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A comparison of analogous 4f- and 5f-element compounds: syntheses and crystal structures of triphenylphosphine oxide complexes of lanthanide(III) and uranium(III) triflates and iodides $[MX_2(OPPh_3)_4][X]$ (X = OTf and M = Ce or U; X = I and M = Nd, Ce, La, U)

Jean-Claude Berthet *, Martine Nierlich, Michel Ephritikhine *

Service de Chimie Moléculaire, DSM/DRECAM, Laboratoire Claude Fréjacques, CNRS URA 331, CEA Saclay, Gif-sur-Yvette Cedex 91191, France

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Abstract

The X-ray crystal structures of the title complexes show that the differences between the U–O and Ln–O distances reflect the variation in the ionic radii of the trivalent uranium and lanthanide ions while the U–I bond lengths are smaller than those predicted from a purely ionic bonding model. The results indicate that the uranium ion interacts more strongly than the lanthanide ions with the softer iodide ligand, and that the counterions would have a major influence on the differentiation of trivalent 4f and 5f ions.

Keywords: Uranium; Lanthanides; Triphenylphosphine oxide; Iodide; Triflate; X-ray crystal structure

1. Introduction

Phosphine oxides are ubiquitous ligands in f-element chemistry, due to their facile coordination to the oxophilic and Lewis acidic lanthanide (Ln) and actinide (An) ions [1]. The R_3PO molecules are able to stabilize a variety of inorganic and organometallic compounds in low or high oxidation states, and have found useful applications in catalysis and liquid–liquid extraction processes. The great majority of compounds which have been crystallographically characterized involve hexamethylphosphoramide (hmpa) or triphenylphosphine oxide (Ph_3PO). A number of hmpa-coordinated complexes of rare earth(II) or (III) halides and Ln(III) triflates have been isolated in order to obtain informations on their structure–reactivity relationship and to understand the strong effect of hmpa on their catalytic properties [2–7]. Phosphine oxides and their derivatives have been widely used in the first steps of the management of the nuclear fuels but subsequent separation of the trivalent lanthanide and actinide ions with oxygen ligands was precluded because of the equally strong oxophilicity of 4f and 5f metals. Though these trivalent ions have very similar chemical properties, the slightly less hard character of the An^{3+} versus Ln^{3+} ions is the chemical feature which makes the Ln(III)/An(III) hydrothermal separation conceivable. The stronger interaction of actinides with heteroatoms softer than oxygen has led to the design of new nitrogen and sulfur polydentate ligands which display better affinity and selectivity toward trivalent actinides [8–10]. However, it has been recently reported that the affinity and selectivity of tri-*n*-octyl phosphine oxide for the Am(III) and Eu(III) ions could be strongly modified by changing the nature of the anionic extraction media [11]. In this context, it seemed to us interesting to compare the structural parameters of analogous phosphine oxide complexes of trivalent uranium and lanthanide ions associated with counterions which have distinct hardness in the Pearson's HSAB

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* Corresponding authors. Fax: +1-6908-6640.

E-mail addresses: berthet@drecam.cea.fr (J.-C. Berthet), nierlich@drecam.cea.fr (M. Nierlich), ephri@drecam.cea.fr (M. Ephritikhine).

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classification, with the aim of evaluating and possibly differentiating the nature of the bonds in these 4f- and 5f-element compounds. Here we present the synthesis and crystal structures of triphenylphosphine oxide complexes of uranium(III) and lanthanides(III) with triflate or iodide counterions, $[MX_2(OPPh_3)_4][X]$ ($X=OTf$ and $M=Ce$ or U [12]; $X=I$ and $M=Nd$, Ce, La, U); the results reveal that the Ln(III)/An(III) discrimination is much influenced by the nature of the X counterion.

2. Results and discussion

2.1. Synthesis of the complexes

The triflate compounds $[M(OTf)_2(OPPh_3)_4][OTf]$ ($M=Ce$, U) have been prepared by reaction of 4 equiv. of Ph_3PO with $Ce(OTf)_3$ in pyridine or $U(OTf)_3$ in dimethoxyethane. After 2 h at 20 °C and upon addition of diethyl ether, the products were isolated as a white (Ce) or red (U) powder in 79% and 85% yield, respectively. Similar treatment of CeI_3 or UI_3 with Ph_3PO in pyridine readily afforded the pale orange (Ce) or violet (U) powder of $[MI_2(OPPh_3)_4][I]$ in 84% and 65% yield, respectively. The $[MX_2(OPPh_3)_4][X]$ ($M=Ce$, U; $X=OTf$, I) have been characterized by their elemental analyses. Single crystals of $[Ce(OTf)_2(OPPh_3)_4][OTf]$ and $[MI_2(OPPh_3)_4][I]$ ($M=Nd$, Ce, La, U), suitable for X-ray diffraction studies, were obtained by slow diffusion of diethyl ether into a pyridine solution containing $Ce(OTf)_3$ or MI_3 and an excess of Ph_3PO. The crystal structure of $[U(OTf)_2(OPPh_3)_4][OTf]$, described in our preliminary report [12], can thus be compared with that of the cerium analogue and also with those of the Sc, Lu and Nd counterparts, which have been recently synthesized from the corresponding metal triflates and Ph_3PO in ethanol [13].

2.2. Crystal structures of the triflate complexes

In the series of the triflate complexes $[M(OTf)_2(OPPh_3)_4][OTf]$, the cerium and uranium derivatives are isomorphous with the recently reported scandium, lutetium and neodymium analogues [13]. Crystals of these compounds are composed of discrete cation and anion pairs, and it has been already found that the smaller Sc(III) and Lu(III) ions are six coordinate, with two monodentate triflate ligands, while the larger Nd(III) ion is seven coordinate, with one monodentate and one bidentate OTf groups. Not surprisingly, the Ce and U complexes are isostructural with the Nd counterpart; a view of the cerium cation is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The crystal structures of these $OPPh_3$ complexes resemble those of the hmpa derivatives $[Ln(OTf)_2(hmpa)_4][OTf]$ [3,4]. In these latter, the triflate ligands adopt a monodentate coordination for all the lanthanides except lanthanum for which the triflate groups are mono- and

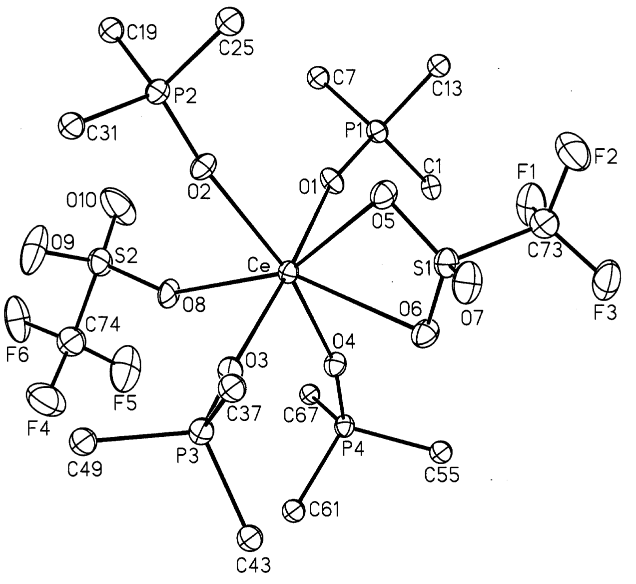

Fig. 1. View of the cation $[Ce(OTf)_2(OPPh_3)_4]^+$ with thermal ellipsoid drawn at the 20% probability level. For clarity, only the *ipso* carbon atoms of the phenyl rings are represented.

Table 1
Selected bond distances (Å) and angles (°) in the $[M(OTf)_2(OPPh_3)_4]^+$ cations

	$[U(OTf)_2(OPPh_3)_4]^{+a}$	$[Ce(OTf)_2(OPPh_3)_4]^+$
Bond distances		
M–O(1)	2.370 (4)	2.365 (5)
M–O(2)	2.352 (4)	2.362 (5)
M–O(3)	2.389 (4)	2.337 (5)
M–O(4)	2.348 (4)	2.352 (5)
⟨M–O(OPPh3)⟩	2.36 (2)	2.35 (2)
M–O(5)	2.645 (5)	2.581 (5)
M–O(6)	2.614 (4)	2.650 (5)
M–O(8)	2.446 (4)	2.444 (5)
P(1)–O(1)	1.502 (4)	1.511 (5)
P(2)–O(2)	1.518 (4)	1.509 (5)
P(3)–O(3)	1.516 (4)	1.507 (5)
P(4)–O(4)	1.520 (4)	1.503 (5)
Bond angles		
M–O(1)–P(1)	173.3 (3)	165.5 (3)
M–O(2)–P(2)	156.2 (3)	170.9 (3)
M–O(3)–P(3)	164.4 (2)	167.5 (3)
M–O(4)–P(4)	151.4 (2)	166.6 (3)
O(1)–M–O(2)	90.30 (15)	88.47 (18)
O(2)–M–O(3)	92.56 (15)	90.03 (18)
O(3)–M–O(4)	87.32 (15)	95.01 (18)
O(1)–M–O(4)	85.60 (15)	84.95 (18)
O(1)–M–O(5)	108.4 (2)	86.52 (17)
O(2)–M–O(5)	72.88 (13)	74.91 (17)
O(2)–M–O(8)	77.95 (14)	79.79 (18)
O(4)–M–O(8)	83.12 (14)	81.64 (17)
O(4)–M–O(6)	72.45 (13)	75.13 (16)

[a] From the preliminary report [12], the oxygen atoms O(3) and O(4) of the uranium complex have been inverted in order to ensure comparison with the cerium analogue.

bidentate. The difference in the coordination numbers of the corresponding $[Ln(OTf)_2(OPPh_3)_4]^+$ and $[Ln(OTf)_2(hmpa)_4]^+$ complexes (Ln = Nd, Ce) is likely due to the greater steric hindrance of hmpa versus Ph_3PO (cone angles: $Ph_3PO = 145°$, $(Me_2N)_3PO = 157°$ [14]). The average Ln–O($OPPh_3$) distances in the seven coordinate complexes are 0.3 Å longer than the average Ln–O(hmpa) distances in the six coordinate compounds [15]. The mean U–O($OPPh_3$) distance of 2.36(2) Å can be compared with the U–O distances found in the other few trivalent uranium complexes with phosphine oxide ligands which have been crystallographically characterized: 2.36(2) Å in $[UI_2\{H_2B(3^tBu,5Me\text{-pyrazolyl})_2\}(OPPh_3)_2]$ [16], 2.389 (6) Å in $[U(C_5H_4Me)_3(OPPh_3)]$ [17], 2.41(4) Å in $[U(COT)(hmpa)_3][BPh_4]$ [18] and 2.461(8) Å in [U(COT) (Cp*)(hmpa)] (COT = η-C_8H_8, Cp* = η-C_5Me_5) [19].

A plot of the average M–O($OPPh_3$) distances versus the ionic radii $r(M^{3+})$ of the six coordinate Sc^{3+} and Lu^{3+} and the seven coordinate Nd^{3+}, Ce^{3+} and U^{3+} ions (Fig. 2) shows a quite perfect linear variation, from 2.07 (2) (Sc) to 2.36(2) Å (U). The mean M–O(η^1-OTf) and M–O(η^2-OTf) distances similarly increase with $r(M^{3+})$, from 2.12(1) (Sc) to 2.446(4) Å (U) and from 2.59(4) (Nd) to 2.63(2) Å (U), respectively. Thus, the corresponding M–O($OPPh_3$) and M–O(OTf) bond lengths in the triflate compounds $[M(OTf)_2(OPPh_3)_4][OTf]$ (M = Ln, U) do not reveal any difference in the nature of the 4f and 5f metal–ligand bonds.

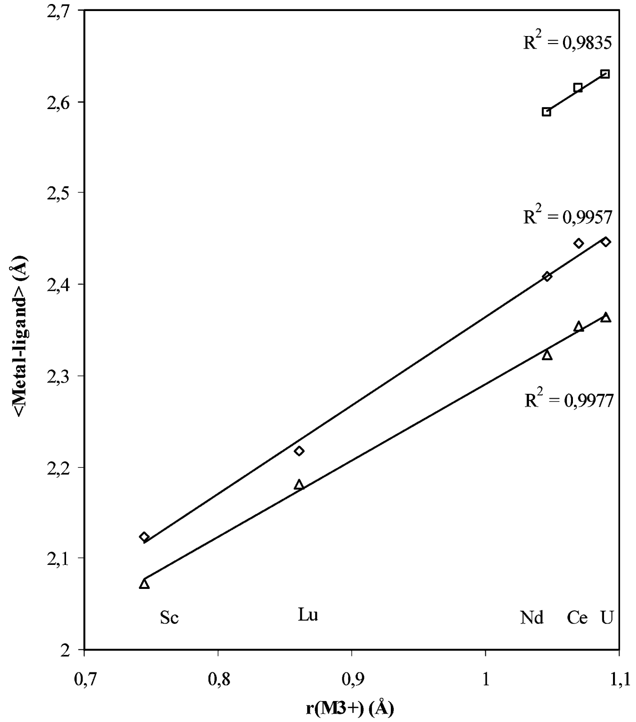

Fig. 2. M–O($OPPh_3$) (△), M–O(η^1-OTf) (◇) and M–O(η^2-OTf) (□) distances as a function of the metal ionic radii in the $[M(OTf)_2(OPPh_3)_4]^+$ cations.

2.3. Crystal structures of the iodide complexes

Crystals of the isostructural iodide complexes $[MI_2(OPPh_3)_4][I]$ (M = Nd, Ce, La, U) are also composed of discrete cation and anion pairs; a view of the uranium cation is shown in Fig. 3 and selected bond distances and angles are listed in Table 2. The geometry around the metal is distorted octahedral with the two iodide ligands in *trans* positions; the structure of the complexes closely resembles that of the hmpa derivatives $[LnI_2(hmpa)_4][I]$ (Ln = Sm [7], Tm [6]). As it was observed with the triflate compounds, the average M–O($OPPh_3$) distances in the iodide series increase linearly with $r(M^{3+})$ (Fig. 4). It is interesting to note that the mean M–O($OPPh_3$) distances of 2.31(3), 2.34(3) and 2.37(2) Å for M = Nd, Ce and U in the six coordinate iodide complexes are quite identical to those of 2.32(2), 2.34(2) and 2.36(2) Å in the seven coordinate triflate counterparts. That these bond lengths do not increase with the increasing coordination number of the M^{3+} ion can be explained by the more Lewis acidic character of the triflate complexes which induces a stronger interaction with the Ph_3PO Lewis base. The distinct steric and electronic effects of the OTf and Br or I ligands have already been noted in the complexes $[SmX_2(hmpa)_4][X]$ (X = Br, I, OTf) where the mean Sm–O(hmpa) distances in the halides are 0.02 Å longer than those in the triflates

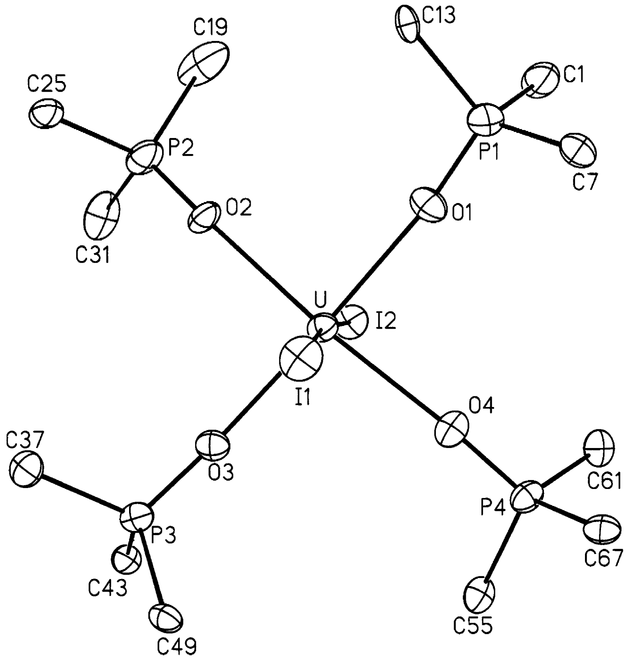

Fig. 3. View of the cation $[UI_2(OPPh_3)_4]^+$ with thermal ellipsoid drawn at the 20% probability level. For clarity, only the *ipso* carbon atoms of the phenyl rings are represented.

Table 2
Selected bond distances (Å) and angles (°) in the $[MI_2(OPPh_3)_4]^+$ cations

	$[LaI_2(OPPh_3)_4]^+$	$[UI_2(OPPh_3)_4]^+$	$[CeI_2(OPPh_3)_4]^+$	$[NdI_2(OPPh_3)_4]^+$
Bond distances				
M–O(1)	2.391 (6)	2.352 (5)	2.366 (3)	2.328 (5)
M–O(2)	2.393 (5)	2.382 (4)	2.368 (3)	2.342 (4)
M–O(3)	2.340 (6)	2.361 (5)	2.325 (3)	2.297 (4)
M–O(4)	2.343 (5)	2.370 (4)	2.318 (4)	2.289 (4)
M–I(1)	3.233 (1)	3.157 (1)	3.206 (1)	3.173 (1)
M–I(2)	3.169 (1)	3.146 (1)	3.145 (1)	3.110 (1)
⟨M–O⟩	2.37 (3)	2.37 (2)	2.34 (3)	2.31 (3)
⟨M–I⟩	3.20 (3)	3.151 (7)	3.17 (3)	3.14 (4)
P(1)–O(1)	1.508 (6)	1.493 (6)	1.503 (3)	1.507 (5)
P(2)–O(2)	1.511 (6)	1.495 (5)	1.508 (4)	1.499 (5)
P(3)–O(3)	1.524 (6)	1.507 (6)	1.511 (4)	1.506 (5)
P(4)–O(4)	1.515 (6)	1.504 (4)	1.515 (4)	1.515 (4)
Bond angles				
I(1)–M–I(2)	174.93 (3)	173.41 (1)	175.39 (1)	175.96 (2)
M–O(1)–P(1)	177.0 (4)	166.6 (4)	176.7 (2)	176.5 (3)
M–O(2)–P(2)	172.4 (4)	159.5 (3)	171.9 (2)	171.3 (3)
M–O(3)–P(3)	171.8 (4)	169.7 (3)	171.8 (2)	172.0 (3)
M–O(4)–P(4)	168.6 (4)	169.6 (3)	168.5 (2)	169.3 (3)
O(1)–M–O(2)	89.4 (2)	89.3 (2)	89.7 (1)	90.0 (2)
O(2)–M–O(3)	90.6 (2)	89.4 (2)	90.4 (1)	90.6 (2)
O(3)–M–O(4)	88.1 (2)	94.8 (2)	88.2 (1)	88.3 (2)
O(4)–M–O(1)	92.3 (2)	87.3 (2)	92.0 (1)	91.5 (2)
I(1)–M–O(1)	83.0 (2)	89.7 (2)	83.11 (9)	83.3 (1)
I(1)–M–O(2)	92.3 (2)	99.1 (1)	92.35 (9)	92.3 (1)
I(1)–M–O(3)	87.7 (2)	84.4 (1)	87.98 (9)	88.1 (1)
I(1)–M–O(4)	90.2 (2)	88.6 (1)	90.14 (9)	90.6 (1)

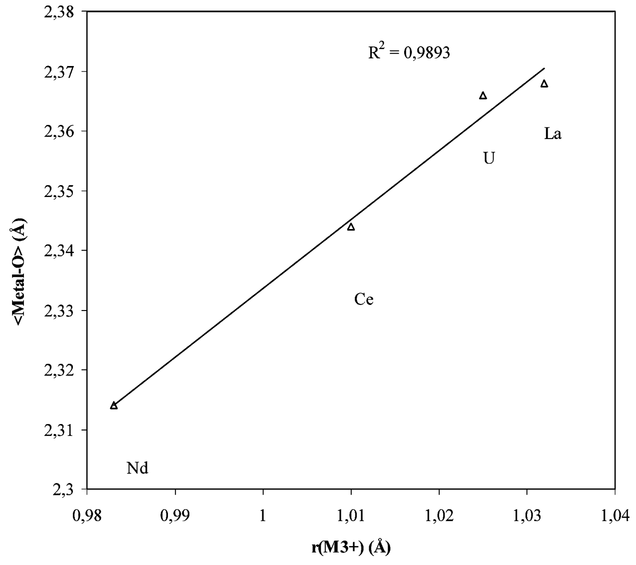

Fig. 4. M–O($OPPh_3$) distances as a function of the ionic metal radii in the $[MI_2(OPPh_3)_4]^+$ cations.

[5]. These observations further confirm that the nature of the counterions has a marked influence on the metal–ligand interactions. However, in both the triflate and iodide compounds, the mean O–P bond lengths are quite identical with a value of 1.51(1) Å, i.e. 0.03 Å longer than in the free ligand. The average Ln–O–P angles are equal to 168(2)° and 172(3)° in the triflate and iodide derivatives, respectively, while the U–O–P angles are more variable with average values of 161(10)° and 166(5)°. These angles are similar to those found in $[UI_2\{H_2B(3^tBu,5Me\text{-pyrazolyl})_2\}(OPPh_3)_2]$ (159.8(10)° and 168.7(9)°) [16] and $[U(C_5H_4Me)_3(OPPh_3)]$ (162.8° (4)) [17]. The tightening of the U–O–P angles with respect to the Ln–O–P angles, if significant, would indicate that the U–O($OPPh_3$) bond has a little less ionic character than the Ln–O($OPPh_3$) bond [20].

The M–I distances vary from 3.110(1) Å (M = Nd) to 3.233(1) Å (M = La) and are similar to those found in other trivalent lanthanide and uranium iodide compounds [6,7,9]. However, the variation of the average M–I distances was found to be different from that of the M–O distances, as shown in Fig. 5. While the usual linear relationship between the Ln–I distances and $r(Ln^{3+})$ is respected, the U–I bond lengths are shorter than those expected from a purely ionic bonding model, by 0.04 Å. This difference seems significant and can be considered with confidence as it is measured from the series of isostructural complexes $[MI_2(OPPh_3)_4][I]$; the shortening of the U–I bonds is larger than the difference due to the variation of $r(Ln^{3+})$, which is well reflected in the variation of the Ln–I distances. It is also noteworthy that the two U–I distances are equal whereas one Ln–I bond length in all the $[LnI_2(OPPh_3)_4][I]$ complexes is ca. 0.07 Å longer than the other, suggesting that a second iodide ligand could be easily dissociated from the lan-

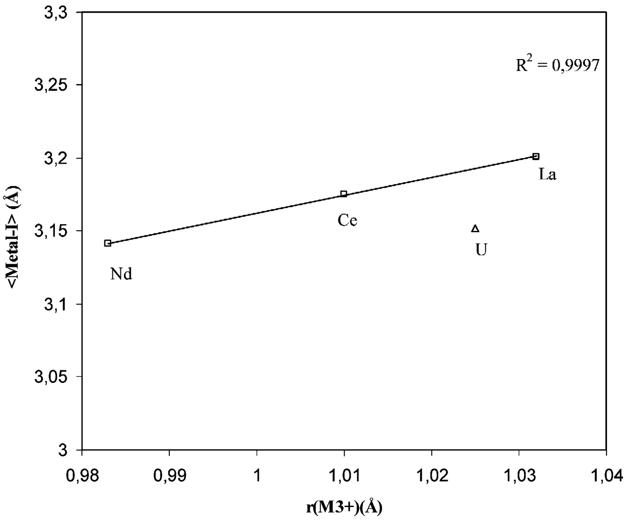

Fig. 5. M–I distances as a function of the ionic metal radii in the $[MI_2(OPPh_3)_4]^+$ cations.

thanide triiodide upon complexation of Ph_3PO. Such a dissociation was observed in the crystallization of $[TmI_3(hmpa)_4]$ from pyridine which afforded crystals of $[TmI_2(hmpa)_4][I] \cdot 5$pyridine and $[TmI(hmpa)_4(py)][I]_2$; however, in the monocationic thulium diodide, the two Tm–I distances are identical by imposed symmetry [6].

The shortening of the U–I distances with respect to the Ln–I distances in the triphenylphosphine oxide complexes $[MI_2(OPPh_3)_4][I]$, while the mean U–O distance corresponds to that expected from a purely ionic bonding model, can be accounted for by the softer (less hard) character of the 5f versus 4f trivalent ions, leading to the creation of a stronger interaction between uranium and soft ligands. We can observe a similar trend, although not so pronounced, in other analogous iodide complexes of uranium(III) and lanthanides(III). In the complexes $[MI_3(THF)_4]$ (M = Ce [21], U [22], La [23]), the mean M–I distances are 3.14(4), 3.13(4) and 3.15(4) Å, respectively. In the isostructural eight coordinate complexes $[MI_3(bipy)_2(py)]$ (M = Ce, U) [9a], the M–I distances are identical (3.22(3) Å) though the ionic radius of uranium(III) is ca. 0.01 Å larger than that of cerium(III), and in the compounds $[MI_3(tpza)L]$ (M = U, La; tpza = tris[(2-pyrazinyl)methyl]amine; L = Me CN, THF), the U–I distances are shorter than the La–I bond lengths with L = THF while the reverse trend is observed with L = MeCN [24].

The better affinity of neutral nitrogen, phosphorus and sulfur ligands for U^{3+} than for Ln^{3+} ions has been similarly assessed from the crystal structures of analogous complexes, by measuring the deviation between the differences [⟨U–X⟩–⟨Ln–X⟩] and $[r(U^{3+}) - r(Ln^{3+})]$ (X = N, P, S); the greatest deviations of 0.1 Å were observed in the compounds $[M(\eta\text{-}C_5H_4Me)_3L]$ [M = Ce or U; L = PMe_3 or $P(OCH_2)_3CEt$] [25] and $[M(btp)_3][I]_3$[M = Ce or U; btp = 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine] [9c]. The crystal structures of the two monocyclooctatetraenyl complexes $[U(COT)(hmpa)_3][BPh_4]$ and $[U(COT)(Cp^*)(hmpa)]$ have also been compared with those of the neodymium(III) analogues. The differences between the average distances ⟨U–X⟩–⟨Nd–X⟩ (X = C, O) in the cations $[M(COT)(hmpa)_3]^+$ (M = Nd or U) simply reflect the +0.04 Å difference between the ionic radii of the trivalent uranium and neodymium ions [18], while the ⟨U–X⟩ bond lengths and especially the ⟨U–C(Cp*)⟩ distance in $[U(COT)(Cp^*)(hmpa)]$ are shorter than expected from a purely ionic model [19]. Thus, after the organometallic complexes $[M(COT)(Cp^*)(hmpa)]$ (M = Nd or U), the series of $[MI_2(OPPh_3)_4][I]$ compounds provide another example of crystal structures in which the more covalent character of the uranium–ligand bond is observed with an anionic ligand, and not with a neutral Lewis base. These results show that counterions can play a major role in the discrimination between Ln(III) and An(III) complexes. This can be of importance in the management of the nuclear wastes, especially in the selective extraction of trivalent actinides from lanthanides. The nature of the counterions X^-, which induce a synergistic effect on the extraction, will have an influence not only on the coordination of neutral extractant molecules L onto the $[MX_{3-n}]^{n+}$ species (n = 1–3), but also on the binding of X^- to the $[ML_x]^{3+}$ complexes. In this context, it has been recently found that in the extraction of Am(III) and Eu(III) from SCN^- and NO_3^- media with tri-*n*-octyl phosphine oxide, the selectivity in favour of Am(III) is much better in the thiocyanate than in the nitrate medium, in relation with the formation constants K of the extracted complexes, $\log K_{Am} - \log K_{Eu}$ being equal to 1.49 for $[M(SCN)_3\{OP(n\text{-}octyl)_3\}_4]$ and 0.23 for the corresponding nitrate complexes. This difference was attributed to the participation of the 5f orbitals of the actinide while binding to the “soft” donor N atom of the thiocyanate ion, leading to some covalency in the bond between Am(III) and SCN^- [11].

3. Conclusion

The synthesis of the triphenylphosphine oxide complexes $[MX_2(OPPh_3)_4][X]$ (X = OTf and M = Ce or U; X = I and M = Nd, Ce, La, U) permitted, with data previously reported in the literature, to compare the structural parameters of analogous lanthanide and uranium compounds. The variations in the distances between the metal and hard oxygen atoms, M–$O(OPPh_3)$ and M–O(OTf), correspond to the differences between the ionic radii of the trivalent M^{3+} ions. In contrast, the U–I bond lengths are 0.04 Å shorter than

Table 3
Crystallographic data of the complexes

	$[LaI_2(OPPh_3)_4][I]$	$[CeI_2(OPPh_3)_4][I]$	$[NdI_2(OPPh_3)_4][I]$	$[UI_2(OPPh_3)_4][I] \cdot 3$pyridine	$[Ce(OTf)_2(OPPh_3)_4][OTf]$	$[U(OTf)_2(OPPh_3)_4][OTf]$
Chemical formula	$C_{72}H_{60}I_3LaO_4P_4$	$C_{72}H_{60}CeI_3O_4P_4$	$C_{72}H_{60}I_3NdO_4P_4$	$C_{87}H_{75}I_3N_3O_4P_4U$	$C_{75}H_{60}F_9CeO_{13}P_4S_3$	$C_{75}H_{60}F_9O_{13}P_4S_3U$
M (g mol^{-1})	1632.69	1633.90	1638.02	1969.11	1700.41	1798.32
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.125 (3)	13.106 (3)	13.089 (3)	20.093 (4)	13.691 (3)	13.6940 (12)
b (Å)	14.056 (3)	14.022 (3)	14.016 (3)	19.723 (4)	15.031 (3)	14.7341 (12)
c (Å)	37.671 (8)	37.630 (8)	37.548 (8)	22.753 (5)	19.361 (4)	19.4198 (15)
α (°)	90.00	90.00	90.00	90.00	94.23 (3)	92.143 (4)
β (°)	95.63 (3)	95.74 (3)	95.88 (3)	115.94 (3)	109.16 (3)	108.393 (4)
γ (°)	90.00	90.00	90.00	90.00	93.73 (3)	91.460 (4)
V (Å^3)	6916 (2)	6881 (2)	6852 (2)	8109 (3)	3736.3 (13)	3713 (13)
Z	4	4	4	4	2	2
ρ_{calcd} (g cm^{-3})	1.568	1.577	1.588	1.613	1.511	1.609
μ (Mo Kα) (mm^{-1})	2.095	2.147	2.249	3.274	0.863	2.441
Crystal size (mm)	0.20 × 0.15 × 0.05	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.10	0.15 × 0.10 × 0.05	0.18 × 0.12 × 0.12
T_{min}/T_{max}	0.683,0.900	0.675,0.813	0.580, 0.800	0.680,0.708	0.900,0.962	0.606,0.617
F (000)	3200	3204	3212	3844	1722	1790
2θ range (°)	2, 24.73	2, 24.73	2, 24.73	2, 24.72	2, 24.70	2, 23.28
T (K)	123 (2)	123 (2)	123 (2)	123 (2)	123 (2)	123 (2)
Number of data collected	29 931	41 279	30 338	49 765	23 307	19 977
Number of unique data	10 678	11 277	10 663	12 770	11 756	10 109
Observed data $[I > 2\sigma(I)]$	5815	8664	7373	6859	8451	7023
R_{int}	0.146	0.038	0.068	0.121	0.082	0.076
Number of parameters	757	757	757	1064	576	946
R_1[a]	0.0578	0.0381	0.0476	0.0744	0.0679	0.0436
wR_2[b]	0.0963	0.0734	0.0878	0.1347	0.1643	0.0773
S	0.929	1.039	0.990	1.040	1.085	1.010
$\Delta\rho_{min}$ (e Å^{-3})	−0.858	−0.906	−0.747	−0.846	−0.730	−0.598
$\Delta\rho_{max}$ (e Å^{-3})	0.789	1.009	1.018	0.933	0.843	1.010

[a] $R_1 = \sum ||F_o| - |F_c|| / |F_o|$ (observed reflections).

[b] $wR_2 = \left[\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2\right]^{1/2}$ (observed reflections).

those expected from a purely ionic bonding model, reflecting a stronger interaction with a partially covalent character between the 5f ion and the soft iodide ligand. The results show the counterions to have a major influence in the differentiation of trivalent lanthanide and actinide ions.

4. Experimental

4.1. General

All experiments were carried out in argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Pyridine-d_5(Eurisotop) was dried over 3 Å molecular sieves and THF-d_8 was distilled over Na/K alloy. ^1H NMR spectra were recorded on a Bruker DPX200 spectrometer and were referenced internally using the residual protio solvent resonances relative to TMS (δ 0). Elemental analyses were carried out by Analytische Laboratorien at Lindlar (Germany). Ph_3PO, $Ce(OTf)_3$, LnI_3 (Ln = Nd, Ce, La) (Aldrich) were dried under vacuum and $[UI_3(pyridine)_4]$ was prepared as described in [22]; the synthesis and crystal structure of $[U(OTf)_2(OPPh_3)_4]$ [OTf] were described in our preliminary report [12].

4.2. Syntheses

4.2.1. $[Ce(OTf)_2(OPPh_3)_4][OTf]$

A flask was charged with Ph_3PO (106 mg, 0.34 mmol) and $Ce(OTf)_3$ (50 mg, 0.085 mmol) and pyridine (10 ml) was distilled into it. The reaction mixture was stirred for 12 h at 20 °C and after filtration, the volume of the light orange solution was reduced to 5 ml. The cream powder of the product which precipitated upon addition of a mixture of pentane and diethyl ether (10 ml each) was filtered off and dried under vacuum (115 mg, 79%).

^1H NMR (THF-d_8, 23 °C): 8.42 (br s, $w_{1/2} = 60$ Hz, *o*-Ph), 7.57 (br t, $J = 7$ Hz, *p*-Ph), 7.40 (br s, $w_{1/2} = 25$ Hz, *m*-Ph). *Anal.* Calc. For $C_{75}H_{60}F_9O_{13}P_4S_3Ce$: C, 52.97; H, 3.55; F, 10.05. Found: C, 52.69; H, 3.79; F, 9.92%.

4.2.2. $CeI_2(OPPh_3)_4][I]$

A flask was charged with Ph_3PO (106 mg, 0.38 mmol) and CeI_3 (50 mg, 0.096 mmol) and pyridine (10 ml) was distilled into it. The reaction mixture was stirred for 2 h at 20 °C and after filtration, the volume of the light orange solution was reduced to 5 ml. The white powder of the product which precipitated upon addition of diethyl ether (15 ml) was filtered off, washed with diethyl ether and dried under vacuum (132 mg, 84%).

^1H NMR (Pyridine-d_5, 23 °C): 7.68 and 7.52 (br s, $w_{1/2} = 35$ Hz). *Anal.* Calc. For $C_{72}H_{60}I_3O_4P_4Ce$: C, 52.92; H, 3.70; I, 23.30. Found: C, 52.69; H, 3.81; I, 23.58%.

4.2.3. $[UI_2(OPPh_3)_4][I]$

A flask was charged with Ph_3PO (89.5 mg, 0.32 mmol) and $[UI_3(pyridine)_4]$ (75 mg, 0.080 mmol) and pyridine (5 ml) was distilled into it. The reaction mixture was stirred for 1 h at 20 °C and after filtration, the dark violet solution was evaporated to dryness. The violet powder of the product was washed with a mixture of diethyl ether (10 ml) and THF (5 ml) and dried under vacuum (91 mg, 65%).

^1H NMR (Pyridine-d_5, 23 °C): 7.7 (br s, $w_{1/2} = 320$ Hz). *Anal.* Calc. For $C_{72}H_{60}I_3O_4P_4U$: C, 49.93; H, 3.49; I, 21.98. Found: C, 49.66; H, 3.58; I, 22.27%.

4.3. Crystallography

X-ray data collection, determination and refinement diffraction collection were carried out on a Nonius diffractometer equipped with a CCD detector. The data were recorded at 123 K. The lattice parameters were determined from all the reflections measured on 10 images recorded with 2° Φ-scans and later refined on all data. A 180° Φ range was scanned with 2° steps and 10 s ($[LaI_2(OPPh_3)_4][I]$, $[UI_2(OPPh_3)_4][I]$) or 8 s ($[CeI_2(OPPh_3)_4][I]$, $[NdI_2(OPPh_3)_4][I]$, $[Ce(OTf)_2(OPPh_3)_4]$ [OTf]) of exposure time per frame with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz polarization and absorption effects [26]. The structures were solved by the heavy-atom method and refined by full-matrix least-squares on F_2 with anisotropic thermal parameters for all non H atoms. H atoms were introduced at equal positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH) times that of the parent atom. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package [27]. Crystals data and details of data collections and structures refinements are given in Table 3.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 212639–212643. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) F.A. Hart, in: G. Wilkinson, R.D. Guillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 3, Pergamon, Oxford, 1987;
(b) T.S. Lobana, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorous Compounds, vol. 2, Wiley, New York, 1992.

[2] (a) Z. Hou, K. Kobayashi, H. Yamazaki, Chem. Lett. (1991) 265;
(b) Z. Hou, Y. Wakatsuki, J. Chem. Soc., Chem. Commun. (1994) 1205;
(c) S. Petriček, A. Demšar, L. Golič, J. Košmrlj, Polyhedron 19 (2000) 199.

[3] T. Imamoto, M. Nishiura, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, Chem. Lett. (1996) 875.

[4] M. Nishiura, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, T. Imamoto, Bull. Soc. Chim. Fr. 134 (1997) 411.

[5] K. Asakura, T. Imamoto, Bull. Chem. Soc. Jpn. 74 (2001) 731.

[6] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, Polyhedron 17 (1998) 3361.

[7] A. Cabrera, M. Salmón, N. Rosas, J. Pérez-Flores, L. Velasco, G. Espinosa-Mérez, J.L. Arias, Polyhedron 17 (1998) 193.

[8] (a) K.A. Gschneidner Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of Rare Earths. Lanthanides/Actinides: Chemistry, vol. 18, Elsevier Science, Amsterdam, 1994;
(b) Actinides and Fission Products Partitioning and Transmutation. Status and Assessment Report, NEA/OECD Report, NEA/OECD, Paris, 1999;
(c) Actinides and Fission Products Partitioning and Transmutation. Proceedings of the Fifth International Information Exchange Meeting, Mol, Belgium, 25–27 Nov. 1998, NEA/OECD Report, NEA/OECD, Paris, 1999;
(d) K.L. Nash, Solvent Extr. Ion Exch. 11 (1993) 729.

[9] (a) C. Rivière, M. Nierlich, M. Ephritikhine, C. Madic, Inorg. Chem. 40 (2001) 4428;
(b) J.C. Berthet, C. Rivière, Y. Miquel, M. Nierlich, C. Madic, M. Ephritikhine, Eur. J. Inorg. Chem. (2002) 1439;
(c) J.C. Berthet, Y. Miquel, P.B. Iveson, M. Nierlich, P. Thuéry, C. Madic, M. Ephritikhine, J. Chem. Soc., Dalton Trans. (2002) 3265.

[10] (a) W. Levason, E.H. Newman, M. Webster, Polyhedron 19 (2000) 2697;
(b) L. Deakin, W. Levason, M.C. Popham, G. Reid, M. Webster, J. Chem. Soc., Dalton Trans. (2000) 2439;
(c) M. Bosson, W. Levason, T. Patel, M.C. Popham, M. Webster, Polyhedron 20 (2001) 2055;
(d) N.J. Hill, W. Levason, M.C. Popham, G. Reid, M. Webster, Polyhedron 21 (2002) 445.

[11] G. Suresh, M.S. Murali, J.N. Mathur, Radichim. Acta 91 (2003) 127.

[12] Preliminary report: J.C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, Eur. J. Inorg. Chem. (1999) 2005.

[13] J. Fawcett, A.W.G. Platt, D.R. Russell, Polyhedron 21 (2002) 287.

[14] J. Marcalo, A. Pires de Matos, Polyhedron 8 (1989) 2431.

[15] T. Imamoto, personal communication.

[16] L. Maria, M.P. Campello, A. Domingos, I. Santos, R. Andersen, J. Chem. Soc., Dalton Trans. (1999) 2015.

[17] J.G. Brennan, R.A. Andersen, A. Zalkin, Inorg. Chem. 25 (1986) 1761.

[18] S.M. Cendrowski-Guillaume, M. Nierlich, M. Ephritikhine, Eur. J. Inorg. Chem. (2001) 1495.

[19] S.M. Cendrowski-Guillaume, G. Le Gland, M. Nierlich, M. Ephritikhine, Eur. J. Inorg. Chem. (2003) 1388.

[20] (a) P.L. Goggin, in: G. Wilkinson, R.D. Guillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987;
(b) G.B. Deacon, B.M. Gatehouse, P.A. White, Polyhedron 8 (1989) 1983.

[21] C. Rivière, J.C. Berthet, M. Nierlich, M. Ephritikhine, unpublished results.

[22] L.R. Avens, S.G. Bott, D.L. Clark, A.P. Sattelberger, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 2248.

[23] A.A. Trifonov, P. Van de Weghe, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 527 (1997) 225.

[24] M. Mazzanti, R. Wietzke, J. Pécault, J.-M. Latour, P. Maldivi, M. Remy, Inorg. Chem. 41 (2002) 2389.

[25] J.G. Brennan, S.D. Stults, R.A. Andersen, A. Zalkin, Organometallics 7 (1988) 1329.

[26] A.L Spek, PLATON, University of Utrecht, The Netherlands, 2000.

[27] G.M. Sheldrick, SHELXTL, University of Göttingen, Germany, distributed by Bruker-AXS, Madison, WI, 1999.