

# Selective complexation of uranium(III) over cerium(III) by 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines: $^1\text{H}$ NMR and X-ray crystallography studies

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Addition of 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (btp) to  $\text{U}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$  in anhydrous pyridine gave the 1:3 complexes  $[\text{M}(\text{btp})_3]\text{I}_3$ , the terdentate nitrogen ligand being completely selective for  $\text{U}^{\text{III}}$  over  $\text{Ce}^{\text{III}}$ , as shown by  $^1\text{H}$  NMR competition experiments; crystal structures of analogous btp complexes of  $\text{U}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$  revealed that the U–N bond distances are significantly shorter than the corresponding Ce–N distances.

Much attention is currently paid to the separation of trivalent minor actinides (americium and curium) from trivalent lanthanides, which represents a challenging goal for the definition of new methods in the management of nuclear wastes.<sup>1</sup> A number of multidentate nitrogen extractants have been designed for the selective complexation of the actinides, and the recently discovered 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (btp) are the most effective so far.<sup>2</sup> The high separation factors have been attributed to the very weakly basic nature of these ligands which results in the formation of stronger actinide–nitrogen bonds with increased covalent character. However, no actinide complex with btp ligands has been isolated and characterized. We have studied the complexation of the triiodides  $\text{U}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$  with two btp molecules, Mebtp and  $\text{Pr}^{\text{n}}\text{btp}$  (Fig. 1) in anhydrous pyridine;  $\text{U}^{\text{III}}$  was used as an actinide analogue of the highly radiotoxic  $\text{Am}^{\text{III}}$  and  $\text{Cm}^{\text{III}}$ , and the similarly sized  $\text{Ce}^{\text{III}}$  was chosen as representative of the lanthanides. For the first time, btp complexes of 4f and 5f elements have been studied both in solution and in the solid state, and the remarkably better affinity of actinides(III) vs. lanthanides(III) for such multidentate ligands has been revealed by  $^1\text{H}$  NMR competition experiments and also by X-ray crystallography, with the direct comparison of the crystal structures of the analogous complexes  $[\text{M}(\text{Pr}^{\text{n}}\text{btp})_3]\text{I}_3$  ( $\text{M} = \text{U}, \text{Ce}$ ).

A  $2 \times 10^{-2}$  M solution of  $\text{U}^{\text{III}}$  in  $[\text{D}_5]\text{pyridine}$  was titrated with Mebtp in the presence of cyclohexane as internal standard. The  $^1\text{H}$  NMR spectra<sup>†</sup> showed that, whatever the number  $n$  of ligand equivalents, only the 1:3 complex  $[\text{U}^{\text{III}}(\text{Mebtp})_3]$  was formed in an immediate and quantitative manner. For  $n > 3$ , free Mebtp was observed in solution, without exchanging with coordinated ligands. The four resonances in the intensity ratio of 18:18:6:3 indicate that the three Mebtp ligands are equivalent in a  $D_3$  symmetrical arrangement. Complexation of  $\text{Ce}^{\text{III}}$  with Mebtp exhibited some differences since for  $n < 3$ , the 1:2 and

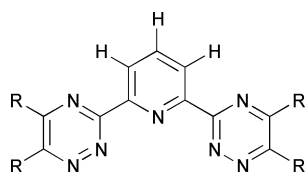
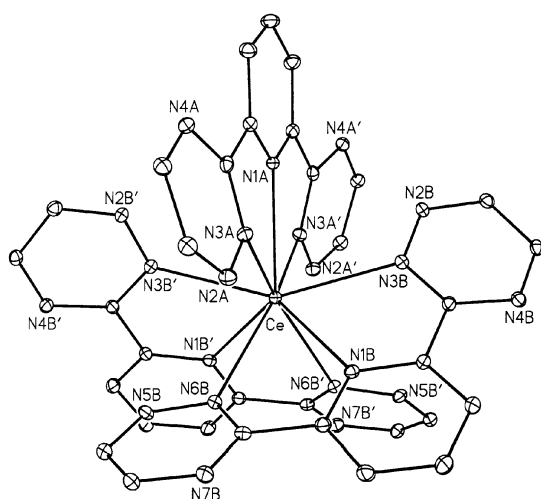


Fig. 1 The Rbtp ligands ( $\text{R} = \text{Me}$  and  $\text{Pr}^{\text{n}}$ ).

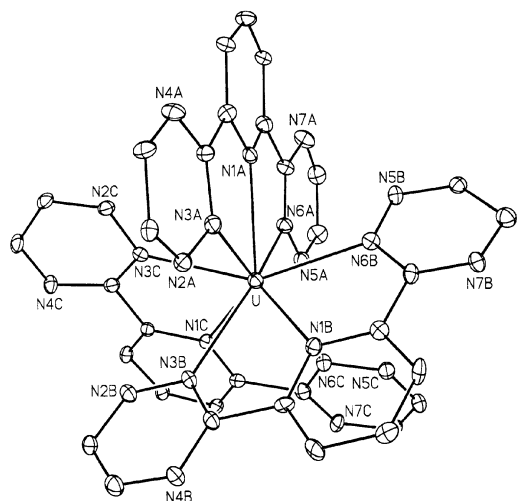
1:3 complexes  $\text{Ce}^{\text{III}}(\text{Mebtp})_2$  and  $\text{Ce}^{\text{III}}(\text{Mebtp})_3$  were formed together. This result is a first indication that  $\text{Ce}^{\text{III}}$  has a lesser affinity for Mebtp than  $\text{U}^{\text{III}}$ . However, the 1:3 complex was the major species for  $n > 2$  and the sole present in solution for  $n \geq 3$ . It is also interesting to note that addition of  $\text{Pr}^{\text{n}}\text{btp}$  to  $\text{Ln}(\text{NO}_3)_3$  in a 1:1 ratio in ethanol resulted in the crystallization of 1:3 complexes containing the  $[\text{Ln}(\text{Pr}^{\text{n}}\text{btp})_3]^{3+}$  cations ( $\text{Ln} = \text{Sm}, \text{Tm}$  and  $\text{Yb}$ ) with a variety of anions.<sup>3</sup> However, this work did not demonstrate, in contrast to the present study, that the 1:3 complexes were actually the dominant species in solution, while crystallization alone implies exceptional stability of the 1:3 complexes. The strong preference for the formation of the 1:3 complexes with respect to the 1:1 and 1:2 complexes is quite exceptional in coordination chemistry,<sup>4</sup> but some 1:3 complexes between lanthanide ions and terdentate nitrogen ligands have been reported.<sup>5</sup>

Even more striking was the competition reaction of  $\text{U}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$  with Mebtp. Only the 1:3 complex  $[\text{U}^{\text{III}}(\text{Mebtp})_3]$  was observed in pyridine solution on addition of 1–3 mol equivalents of Mebtp to 1 mol equivalent of both  $\text{U}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$ ; no cerium complex could be detected. The two  $\text{Ce}^{\text{III}}$  complexes  $\text{Ce}^{\text{III}}(\text{Mebtp})_2$  and  $\text{Ce}^{\text{III}}(\text{Mebtp})_3$  then appeared as more ligand was added (3–6 mol equivalents) and finally, only  $[\text{U}^{\text{III}}(\text{Mebtp})_3]$  and  $[\text{Ce}^{\text{III}}(\text{Mebtp})_3]$  were observed with an excess of ligand. Similar observations were made when Mebtp was replaced with  $\text{Pr}^{\text{n}}\text{btp}$ , and these results clearly demonstrate that these very efficient complexants are completely selective for uranium(III) over cerium(III). By considering that 5% of the cerium complex could be easily detected in solution by  $^1\text{H}$  NMR, the selectivity factor is certainly higher than 20. This value can be compared with those obtained for the actinide(III)–lanthanide(III) separation ( $\text{Am}^{\text{III}}/\text{Eu}^{\text{III}}$ ) with btp ligands from aqueous nitric acid solutions, which lie between 50 and 150 and are ten times greater than those observed with other terdentate nitrogen ligands such as 2,2':6',2''-terpyridine or 2,4,6-tri(2-pyridyl)-1,3,5-triazine.<sup>2</sup>

Single crystals of  $[\text{Ce}(\text{Mebtp})_3]\text{I}_3 \cdot 9\text{C}_5\text{H}_5\text{N}$  (red),  $[\text{Ce}(\text{Pr}^{\text{n}}\text{btp})_3]\text{I}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$  (orange) and  $[\text{U}(\text{Pr}^{\text{n}}\text{btp})_3]\text{I}_3 \cdot 4\text{C}_5\text{H}_5\text{N}$  (brown) were obtained by slow diffusion of pentane into pyridine solutions and their structures were determined.<sup>‡</sup> The crystals are composed of discrete  $[\text{M}(\text{btp})_3]^{3+}$  cations, iodide anions and pyridine molecules. The structures of the cations are very similar; those of  $[\text{Ce}(\text{Mebtp})_3]^{3+}$  and  $[\text{U}(\text{Pr}^{\text{n}}\text{btp})_3]^{3+}$  are shown in Figs. 2 and 3, respectively, together with selected data. The metal centres are nine coordinate in a slightly distorted tricapped trigonal prismatic configuration, each btp ligand being attached *via* the nitrogen atom of the pyridine fragment ( $\text{N}_p$  or  $\text{N}1$  in Figures) which occupies the capping position and the nitrogen atoms at the 2 position of the triazine rings ( $\text{N}_t$  or  $\text{N}3$  and  $\text{N}6$  in Figures). These structures are equivalent to those found in the lanthanide cations  $[\text{Ln}(\text{Pr}^{\text{n}}\text{btp})_3]^{3+}$  ( $\text{Ln} = \text{Sm}, \text{Tm}, \text{Yb}$ ).<sup>3</sup> Of special interest is the comparison of the metal–nitrogen bond distances in these cations. The Ce– $\text{N}_p$  distances



**Fig. 2** Crystal structure of the cation  $[\text{Ce}(\text{Mebtp})_3]^{3+}$ . Methyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ce–N1A 2.641(6), Ce–N1B 2.624(4), Ce–N3A 2.613(5), Ce–N3B 2.598(5), Ce–N6B 2.625(5); N1A–Ce–N1B 120.7(1), N1B–Ce–N1B' 118.7(2). Primed atoms are related to unlabelled atoms by the two-fold axis.



**Fig. 3** Crystal structure of the cation  $[\text{U}(\text{Pr}^{\text{nbtp}})_3]^{3+}$ . Propyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ); the corresponding values in the analogous cerium cation are given in square brackets: U–N1A 2.56(2) [2.63(2)], U–N1B 2.53(2) [2.65(2)], U–N1C 2.56(2) [2.65(2)], U–N3A 2.54(2) [2.57(2)], U–N6A 2.57(3) [2.64(2)], U–N3B 2.56(2) [2.66(2)], U–N6B 2.53(3) [2.61(2)], U–N3C 2.52(3) [2.54(2)], U–N6C 2.53(3) [2.59(2)]; N1A–U–N1B 122.1(8) [116.9(7)], N1A–U–N1C 118.6(8) [121.9(5)], N1B–U–N1C 119.4(8) [121.2(6)].

in  $[\text{Ce}(\text{Mebtp})_3]^{3+}$  are equal to 2.624(4) and 2.641(6) Å with an average value of 2.63(1) Å whereas the Ce–N<sub>t</sub> bond lengths range from 2.598(5) to 2.625(5) Å with a mean value of 2.61(2) Å. Very similar distances are found in  $[\text{Ce}(\text{Pr}^{\text{nbtp}})_3]^{3+}$  [ $\langle \text{Ce}–\text{N}_p \rangle = 2.64(1)$  Å and  $\langle \text{Ce}–\text{N}_t \rangle = 2.60(4)$  Å], indicating that the different alkyl groups at the 5 and 6 positions of the triazine moiety have no significant effect on the metal coordination sphere. These average Ce–N<sub>p</sub> and Ce–N<sub>t</sub> distances appear longer than the corresponding distances in the other  $[\text{Ln}(\text{Pr}^{\text{nbtp}})_3]^{3+}$  cations: 2.57(3) and 2.57(3) Å (Sm), 2.49(2) and 2.50(2) Å (Tm), 2.46(2) and 2.48(2) Å (Yb); this order is in agreement with the variation of the ionic radii of the metals.<sup>6</sup> In the cation  $[\text{U}(\text{Pr}^{\text{nbtp}})_3]^{3+}$ , the U–N<sub>p</sub> bond lengths vary from 2.53(2) to 2.56(2) Å and the U–N<sub>t</sub> distances range from 2.52(3) to 2.57(3) Å. These metal–nitrogen distances are shorter than those found in the cerium analogue, by 0.09 and 0.06 Å, if the average values are considered, while U<sup>III</sup> and Ce<sup>III</sup> have similar ionic radii.<sup>6</sup> Such a difference, which has never been observed

in other pairs of analogous uranium and lanthanide complexes with neutral N-donor ligands,<sup>4,7</sup> could reflect some uranium to nitrogen  $\pi$ -back bonding<sup>8</sup> and some degree of covalency in the U–N bond. The distinctive structural features of the  $[\text{U}(\text{Pr}^{\text{nbtp}})_3]^{3+}$  cation, in comparison with its Ce<sup>III</sup> counterpart, should be related to the outstanding capacity of btp molecules to coordinate trivalent actinides in preference to trivalent lanthanides, and can be attributed to the much softer character of the N atoms in this weakly basic ligand.

## Notes and references

<sup>†</sup>  $^1\text{H}$  NMR spectra (200 MHz, 30  $^\circ\text{C}$  in  $[\text{D}_5]_2\text{pyridine}$ ):  $[\text{Ce}(\text{Mebtp})_2]\text{I}_3$ ,  $\delta$  0.42 (6 H, s, Me), 1.33 (6 H, s, Me), 11.36 (1 H, t, 4-py), 12.06 (2 H, d, 3,5-py);  $[\text{Ce}(\text{Mebtp})_3]\text{I}_3$ ,  $\delta$  –0.41 (6 H, s, Me), 0.55 (6 H, s, Me), 11.91 (1 H, t, 4-py), 12.28 (2 H, d, 3,5-py);  $[\text{U}(\text{Mebtp})_3]\text{I}_3$ ,  $\delta$  –18.04 (6 H, s, Me), 4.59 (6 H, s, Me), 5.64 (1 H, t, 4-py), 33.95 (2 H, d, 3,5-py). The coupling constants are equal to 6–8 Hz; 4-py and 3,5-py denote the H atoms at the 4 and 3,5 positions of the pyridine ring, respectively.

<sup>‡</sup> Crystal data for  $[\text{Ce}(\text{Mebtp})_3]\text{I}_3 \cdot 9\text{C}_5\text{H}_5\text{N}$ :  $\text{C}_{90}\text{H}_{90}\text{I}_3\text{N}_{30}\text{Ce}$ ,  $M = 2112.74$ , monoclinic, space group  $P2_1/n$ ,  $a = 14.078(3)$ ,  $b = 13.889(3)$ ,  $c = 24.741(5)$  Å,  $\beta = 101.94(3)^\circ$ ,  $V = 4732.9(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.483$  g cm<sup>–3</sup>,  $\mu = 1.520$  mm<sup>–1</sup>,  $F(000) = 2114$ ,  $R_1 = 0.052$ ,  $wR_2 = 0.117$ ,  $S = 1.026$  for 7635 observed reflections with  $I > 2\sigma(I)$  ( $R_{\text{int}} = 0.075$ ) and 508 parameters.

For  $[\text{Ce}(\text{Pr}^{\text{nbtp}})_3]\text{I}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ :  $\text{C}_{84}\text{H}_{108}\text{I}_3\text{N}_{24}\text{Ce}$ ,  $M = 1974.76$ , monoclinic, space group  $Pc$ ,  $a = 13.576(2)$ ,  $b = 19.695(2)$ ,  $c = 16.643(2)$  Å,  $\beta = 95.095(4)^\circ$ ,  $V = 4432.4(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.480$  g cm<sup>–3</sup>,  $\mu = 1.615$  mm<sup>–1</sup>,  $F(000) = 1994$ ,  $R_1 = 0.093$ ,  $wR_2 = 0.158$ ,  $S = 0.956$  for 12500 observed reflections with  $I > 2\sigma(I)$  ( $R_{\text{int}} = 0.117$ ) and 974 parameters. The structure was refined as corresponding to a racemic twin with  $x = 0.25(4)$ .

For  $[\text{U}(\text{Pr}^{\text{nbtp}})_3]\text{I}_3 \cdot 4\text{C}_5\text{H}_5\text{N}$ :  $\text{C}_{89}\text{H}_{113}\text{I}_3\text{N}_{25}\text{U}$ ,  $M = 2151.77$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.431(1)$ ,  $b = 16.509(1)$ ,  $c = 21.140(2)$  Å,  $\alpha = 80.601(4)$ ,  $\beta = 88.755(4)$ ,  $\gamma = 83.588(5)^\circ$ ,  $V = 4595.4(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.555$  g cm<sup>–3</sup>,  $\mu = 2.832$  mm<sup>–1</sup>,  $F(000) = 2146$ ,  $R_1 = 0.084$ ,  $wR_2 = 0.174$ ,  $S = 0.990$  for 15377 observed reflections with  $I > 2\sigma(I)$  ( $R_{\text{int}} = 0.093$ ) and 1011 parameters.

The data were collected at 123 K on a Nonius Kappa-CCD area detector diffractometer using graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods. Absorption effects were empirically corrected, except in  $[\text{Ce}(\text{Mebtp})_3]\text{I}_3 \cdot 9\text{C}_5\text{H}_5\text{N}$ , with the program DELABS from PLATON.<sup>9</sup> Some pyridine molecules in all three compounds were found to be disordered as well as the propyl groups and two iodide ions in  $[\text{U}(\text{Pr}^{\text{nbtp}})_3]\text{I}_3 \cdot 4\text{C}_5\text{H}_5\text{N}$ . Hydrogen atoms were included at calculated positions as riding atoms, except those of the disordered fragments or molecules. All non-hydrogen atoms were refined anisotropically, except those of the disordered fragments and some pyridine molecules. The structures were refined by full-matrix least-squares on  $F^2$  with SHELXTL.<sup>10</sup>

CCDC reference numbers 161597–161599. See <http://www.rsc.org/suppdata/cc/b1/b103606h/> for crystallographic data in CIF or other electronic format.

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