{54}I_3N_{14}U$: C, 42.72; H, 3.56; I, 25.10; N, 12.92. Found: C, 42.50; H, 3.60; I, 22.16; N, 12.13%.

$[U(ntb)_2]I_3$ 1a. A blue solution of $[UI_3(thf)_4]$ (44.5 mg, 0.049 mmol) in pyridine (1.5 mL) was added to a stirred white suspension of ntb (40 mg 0.098 mmol) in pyridine (2 mL). The reaction mixture, which became dark green after few minutes, was stirred for 30 min at room temperature. n-Hexane (3 mL) was added to the resulting green solution and a green solid formed, which was collected and washed with n-hexane (50 mg, yield: 71%). ^{1}H NMR (400 MHz, CD_5N, 298 K): δ 17.2 (3 H, s, broad, NH), 8.23 (6 H, s, broad, H^3), 7.34 (3 H, s, broad, H^6), 6.94 (3 H, s, broad, H^5), −7.39 (3 H, s, broad, CH$_2^b$) and −7.87 (3 H, s, broad, CH$_2^a$). Calc. for $[U(ntb)I_3]\cdot C_6H_{14}$, $C_{54}H_{56}I_3N_{14}U$: C, 42.68; H, 3.68; I, 25.06; N, 12.90. Found: C, 42.57; H, 3.42; I, 22.66; N, 13.50%.

$[U(tpa)I_3(py)]$ 2. 19.2 mg (0.066 mmol) of tpa were added to a stirred solution of $[UI_3(thf)_4]$ (60 mg, 0.066 mmol) in pyridine (1 mL). The solution was stirred for 30 minutes and then n-hexane (1.5 mL) added to the resulting brown solution to give a brown crystalline solid (56 mg, yield: 86%). X-Ray quality crystals of $[U(tpa)I_3(py)]$ were obtained by slow diffusion of n-hexane into a pyridine–acetonitrile (90:10) solution of the complex. Calc. for $[U(tpa)I_3(py)]\cdot py$, $C_{28}H_{28}I_3N_6U$: C, 31.49; H, 2.67; I, 35.70; N, 7.87. Found: C, 31.16; H, 2.50; I, 32.84; N, 7.55%. ^{1}H NMR (400 MHz, CD_5N, 298 K): δ 15.78 (3 H, t, $J = 7$, H^4), 15.14 (3 H, s, broad, H^6), 10.18 (3 H, d, $J = 7$, H^3), 7.82 (3 H, d, $J = 7$ Hz, H^5) and 0.12 (6 H, s, CH$_2$).

$[La(tpa)I_3(py)]$ 3. 27.2 mg (0.094 mmol) of tpa were added to a solution of LaI_3 (48.8 mg, 0.094 mmol) in pyridine (2 mL). The solution was stirred for 5 minutes and then filtered. Addition of hexane (3 ml) resulted in the formation of a white solid (70 mg, 83%). Λ_M at 293 K for a 10^{-3} M acetonitrile solution of $[La(tpa)I_3(py)] = 282\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H NMR (400 MHz, C_5D_5N, 298 K) : δ 9.56 (3 H, d, H^6), 7.35 (3 H, t, H^4), 7.10 (3 H, d, H^3), 6.80 (3 H, d, H^5) and 4.59 (6 H, s, CH$_2$). ^{1}H NMR spectrum of a 1:2 solution of $[LaI_3(thf)_4]$ and tpa in CD_3CN (400 MHz, 298 K): δ 8.38 (3 H, d, H^6), 7.33 (3 H,t, H^5), 8.01 (3 H, t, H^4), 7.67 (3 H, d, H^3) and 4.70 (6 H, s, CH$_2$). Λ_M at 293 K for a 1.4×10^{-3} M acetonitrile solution of $[La(tpa)_2]I_3$ prepared *in situ* $= 374\ \Omega^{-1}\ cm^2\ mol^{-1}$. ESMS of $[La(tpa)_2]I_3$ prepared *in situ*: *m*/*z* 972.7 ($[La(tpa)_2I_2]^+$).

X-Ray crystallography

All diffraction data were taken using a Bruker SMART CCD area detector three-circle diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). To prevent oxidation and solvent loss the crystals were mounted in a capillary tube with some of the crystallisation solvent in the glovebox and quickly transferred to a stream of cold nitrogen at 143 K on the diffractometer.

Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Bruker SMART program[20] were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the SADABS Bruker program.[20] Space groups were determined from systematic absences, and confirmed by successful solution of the structure (see Table 1). The structures were solved by direct methods using the SHELXTL 5.03 package,[21] and all atoms were found by Fourier difference syntheses. All non-hydrogen atoms were anisotropically refined on F^2. Hydrogen atoms were included in calculated positions and refined isotropically.

CCDC reference number 186/2179.

See http://www.rsc.org/suppdata/dt/b0/b004179n/ for crystallographic files in .cif format.

Results

ntb Complexes

NMR Solution studies. The reaction of $[UI_3(L)_4]$ and $[LaI_3(L)_4]$ (L = thf or py) with the ligand ntb in pyridine was

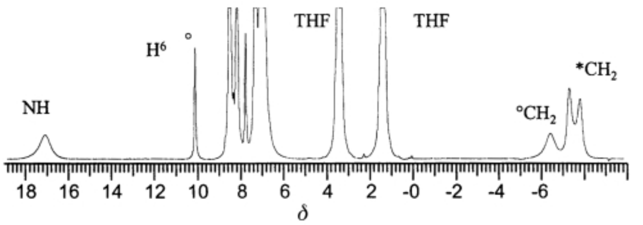


Fig. 1 ^1H NMR spectra of a pyridine solution of $[UI_3(thf)_4]$ and ntb at ratio 1 : 0.5 (°, 1 : 1 complex; *, 1 : 2 complex).

followed by NMR spectroscopy in order to determine the number and nature of the species formed at different ligand : metal ratios. Study of the reaction in other solvents such as thf or acetonitrile was prevented by insolubility of the ntb complexes. Proton NMR spectra were recorded for solutions of $[MI_3(L)_4]$ (M = La or U) and ntb in deuteriated pyridine at different ntb : metal ratios (Fig. 1). At ratios ranging from 0.5 to 2 : 1 the proton spectra indicated the presence of two sets of signals which were attributed to a bis(ntb) complex and to a mono(ntb) species. At a ratio of 2 : 1 the spectrum at 298 K shows only one set of signals which was attributed to the bis(ligand) complex. The spectrum of the bis(ntb) complex of uranium shows four signals for the benzimidazole ring and two signals for the methylene protons, consistent with solution species in which all chelating arms of the ntb ligand are equivalent. The presence of two signals for the two methylene protons at room temperature is consistent with a D_3 symmetric species. The two methylene signals, which are broad and overlapped at 298 K, become sharp and well separated at 273 K. This indicates that at this temperature the conformation of the bis(ntb) complex is fixed on the NMR timescale, while at room temperature slow fluxional motions are present. Coalescence to the dynamically averaged D_{3h}-symmetrical structure occurs at 323 K in deuteriated pyridine. A similar conformational rigidity of the bis(ntb) complex in solution was also observed for lanthanides(III) (Eu and Nd) in the presence of triflate or perchlorate counter ions.[22] The spectrum of the lanthanum bis(ntb) complex shows four signals for the benzimidazole ring and only one very broad signal for the methylene protons consistent with a fluxional D_{3h} symmetric species in solution. Only one resonance is observed for the methylene protons of the mono(ntb) complex of U and La consistent with a fluxional C_{3v} symmetric solution species. The signal of the methylene protons of the mono(ntb) complex of U becomes very broad at low temperature (243 K). This indicates a higher conformational mobility with respect to the bis(ligand) species.

The quotient K_2/K_1 of the stepwise formation constants of the 2 : 1 and 1 : 1 complexes was estimated after integration of the NMR signals to be 8 ± 1 for U and 35 ± 4 for La from eqn. (1)

$$\frac{K_2}{K_1} = (a-1)\frac{[ML_2]}{[ML]} + (2a-1)\left(\frac{[ML_2]}{[ML]}\right)^2 \qquad (1)$$

where L = ntb, a is the initial M : L ratio, and $[ML_2]/[ML] = (I_{ML_2}/2)/I_{ML}$. These values show a similar preference of U^{III} and La^{III} for formation of the bis(ntb) adducts with respect to the mono(ntb) complexes. We have recently reported in a preliminary communication the preference of lanthanide ions in anhydrous acetonitrile in the presence of triflate as counter ion for the formation of bis(ntb) complexes with respect to the mono(ntb) complexes.[22] This behaviour, which is rather unusual in co-ordination chemistry, had been related to the presence in solution, as well as in the solid state, of strong π–π interactions[23] between benzimidazole rings. The value of K_2/K_1 (115 ± 14) found for the stepwise formation constants of the 2 : 1 and 1 : 1 complexes $[La(ntb)_2][Otf]_3$ and $[La(ntb)][Otf]_3$ ($Otf = O_3SCF_3$) in pyridine is larger than the one found in the presence of the more co-ordinating iodide counter ion (35 ± 4). However the value found for the stepwise formation constants of these 2 : 1 and 1 : 1 complexes in acetonitrile is lower than 1 (0.03 ± 0.003). The larger value found in pyridine for the lanthanum ion could be due to an enhancement of the stacking interaction in the less polar solvent.[24]

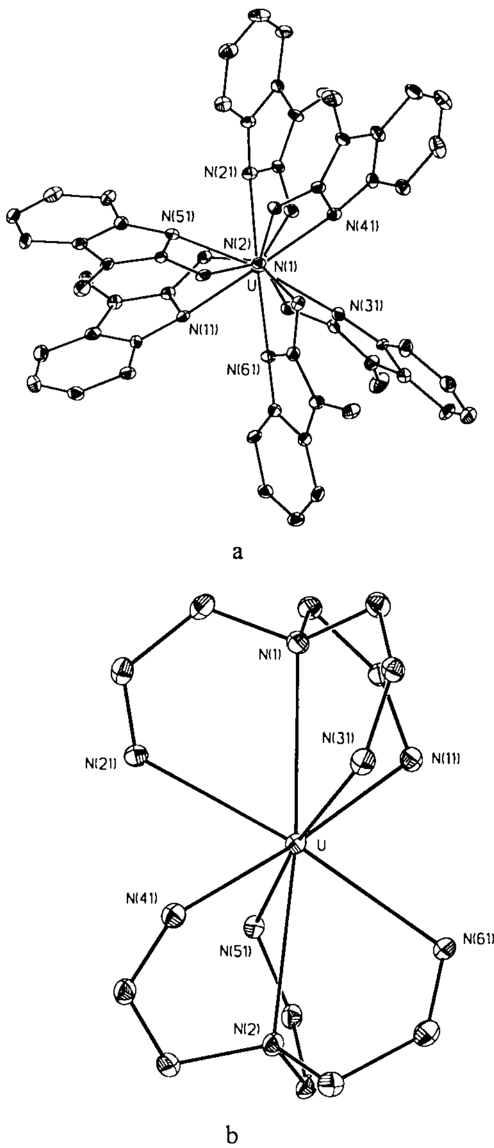


Fig. 2 (a) Side view of the crystal structure of the cation $[U(Mentb)_2]^{3+}$ with thermal ellipsoids at 30% probability. (b) Co-ordination environment of U in $[U(Mentb)_2]^{3+}$.

Crystal and molecular structure of $[U(Mentb)_2]I_3 \cdot 3py$ 1. Reaction of $[UI_3(thf)_4]$ with two equivalents of Mentb in pyridine gave the bis(ligand) uranium(III) complex $[U(Mentb)_2]I_3 \cdot 3py$ **1**. This is very insoluble in pyridine or thf but can be recrystallised from an acetonitrile–pyridine mixture. It is the first crystallographically characterised complex of uranium(III) containing only neutral N-donor ligands. The crystal structure of the cation $[U(Mentb)_2]^{3+}$ is shown in Fig. 2 and selected interatomic distances and angles are given in Table 2. The U^{III} is eight-co-ordinated by two tetradentate Mentb ligands with the ligand arms wrapped around the metal in a pseudo-D_3 symmetric arrangement. The geometry can be described as a distorted bicapped trigonal antiprism with the two apical aliphatic nitrogens in the capping positions. The U–N distances range from 2.527(6) to 2.562(5) Å for the benzimidazole nitrogens, while larger values are found for the nitrogen atoms from the tertiary amines (2.750(5) and 2.756(5) Å). These values are in the range (2.98–2.509 Å)[4,16,25] of distances reported and are similar to those found for the La–N distances in the analogous

Table 1 Crystallographic data for the three structures

	$[U(Mentb)_2]I_3\cdot 3py$ **1**	$[U(tpa)I_3(py)]$ **2**	$[La(tpa)I_3(py)]$ **3**
Formula	$C_{69}H_{69}I_3N_{17}U$	$C_{23}H_{23}I_3N_5U$	$C_{23}H_{23}I_3N_5La$
M	1755.14	988.19	889.07
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1$	$P2_1$
a/Å	21.598(4)	9.6979(6)	9.7180(5)
b/Å	22.296(5)	15.3561(9)	15.3889(8)
c/Å	27.992(6)	9.9489(6)	9.9741(5)
β/Å		115.894(1)	115.826(1)
V/Å^3	13480(5)	1332.86(14)	1342.64(12)
Z	8	2	2
μ(Mo-Kα)/mm^{-1}	3.838	9.583	5.060
T/K	193	193	193
$R1$, $wR2^a$	0.0422, 0.0942	0.0425, 0.1091	0.0388, 0.1037
Reflections collected	85248	8613	8639
Independent reflections/R(int)	16728/0.1116	5730/0.0581	6035/0.0394
Reflections observed ($I > 2\sigma(I)$)	9116	5532	5890

^{a} Structure was refined on F_o^2 using all data.

Table 2 Selected bond distances (Å) and angles (°) in $[U(Mentb)_2]I_3\cdot 3py$

U–N(51)	2.527(6)	U–N(61)	2.562(5)
U–N(11)	2.543(5)	U–N(31)	2.576(6)
U–N(21)	2.554(6)	U–N(1)	2.750(5)
U–N(41)	2.555(5)	U–N(2)	2.756(5)
N(51)–U–N(11)	78.1(2)	N(61)–U–N(31)	76.0(2)
N(51)–U–N(21)	80.2(2)	N(51)–U–N(1)	117.7(2)
N(11)–U–N(21)	100.3(2)	N(11)–U–N(1)	63.0(2)
N(51)–U–N(41)	103.8(2)	N(21)–U–N(1)	62.9(2)
N(11)–U–N(41)	175.5(2)	N(41)–U–N(1)	112.7(2)
N(21)–U–N(41)	76.3(2)	N(61)–U–N(1)	123.0(2)
N(51)–U–N(61)	98.0(2)	N(31)–U–N(1)	63.1(2)
N(11)–U–N(61)	85.2(2)	N(51)–U–N(2)	62.7(2)
N(21)–U–N(61)	173.6(2)	N(11)–U–N(2)	122.2(2)
N(41)–U–N(61)	98.4(2)	N(21)–U–N(2)	111.9(2)
N(51)–U–N(31)	172.1(2)	N(41)–U–N(2)	62.1(2)
N(11)–U–N(31)	96.0(2)	N(61)–U–N(2)	62.1(2)
N(21)–U–N(31)	106.3(2)	N(31)–U–N(2)	117.5(2)
N(41)–U–N(31)	82.4(2)	N(1)–U–N(2)	173.9(2)

complex $[La(Mentb)_2][ClO_4]_3$ (2.54(1)–2.58(1) Å for the benzimidazole nitrogens and 2.73(1), 2.77(1) Å for the tertiary amine nitrogens).[26] The metal ion and the two apical tertiary amine nitrogens are aligned on the pseudo-C_3 axis (N(1)–U–N(2), 173.9(2)°).

The two ligands show the same right- or left-handed helical arrangement in each cation to give a chiral enantiomer. The complex crystallises with pairs of enantiomeric cations resulting in a racemic crystal. The values of the interplanar angles between closely adjacent benzimidazole rings (13.0, 13.7, 25.8°) and the values of the interplanar distances (3.7, 3.4, 3.3 Å) are in consistent with the presence of strong intramolecular π–π interactions between the benzimidazole rings.

tpa Complexes

Reaction of $[MI_3(thf)_4]$ (M = U or La) with one equivalent of tpa in pyridine yields the 1:1 complexes $[M(tpa)I_3(py)]$ (M = U **2** or La **3**). It is worth noting that reduction of tpa by $[UI_3(thf)_4]$ was never observed either in pyridine or in acetonitrile even after leaving the solution standing for a long period of time.

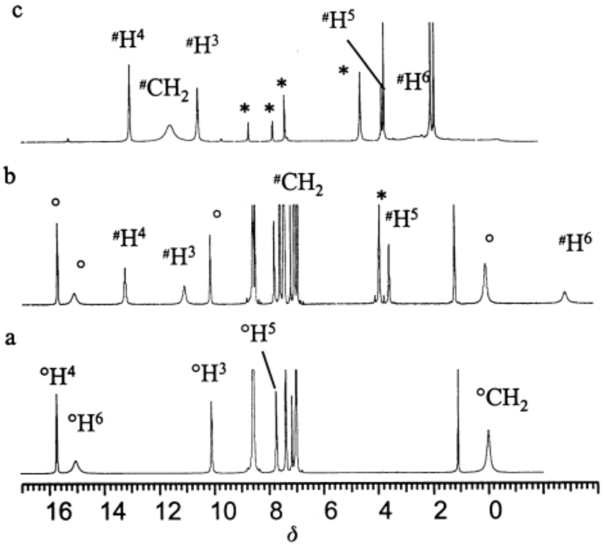


Fig. 3 ^{1}H NMR spectra of pyridine solutions of $[UI_3(py)_4]$ and tpa at ratio 1:1 (a) and 1:3 (b) and of an acetonitrile solution of $[UI_3(thf)_4]$ and tpa at ratio 1:3 (c) (*, "free" ligand; °, 1:1 complex; #, 2:1 complex).

NMR Solution studies. NMR studies have been carried out to investigate the solution structure of the uranium and lanthanum complexes of tpa formed at different ligand to metal ratios, and to assess the influence of the solvent and of the nature of the metal on the formation constants of these complexes. When tpa is increasingly added to solutions of $[MI_3(thf)_4]$ or $[MI_3(py)_4]$ (M = U or La) in acetonitrile or pyridine the proton NMR spectra show, for ratios $0 < \text{tpa}:\text{M} \leq 1:1$, only one set of signals for the tpa ligand with four resonances for the 12 pyridine protons and a single signal for the six methylene protons. These signals have been assigned to the 1:1 complexes of tpa. The spectral features are consistent with threefold symmetry of the solution species in which all chelating arms of the tpa ligand are equivalent. This symmetry, which is not present in the crystal structure of the complexes $[U(tpa)I_3(py)]$ **2** and $[La(tpa)I_3(py)]$ **3**, can be explained by a fast exchange between the co-ordinated and bulk solvent. Additionally, the chemical shift equivalence of the methylene protons requires conformational mobility of the ligand arms in solution. A large shift of the tpa protons accompanied by line broadening is observed for the uranium complex for which the assignment of the NMR signals (in acetonitrile and pyridine) has been confirmed by two-dimensional homonuclear COSY. In acetonitrile the protons H6 (δ 11.06) and H4 (δ 15.78) are shifted to low field while the methylene protons (δ 2.28) are shifted upfield. A significantly larger shift is observed in pyridine solution for H6 (δ 15.14) and for the methylene protons (δ 0.12). This difference could be explained by the presence of an increased number of iodide ions co-ordinated to the metal due to the lower polarity of pyridine relative to acetonitrile. A conductivity measurement performed on a 10^{-3} M acetonitrile solution of the mono(tpa) complex $[La(tpa)I_3(py)]$ showed the presence of a 1:2 electrolyte, consistent agreement with the presence in solution of only one co-ordinated iodide (Λ_M at 293 K = 282 Ω^{-1} cm^2 mol^{-1} which is in the range of values (220–300) reported for 2:1 electrolytes in acetonitrile[27]).

When tpa is increasingly added to a solution of $[MI_3(thf)_4]$ or $[MI_3(py)_4]$ (M = U or La) and tpa in pyridine at ratios $1 \leq \text{tpa}:\text{M} \leq 3:1$ the proton NMR spectra show two new sets of signals which are attributed to the "free" ligand and to a bis(tpa) complex (Fig. 3b). The assignment of the NMR signals has been confirmed by two-dimensional homonuclear COSY and two-dimensional NOESY. The set of signals assigned to the bis(tpa) species shows a single resonance for the six methylene protons and four resonances for the pyridine protons indicating the presence of solution species having a threefold

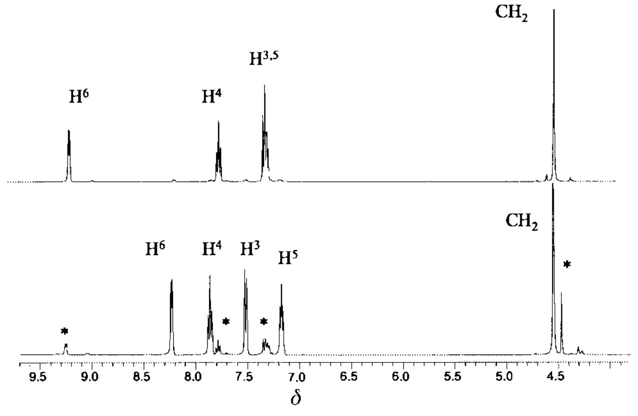


Fig. 4 ^{1}H NMR spectra of acetonitrile solutions of [LaI$_3$(thf)$_4$] and tpa at ratio 1 : 1 (a) and 1 : 7 (b) (*, 1 : 1 complex).

symmetry in which all the pyridyl arms of the two tpa ligands are equivalent. The signal of the six methylene protons and the H6 signal display very different chemical shifts for the bis(tpa) uranium(III) complex with respect to the mono(tpa) complex (Fig. 3b and 3a). These features seems to indicate a different geometric arrangement of tpa in the mono- and bis-(ligand) complexes. A very similar value of K_2 (13 ± 2 L mol^{-1} for U and 10 ± 2 L mol^{-1} for La) was found from the integration of the NMR signals for the two ions.

When tpa is gradually added to a solution of [MI$_3$(thf)$_4$] (M = U or La) and tpa in acetonitrile two new sets of signals, attributed to the "free" ligand and to a bis(tpa) complex, appear in the spectrum for ratios $1 \le$ tpa : M $< 2 : 1$ (Fig. 4 shows the spectra for La at 1 : 1 and 1 : 7 ratios). The presence of a single signal for the methylene protons in pyridine and in acetonitrile indicates that the bis(tpa) complex displays at room temperature a dynamically averaged D_{3h} symmetry and shows an higher fluxionality of the ligand arms with respect to the bis(ntb) complex. Similar bis(ligand) complex : mono(ligand) complex ratios are observed for La and U. At a tpa : metal ratio > 2 : 1 the NMR spectra show only two sets of signals for La and U (Fig. 3c) attributed to the "free" ligand and to the bis(tpa) complex. This indicates that the value of the stepwise formation constant K_2 is much higher in acetonitrile than in pyridine (its high value prevents its determination by integration of NMR signals). The value of the conductivity measured on a 10^{-3} M acetonitrile solution of the bis(tpa) complex (Λ_M at 293 K = 374 Ω^{-1} cm^2 mol^{-1} which is in the range (340–420 Ω^{-1} cm^2 mol^{-1}) reported for 3 : 1 electrolytes in acetonitrile[27]) indicates the presence in solution of a 3 : 1 electrolyte and therefore the absence of co-ordinated iodide. Therefore the lower value of K_2 in pyridine can be explained by the presence of co-ordinated iodides in the pyridine solvent, less polar than acetonitrile, which makes the co-ordination of a second tpa more difficult. While it was impossible to record an electrospray mass spectrum for the bis(tpa) uranium complex due to its extreme air sensitivity, the electrospray mass spectrum of a 1 : 3 solution of [LaI$_3$(thf)$_4$] and tpa in acetonitrile shows the presence of a peak at $m/z = 973$ corresponding to the monocation [La(tpa)$_2$I$_2$]$^+$. This result strongly supports the presence of a bis(tpa) complex in solution. The presence of two iodides in the observed adduct [La(tpa)$_2$I$_2$]$^+$ is due to reassociation of the counter ions during the ESMS experiment.

Table 3 Selected bond distances (Å) and angles (°) in [U(tpa)I$_3$(py)] and [La(tpa)I$_3$(py)]

	U	La
M–N(1)	2.650(7)	2.670(5)
M–N(2)	2.67(1)	2.676(6)
M–N(3)	2.629(8)	2.675(6)
M–N(4)	2.663(7)	2.712(5)
M–N(5)	2.706(8)	2.720(6)
M–I(3)	3.1893(7)	3.2095(5)
M–I(1)	3.2612(7)	3.2885(6)
M–I(2)	3.2944(7)	3.3189(5)
N(3)–M–N(1)	115.6(3)	115.3(2)
N(3)–M–N(4)	63.7(3)	63.4(2)
N(1)–M–N(4)	64.2(2)	63.7(2)
N(3)–M–N(2)	107.8(3)	106.6(2)
N(1)–M–N(2)	76.6(3)	76.6(2)
N(4)–M–N(2)	61.7(3)	61.1(2)
N(3)–M–N(5)	81.5(3)	82.0(2)
N(1)–M–N(5)	135.7(3)	136.2(2)
N(4)–M–N(5)	145.0(3)	145.2(2)
N(2)–M–N(5)	139.7(3)	139.7(2)
N(3)–M–I(3)	160.1(2)	161.0(1)
N(1)–M–I(3)	81.3(2)	80.9(1)
N(4)–M–I(3)	136.1(2)	135.5(1)
N(2)–M–I(3)	85.6(2)	86.0(1)
N(5)–M–I(3)	78.8(2)	79.3(1)
N(3)–M–I(1)	74.4(2)	74.5(1)
N(1)–M–I(1)	69.8(2)	70.3(1)
N(4)–M–I(1)	89.1(2)	89.2(1)
N(2)–M–I(1)	142.8(2)	143.1(1)
N(5)–M–I(1)	77.4(2)	77.2(1)
I(3)–M–I(1)	104.06(2)	104.08(2)
N(3)–M–I(2)	73.9(2)	73.7(1)
N(1)–M–I(2)	145.9(2)	145.6(1)
N(4)–M–I(2)	96.4(2)	96.4(1)
N(2)–M–I(2)	69.4(2)	69.1(1)
N(5)–M–I(2)	76.3(2)	76.3(1)
I(3)–M–I(2)	98.25(2)	98.77(2)
I(1)–M–I(2)	141.19(2)	140.80(2)

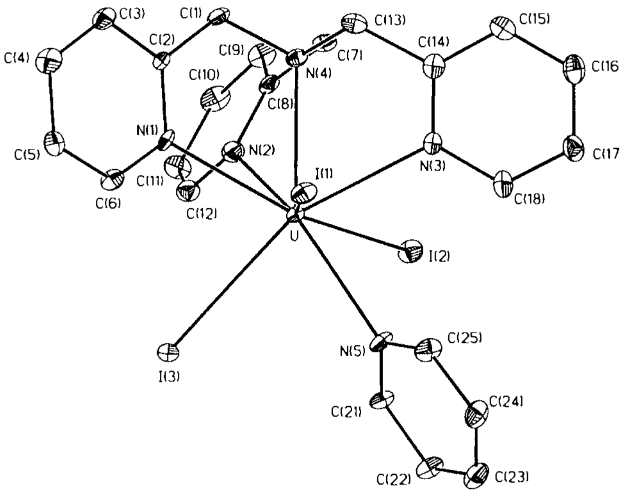


Fig. 5 Side view of the crystal structure of [U(tpa)I$_3$(py)] with thermal ellipsoids at 30% probability.

Crystal and molecular structure of [U(tpa)I$_3$(py)] 2 and [La(tpa)I$_3$(py)] 3. Brown X-ray quality crystals of [U(tpa)I$_3$(py)] **2** and colorless crystals of [La(tpa)I$_3$(py)] **3** were grown by slow diffusion of n-hexane into a pyridine–acetonitrile solution of the complexes. The two complexes are isostructural and accordingly only the uranium one is shown in Fig. 5. Selected interatomic distances and angles are in Table 3. Polytopal analysis indicates that the co-ordination geometry of **2** and **3** (Fig. 6) is best described as a highly distorted dodecahedron formed by the tetradentate tpa, three iodide ions and a pyridine molecule, and values of the angles δ and φ are presented in Table 4. (Polytopal analysis is a method of assessing the conformity of the co-ordination polyhedron formed by the ligating atoms to certain ideal polyhedra, by means of comparing diagnostic internal angles.[28,29]) The dodecahedron can be viewed as a pair of interpenetrating tetrahedra where the atoms I(2), I(1), I(3), N(4) occupy the B vertices which define a flattened tetrahedron and N(2), N(1), N(5), N(3) occupy the A vertices which define an elongated tetrahedron. The mean φ

Table 4 Values of δ and φ/° in [U(tpa)I_3(py)] and [La(tpa)I_3(py)]

Atoms		[U(tpa)I_3(py)] Around U	[La(tpa)I_3(py)] Around La	Idealised polyhedra Atoms[a]	*DD*	*SAPR*	*BCTP*
N(5)[N(1)I(3)]N(1)	δ	43.8	44.1	1(57)3	29.5	0.0	21.8
N(5)[I(2)I(3)]N(2)	δ	52.6	52.7	1(67)4	29.5	0.0	0.0
N(3)[I(1)N(4)]N(1)	δ	33.7	33.6	2(58)3	29.5	52.5	48.2
N(3)[I(2)N(4)]N(2)	δ	21.0	20.04	2(68)4	29.5	52.5	48.2
	φ	6.6	6.9	5634	0.0	24.5	14.1

[a] Polyhedral vertices defined as: 1 [N(5)], 2 [N(3)], 3 [N(1)], 4 [N(2)], 5 [I(1)], 6 [I(2)], 7 [I(3)], 8 [N(4)].

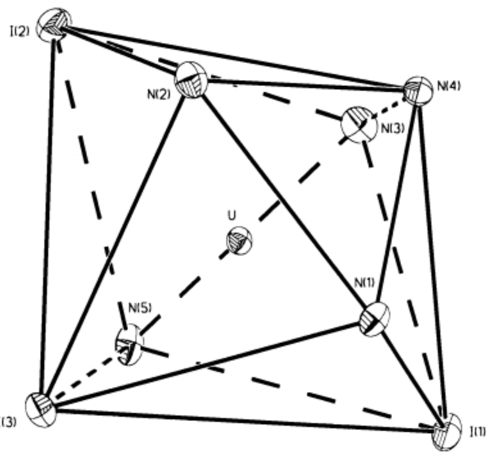


Fig. 6 The co-ordination geometry around the U in [U(tpa)I_3(py)].

angle (6.6° for U and 6.9° for La) and the δ angles show that the geometry of **2** and **3** is considerably distorted from a dodecahedron along the pathway of the bicapped trigonal prism. The La–N distances range from 2.720(6) to 2.670(5) Å and the U–N distances from 2.706(8) to 2.629(8) Å with the longer distance associated with the pyridine molecule. These values are in the range of La–N (2.79–2.60 Å)[16,30,31] and U–N (2.98–2.509 Å)[4,16,25] distances reported. In the lanthanum complex the metal–tertiary amine nitrogen distance is longer than the metal–pyridyl nitrogen distances which all have very similar values. In the uranium complex, while the metal–tertiary amine nitrogen distance is similar to the value found for two of the three metal–pyridyl distances, the value of the U–N distance (U–N3 2.629(8) Å) for the pyridyl group facing one of the iodide ligands (N3–U–I3 160.11(19)°) is significantly shorter than the other U–pyridyl distances (U–N2 2.67(1), U–N1 2.650(7) Å) and than the average La–pyridyl distance (2.673 Å). Since La^{III} and U^{III} have the same ionic radius these differences in bond distances between the two isostructural complexes could indicate the presence of some degree of covalency in the U^{III}–tpa interaction.

Discussion

While the reaction of [UI_3(thf)$_4$] with neutral tridentate heterocyclic imines like terpyridine or 2,4,6-tris(2-pyridyl)-1,3,5-triazine can result,[32] depending on the reaction conditions, in the reduction of the imine, the reduction of tpa and ntb by U^{III} was never observed. In fact the uranium(III) complexes of ntb and tpa (bis(ligand) and mono(ligand)) are stable over long periods of time in solution in absence of water or oxygen.

We have determined the solid state and solution state structure of mono(ligand) and bis(ligand) complexes of U^{III} and La^{III} with tpa and ntb. Bond lengths for isostructural compounds will follow from their ionic radii and their co-ordination number if there is no covalent contribution to the bond.[14] The same values of the bond distances were found for the bis(Mentb) complexes of U^{III} and La^{III}. The differences found in the M–N bond distances in the isostructural complexes [M(tpa)I_3(py)] of La^{III} and U^{III} are probably still too small to be related in themselves to a difference in the metal–ligand interaction. However the lack of large differences in the type of metal–ligand interaction is consistent with metal extraction experiments which show a low Am^{III}/Eu^{III} separation factor for tpa. We are now investigating the differences in M–N bond distances in isostructural complexes of U^{III} and La^{III} containing ligands with softer character and higher Am^{III}/Eu^{III} separation factors (such as tpza), and which are therefore likely to give rise to stronger U–N interactions.

NMR solution studies in pyridine show a strong difference in the behavior of ntb and tpa toward complexation of iodides of La and U. At a ntb : metal ratio of 0.5 : 1 the bis(ligand) complex is already present in solution in greater quantity than the mono(ligand) complex for both La and U and at a ratio of 2 : 1 only the bis(ligand) species exists in solution. On the other hand the bis(tpa) complexes of La and U appear in pyridine solution only at tpa : metal ratios larger than 1 : 1, and even at ratios larger than 3 : 1 the mono(tpa) species is still present in solution. Therefore a much greater stability of the bis(ligand) iodide complexes is observed for ntb than for tpa. Since the pyridine and the benzimidazole nitrogens have very similar electron density ($pK_{a\ \mathrm{pyridine}} = 5.25$ and $pK_{a\ \mathrm{benzimidazole}} = 5.5$), this difference is probably due to the capability of the benzimidazole arms to form strong π–π interactions.[22,33]

Changing the anion in the La/ntb system from iodide to triflate increases K_2/K_1 from 35 ± 4 to 115 ± 14. This behaviour is consistent with the fact that the triflates are less strongly co-ordinating than iodides and therefore are less likely to compete with binding of the second ligand molecule. The same reasoning can be used to explain that the bis(tpa) complex is more favored in acetonitrile than in pyridine. However, the opposite effect is observed for the triflate ntb complexes where K_2/K_1 is as low as 0.03 ± 0.003 in acetonitrile *vs.* 115 ± 14 in pyridine. In this case it appears that the π–π stacking interactions are diminished in the more polar acetonitrile solvent. Minor entropic differences are expected for the reaction in the two solvents. Therefore the enthalpic contribution associated to these π–π interactions should be the dominant factor. Further structural and complexation studies of complexes of La^{III} and U^{III} containing heterocyclic imines with increased π–acceptor character are in progress.

On the other hand, change of the tripodal amine introduces the possibility to tune the reactivity of the system. Indeed, the tris(benzimidazolyl) ligands strongly favor the formation of bis(tripod) complexes and allow us to obtain rather unique uranium(III) complexes containing only neutral N-donor ligands. Conversely the use of tpa allows the isolation of a monotripod complex of U^{III}. This complex presents binding sites for both neutral and anionic ligands, and thus seems very promising for the study of uranium(III) reactivity. The iodide ligands can easily be displaced by a second tripodal ligand to give the bis(tripod) complex. The lower stability of the bis(tpa) uranium(III) complex makes it reactive towards H_2O and alcohols, which is not observed for the bis(ntb) uranium(III) complex probably owing to the inaccessibility of the metal center in this complex which is highly stabilised by the π–π interactions between the benzimidazole rings. Detailed studies of the reactivity of the bis(tpa) complex are in progress.

Tripodal ligands appears to be attractive ancillary ligands for the development of uranium(III) co-ordination chemistry in view of their resistance to metal reduction and of the synthetically easy access to functionalised analogs with different steric and electronic properties.

Acknowledgements

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