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A rare uranium(III) complex of a tripodal aromatic amine and its lanthanum analogue

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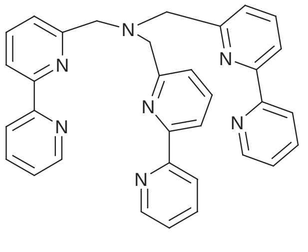
The crystal structure of the first U(III) complex of the heptadentate tripodal aromatic amine tris[(2,2′-bipyridin-6-yl)methyl]amine and of its La(III) analogue have been determined.

While there has been a renewal of interest in the organometallic chemistry of uranium(III),[1] the development of the coordination chemistry of U(III) has lagged behind[2] and the number of structurally characterized U(III) complexes containing N-donor ligands is very limited.[3] Aromatic amines are ligands of great interest in the coordination chemistry of f block elements for their potential application in actinide(III)/lanthanide(III) separation, a difficult problem in nuclear waste disposal.[4] Indeed, they have been reported to complex actinides(III) more strongly than lanthanides(III), owing to a greater covalent contribution to the metal–amine bonding.[5] While an increasing number of lanthanide complexes of aromatic amines have been reported in the last few years, very little is known about the coordination chemistry of actinides(III) with these ligands.[2] The preparation of U(III) complexes of 1,10-phenanthroline and 2,2′-bipyridine was reported several years ago by Hart and Tajik, who were unable to characterize the complexes due to their extreme reactivity with traces of oxygen or moisture.[6] In order to gain more insight into the chemistry of f elements with nitrogen donor ligands, we have started to study the coordination chemistry of Ln(III) and An(III) with the tripodal aromatic amines.[7] The synthesis and some physical properties of Ru(II), Fe(II), Cr(II), Cr(III)[8] and Eu(III)[9] complexes of tris[(2,2′-bipyridin-6-yl)methyl]amine (tbpa) have been described, but to our knowledge there are no crystallographic reports on tbpa complexes.



tbpa

In this communication we report the synthesis and the molecular structure of the first U(III) complex of an aromatic amine, [U(tbpa)I_2]I·py **1** and those of the related lanthanum(III) complex [La(tbpa)(H_2O)(η^2-ClO_4)][ClO_4]$_2$·2$CHCl_3$·MeOH **2**. Complex **1** was prepared by reacting $UI_3(thf)_4$[10] with tbpa in pyridine under argon;† the replacement of the iodide ion and of the four thf ligands of the starting complex $UI_3(thf)_4$ by the heptadentate tbpa results in an increased reactivity towards oxygen and water. The crystal structure of **1**‡ consists of cation–anion pairs and a molecule of pyridine connected by hydrogen bonding to three different cations and one anion. The crystal structure of the cation is shown in Fig. 1. The uranium atom is 9-coordinate with tbpa and two iodine anions with approximately a capped square antiprism coordination geometry. The tertiary amine nitrogen N(7) lies on the expanded face formed by the three bipyridyl nitrogen atoms N(1), N(3), N(5) of tbpa and I(1). The tbpa ligand is bound asymmetrically with U–N distances ranging from 2.697(4) Å for N(7) to 2.595(4) Å for the bipyridyl nitrogens. These values are in the range of U(III)–N distances previously reported.[3,11]

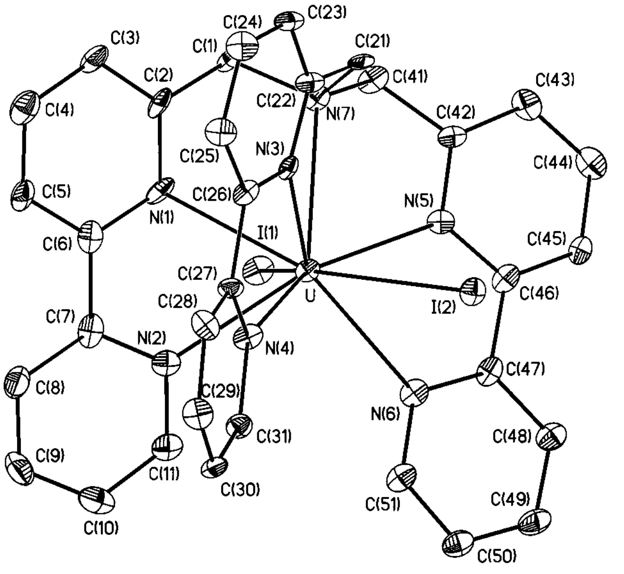


Fig. 1 Crystal structure of the cation of [U(tbpa)I_2]I·py **1** with thermal ellipsoids at 30% probability. Selected bond lengths (Å): U–N(1) 2.595(4), U–N(2) 2.635(4), U–N(3) 2.643(3), U–N(4) 2.657(4), U–N(5) 2.614(4), U–N(6) 2.635(4), U–N(7) 2.697(4), U–I(1) 3.2568(8), U–I(2) 3.3286(7).

Complex **2** was obtained by reaction of La(ClO_4)$_3$·6H_2O with tbpa in acetonitrile.§ The crystal structure of the cation in **2** is shown in Fig. 2. The lanthanum ion is 10-coordinate with tbpa, one water molecule and a bidentate perchlorate. The coordination geometry is not regular. Again, tbpa is asymmetrically bound with distortion of the bipyridine moiety. The average La–N distance (2.728 Å) is longer than the value found for the [La(bipy)$_2$(NO_3)$_3$] complex [2.66(1) Å],[12] and of those found for the 10-coordinate complexes [La(phen)$_2$(NO_3)$_3$] and [La(terpy)$_2$(NO_3)$_2$]$^+$ [2.67(3) and 2.68(3) Å].[13]

NMR studies in acetonitrile solution show that both complexes are stable toward the dissociation of the organic ligand. The NMR spectrum of the La complex shows only one resonance for the methylene protons and seven overlapping resonances for the bipyridine protons. These features are consistent with a three-fold symmetry of the solution species in which all chelating arms of the tbpa ligand are equivalent or in fast

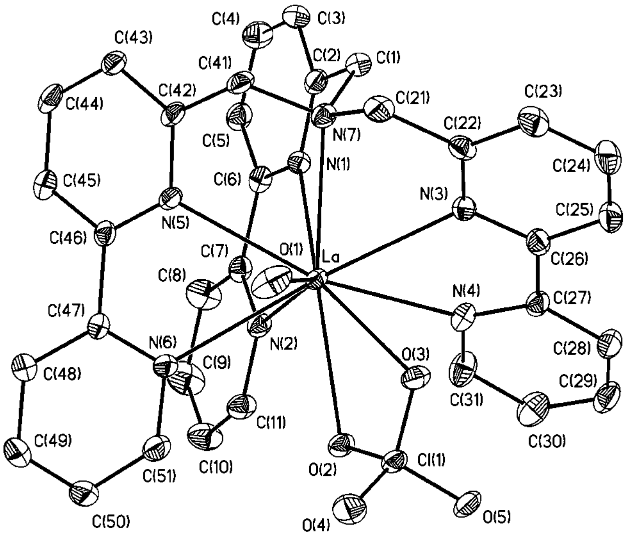


Fig. 2 Crystal structure of the cation of [La(tbpa)(H_2O)(η^2-ClO_4)]-[ClO_4]$_2$·2$CHCl_3$·MeOH **2** with thermal ellipsoids at 30% probability. Selected bond lengths (Å): La–N(1) 2.704(3), La–N(2) 2.693(3), La–N(3) 2.729(3), La–N(4) 2.762(3), La–N(5) 2.688(3), La–N(6) 2.797(3), La–N(7) 2.723(3), La–O(3) 2.763(3), La–O(1) 2.492(3), La–O(2) 2.671(3).

exchange on the NMR time scale. In addition, the chemical shift equivalence of the methylene protons requires a conformational mobility of the ligand arms in solution which was not observed for the ruthenium complex of tbpa.[8] The proton spectrum of the uranium complex at room temperature in acetonitrile shows 8 broad peaks between δ 20 and −10. At lower temperature (−30 °C) the spectrum shows a large number (at least 24) of narrower signals. These features can be explained by the presence at room temperature of an exchange between different ligand conformations.

The number of well characterized coordination compounds of uranium(III) remains very limited because of the extreme ease with which they oxidize to U(IV). Complex **1** is a rare example of a structurally characterized coordination derivative of U(III) and the first, to our knowledge, containing only an aromatic amine as ancillary ligand. The structural data show that the difference between the metal to nitrogen distance and the ionic radius of the metal is essentially the same for La (1.458 Å) and U (1.476 Å) [a value of the ionic radius of 1.163 Å for 9-coordinated U(III) was calculated as described by Raymond and Eigenbrot[14]]. In addition the C–N and the C–C distances for the bipy rings appear to be very similar in the La and U complexes. Surprisingly, these results appear to indicate the occurrence of a similar ionic type of bonding between tbpa and U or La [though we note that the crystal structure of the iodide complex of La(III) with tbpa would allow a better comparison]. The coordination properties of iodide complexes of lanthanides(III) and uranium(III) complexes with tripodal aromatic amines having different soft character is currently under study together with their extraction properties.

Notes and references

† Complex **1**. A solution of tbpa (0.033 mmol) in pyridine (1 mL) was added to a blue solution of $UI_3(thf)_4$ (0.033 mmol) in pyridine (1 mL) to give a brown solution. After standing for two days at room temperature a brown crystalline precipitate formed (0.023 mmol, 71%). Brown crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of hexane into a pyridine–acetonitrile solution {Calc. for [U(tbpa)I_2]I, $C_{33}H_{27}I_3N_7U$: C, 34.75; H, 2.39; N, 8.60. Found: C, 34.20; H, 2.60; N, 8.29%}.

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 level were always kept at less than 1 ppm. The solvents were purchased in their anhydrous form and distilled from K or CaH_2 under argon. Solid or solution samples of **1** were stored in the glovebox in glass vessels sealed with silicon greased stoppers.

‡ Crystal data for complex **1**. [U(tbpa)I_2]I·Py, $C_{38}H_{32}I_3N_8U$: M = 1219.45, monoclinic, $P2_1/c$, a = 9.736(2), b = 17,951(4), c = 22.436(5) Å, β = 95.52(3)°, V = 3903.0(13) Å^3, Z = 4, D_c = 2.075 g cm^{-3}, μ = 6.570 mm^{-1}. 6901 Independent reflections ($2\theta_{max}$ = 52) were collected at 143 K. Refinement using the SHELXTL 5.05 package on all data converged at R_1 [$F > 4\sigma(F)$] = 0.0543, $wR2$ = 0.1183. Crystals of **1** very quickly oxidised in air and lost solvent rapidly. To prevent oxidation and solvent loss the crystals were mounted in a capillary tube with some of the crystallisation solvent in the glove box.

Crystal data for complex **2**. [La(tbpa)(H_2O)(η^2-ClO_4)][ClO_4]$_2$·2$CHCl_3$·MeOH, $C_{36}H_{35}N_7O_{14}Cl_9La$: M = 1247.67, triclinic, $P\bar{1}$, a = 11.90850(10), b = 13.3371(2), c = 18.2306(3) Å, α = 69.6470(10), β = 87.5360(10), γ = 64.0780(10)°, V = 2421.07(6) Å^3, Z = 2, D_c = 1.711 g cm^{-3}, μ = 1.448 mm^{-1}. 6844 Independent reflections ($2\theta_{max}$ = 52) were collected at 143 K. Refinement using the SHELXTL 5.05 package on all data converged at R_1 [$F > 4\sigma(F)$] = 0.0353, $wR2$ = 0.0901. The molecules of MeOH and $CHCl_3$ and one of the perchlorate counter ions are disordered with a site occupancy factor of 0.5. CCDC number 186/1234. See http://www.rsc.org/suppdata/dt/1998/4087/ for crystallographic files in .cif format.

§ Complex **2**. The ligand tbpa (0.23 mmol) was added to a solution of La(ClO_4)$_3$·7H_2O (0.23 mmol) in acetonitrile (5 mL). The resulting pale yellow solution was stirred for 1 h and then concentrated (1 mL). After standing overnight, a white precipitate formed which was collected by filtration, washed with diethyl ether and dried (0.12 mmol, 52 %). ^{1}H NMR (CD_3CN, 200 MHz): δ 8.29 (d, J = 4.4, 3H), 8.17 (t, J = 6.6 Hz, 3H), 8.08 (m, 9H), 7.50 (m, 6H), 4.57 (s, 6H, CH_2). FAB$^+$: m/z 858 [La(tbpa)(ClO_4)$_2$]$^+$ {Calc. for [La(tbpa)(H_2O)(η^2-ClO_4)][ClO_4]$_2$·0.5Et_2O, $C_{35}H_{32}N_7Cl_3O_{12.5}La$: C, 42.21; H, 3.24; N, 9.85. Found: C, 42.55; H, 3.24; N, 10.07%}.

Colourless crystals of **2** suitable for X-ray analysis were obtained by leaving a concentrated solution of tbpa and La(ClO_4)$_3$·7H_2O (0.06 mmol) in MeOH (0.7 mL)–$CHCl_3$ (0.5 mL) standing overnight at room temperature.

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