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Dissolution of Lanthanide and Actinide Metals Using Iodine and 2-Propanol. Synthesis and X-ray Crystal Structures of $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La, Ce) and $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$

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Reaction of lanthanum, cerium, or neodymium metals with $^3/_2$ equiv of iodine in 2-propanol leads to formation of the alcohol adducts $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La (**1**), Ce (**2**), Nd (**3**)) in good yield. Reaction of thorium metal turnings with 2 equiv of iodine in 2-propanol produces the dimeric halide−alkoxide complex $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**). The molecular structures of **1**, **2**, and **4** have been determined by means of single-crystal X-ray diffraction studies. **1** and **2** are found to be isostructural, and consist of seven-coordinate metal centers best described as capped trigonal prisms in which an iodide ligand caps a rectangular face defined by the four 2-propanol oxygen atoms. Ln−I bond lengths lie in the ranges 3.180(1)−3.224(1) for **1** and 3.157(1)−3.191(1) Å for **2**, while Ln−O distances to the 2-propanol ligands average 2.509(7) and 2.488(5) Å for **1** and **2**, respectively. **4** exhibits an edge-shared bioctahedral geometry with 2-propoxide ligands occupying bridging positions. Bridging Th−O distances in **4** are 2.327(6) and 2.399(6) Å, while the Th−O distance to the terminal 2-propoxide ligand is extremely short at 2.056(7) Å. The Th−O bond length to the 2-propanol ligand is characteristically long at 2.437(6) Å, while Th−I distances are 3.094(1) and 3.104(1) Å. Crystal data for **1** (at −70 °C): orthorhombic space group *Pbca*, $a = 17.240(3)$ Å, $b = 13.944(2)$ Å, $c = 19.178(2)$ Å, $V = 4610.3$ Å^3, $d_{calc} = 2.190$ g cm^{-3}, $Z = 8$, $R = 0.0439$, $R_w = 0.0739$. Crystal data for **2** (at −70 °C): orthorhombic space group *Pbca*, $a = 17.199(3)$ Å, $b = 13.884(3)$ Å, $c = 19.153(4)$ Å, $V = 4573.5$ Å^3, $d_{calc} = 2.211$ g cm^{-3}, $Z = 8$, $R = 0.0352$, $R_w = 0.0619$. Crystal data for **4** (at −48 °C): triclinic space group $P\bar{1}$, $a = 9.658(2)$ Å, $b = 9.754(2)$ Å, $c = 11.563(2)$ Å, $\alpha = 109.41(3)°$, $\beta = 95.18(3)°$, $\gamma = 117.33(3)°$, $V = 873.5$ Å^3, $d_{calc} = 2.521$ g cm^{-3}, $Z = 1$, $R = 0.0319$, $R_w = 0.0506$.

Introduction

The direct oxidation of reactive metals with alcohols (eq 1) offers a straightforward synthetic route to a number of metal alkoxide compounds.[2] It is not, however, a route that is

$$M + xROH \rightarrow M(OR)_x + (x/2)H_2 \qquad (1)$$

generally applicable to oxophilic metals, including many of the actinides and lanthanides where passivation of the metal surface may occur. In the case of the lanthanide metals, a number of methodologies have been employed to overcome the problem of surface passivation including the use of catalytic[3−5] or stoichiometric[6,7] quantities of mercuric salts, the electrolytic dissolution of the metals in alcohol solvents in the presence of a tetraalkylammonium halide,[8] and the use of reactive chelating alcohols such as 2-methoxyethanol.[8,9] The reaction of lanthanide metals with gaseous hydrogen chloride in alcohol solvent has been reported to lead to formation of the lanthanide trichloride rather than an alkoxide species.[10]

We recently reported the formation of the dimeric uranium iodo-alkoxide complex $U_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ by direct reaction of uranium metal with alcohol using iodine as the co-oxidant (eq 2).[11] This reaction thus represents a facile, single-step route

$$U + I_2 \xrightarrow{HO\text{-}i\text{-}Pr} {}^1/_2U_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2 \qquad (2)$$

from uranium metal directly into uranium alkoxide chemistry. Metathesis reactions of the halide ligands can now be envisioned to provide a general route to bimetallic or heterobimetallic actinide alkoxide complexes. Given the current high interest in the use of such heterometallic alkoxide complexes as precursors to molecular materials, we were interested in determining whether similar metal/iodine/alcohol reactions would provide a generally applicable single-step route into mixed halide−alkoxide complexes of other reactive actinide and lanthanide metals.

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Table 1. Summary of Crystallographic Data[a]

	1	**2**	**4**
empirical formula	$C_{12}H_{32}I_3LaO_4$	$C_{12}H_{32}CeI_3O_4$	$C_{18}H_{42}I_4O_6Th_2$
color; habit	colorless plate	pale yellow block	clear block
crystal dimens, mm	0.3 × 0.18 × 0.13	0.325 × 0.40 × 0.425	0.15 × 0.2 × 0.25
space group	*Pbca*	*Pbca*	$P\bar{1}$
a, Å	17.240(3)	17.199(3)	9.658(2)
b, Å	13.944(2)	13.884(3)	9.754(2)
c, Å	19.178(2)	19.153(4)	11.563(2)
α, deg			109.41(3)
β, deg			95.18(3)
γ, deg			117.33(3)
V, Å^3	4610.3	4573.5	873.5
Z (molecules/cell)	8	8	1
fw	760.0	761.2	1326.2
d_{calc}, g cm^{-3}	2.190	2.211	2.521
abs coeff, cm^{-1}	58.79	60.48	123.25
λ(Mo Kα)	0.710 73	0.710 73	0.710 73
temp, °C	−70	−70	−48
2θ range, deg	2.0−50.0	4.0−50.0	2.0−50.0
no. of measd reflns	5650	4491	5809
no. of unique intensities	4047	4024	2661
no. of obsd reflns	3447 ($F > 4.0\sigma(F)$)	3354 ($F > 4.0\sigma(F)$)	2467 ($F > 4.0\sigma(F)$)
$R(F)^b$	0.044	0.035	0.032
$R_w(F)^c$	0.074	0.062	0.051
goodness-of-fit	2.30	0.98	1.50

[a] **1** = $LaI_3(HO\text{-}i\text{-}Pr)_4$, **2** = $CeI_3(HO\text{-}i\text{-}Pr)_4$, **4** = $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Results and Discussion

Lanthanide metal powders (Ln = La, Nd) or turnings (Ln = Ce) were found to react smoothly with $^3/_2$ equiv of iodine in 2-propanol to yield the tetrakis(2-propanol) adducts of the corresponding lanthanide triiodide (eq 3) in moderate to good

$$\mathrm{Ln} + {}^3/_2\mathrm{I}_2 \xrightarrow{\mathrm{HO}\text{-}i\text{-}\mathrm{Pr}} \underset{\mathbf{1-3}}{\mathrm{LnI}_3(\mathrm{HO}\text{-}i\text{-}\mathrm{Pr})_4} \qquad (3)$$

$$\mathrm{Ln} = \mathrm{La}\ (\mathbf{1}),\ \mathrm{Ce}\ (\mathbf{2}),\ \mathrm{Nd}\ (\mathbf{3})$$

yields (La 86%, Ce 85%, Nd 58%). The presence of coordinated 2-propanol ligands in **1**−**3** is indicated spectroscopically by strong, broad IR absorptions in the 3200−3300 cm^{-1} region, broad −OH resonances in the ^{1}H NMR spectra, and also by the relatively acute Ln−O-C angles in the X-ray crystal structures of **1** and **2** (*vide infra*). The reaction proceeds equally well for both lanthanide metal powders and turnings, and the presence of oxide coatings on the metals does not appear to interfere significantly with either the rate or yield of the reaction. This behavior may be contrasted with that of uranium metal, where carefully cleaned[12] turnings have to be employed in order to optimize the yield of the reaction.[11] A cold water bath is used to moderate the temperature of the mildly exothermic reactions, and we have found that the reactions can be scaled-up to give synthetically useful quantities of products (20 g of $LnI_3(HO\text{-}i\text{-}Pr)_4$).

Thorium metal turnings are seen to be consumed within several hours when allowed to react with 2 equiv of iodine in 2-propanol solvent. Crystallization from toluene results in the isolation of $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**) in moderate yield (eq 4). Room-temperature ^{1}H NMR spectra of **4** in benzene-d_6 show

$$\mathrm{Th} + 2\mathrm{I}_2 \xrightarrow{\mathrm{HO}\text{-}i\text{-}\mathrm{Pr}} {}^1/_2\mathrm{Th}_2\mathrm{I}_4(\mathrm{O}\text{-}i\text{-}\mathrm{Pr})_4(\mathrm{HO}\text{-}i\text{-}\mathrm{Pr})_2 \qquad (4)$$

only one 2-propyl resonance, indicating that a rapid fluxional process is operating in solution. This process could involve rapid scrambling of the −OH protons over all alkoxide sites, rapid bridge−terminal alkoxide ligand exchange, or a combination of these two mechanisms. The fluxional behavior could not be frozen out at temperatures down to −80 °C. A similar fluxional process has been observed previously in the thorium alcoholate complex $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$.[13] It may be proposed that the product which initially crystallizes directly from the 2-propanol reaction medium (see Experimental Section) is $[ThI(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_4]I$, by analogy with the behavior previously observed for uranium,[11,14] but rapid loss of 2-propanol from this complex precluded its full characterization. However, dissolution of the initial reaction product in toluene followed by removal of all solvent *in vacuo* resulted in smooth conversion to the dimeric species $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**), as is observed in the analogous uranium system.[11]

Structural Studies. A summary of data collection and processing parameters for **1**, **2**, and **4** is given in Table 1.

$LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La (1), Ce (2)). The two 2-propanol adducts subjected to X-ray diffraction analysis, $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La (**1**), Ce (**2**)), are isostructural, and hence their solid-state structures are discussed concurrently. Crystals of compound **1** were grown by cooling a concentrated 2-propanol solution to −40 °C, while crystals of **2** were grown by slow evaporation of a 2-propanol solution in the drybox atmosphere, and both structures were determined from diffraction data collected at −70 °C. The compounds crystallize in the orthorhombic space group *Pbca* as discrete molecules with no unusual intermolecular contacts. An ORTEP plot of the molecular structure, giving the atom-numbering scheme used in the tables, is depicted in Figure 1. Fractional coordinates and isotropic thermal parameters for **1** and **2** are given in Tables 2 and 3, respectively, while selected bond lengths and angles are presented in Table 4.

The molecular geometry about the lanthanide metal center is somewhat distorted but is best described as a capped trigonal prism in which I(3) caps the rectangular face defined by the four 2-propanol oxygen atoms. In this respect, the geometry

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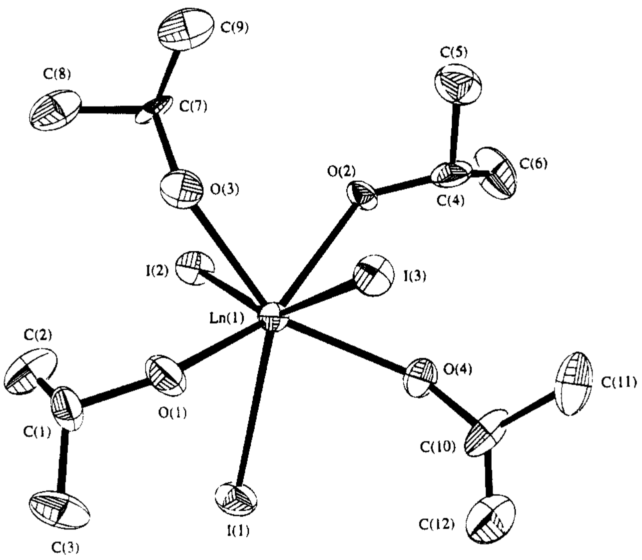

Figure 1. ORTEP plot (50% probability ellipsoids) of the solid-state structure of $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La (**1**), Ce (**2**)) giving the atom-numbering scheme used in the tables.

Table 2. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $LaI_3(HO\text{-}i\text{-}Pr)_4$ (**1**)

	10^4x	10^4y	10^4z	$U(eq)^a$
La(1)	2182(1)	1044(1)	38(1)	15(1)
I(1)	3384(1)	−342(1)	830(1)	26(1)
I(2)	981(1)	−394(1)	738(1)	23(1)
I(3)	2673(1)	2850(1)	−914(1)	20(1)
O(1)	2820(4)	2256(6)	816(4)	26(3)
C(1)	2898(7)	2380(10)	1587(6)	35(4)
C(2)	2275(7)	1775(12)	1930(8)	51(5)
C(3)	3678(6)	2162(9)	1828(7)	33(4)
O(2)	1175(4)	774(5)	−897(3)	16(2)
C(4)	1255(6)	855(7)	−1651(6)	24(3)
C(5)	748(6)	1707(8)	−1903(6)	31(4)
C(6)	1034(8)	-64(9)	−2001(6)	38(4)
O(3)	1154(4)	2205(5)	388(4)	26(2)
C(7)	302(5)	2177(7)	467(6)	18(3)
C(8)	85(7)	2338(8)	1229(6)	32(4)
C(9)	−58(7)	2872(9)	−3(7)	33(4)
O(4)	2905(4)	253(5)	−938(4)	22(2)
C(10)	3622(6)	442(7)	−1338(6)	25(3)
C(11)	3412(11)	461(16)	−2101(8)	78(8)
C(12)	4235(8)	-262(11)	−1163(8)	50(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $CeI_3(HO\text{-}i\text{-}Pr)_4$ (**2**)

	10^4x	10^4y	10^4z	$U(eq)$
Ce(1)	7819(1)	1043(1)	4977(1)	21(1)
I(1)	6605(1)	−327(1)	4201(1)	33(1)
I(2)	9005(1)	−387(1)	4265(1)	28(1)
I(3)	7321(1)	2839(1)	5911(1)	25(1)
O(1)	7195(3)	2218(5)	4172(3)	30(2)
C(1)	7147(6)	2255(12)	3400(5)	66(5)
C(2)	7752(6)	1843(14)	3088(6)	92(6)
C(3)	6322(5)	2166(6)	3185(4)	43(3)
O(2)	8821(3)	759(4)	5891(3)	27(2)
C(4)	8775(5)	884(5)	6659(4)	28(2)
C(5)	9291(5)	1702(6)	6881(5)	41(3)
C(6)	8963(5)	−51(7)	7012(4)	42(3)
O(3)	8838(3)	2203(4)	4618(3)	30(2)
C(7)	9681(4)	2158(5)	4528(4)	27(2)
C(8)	9895(5)	2327(7)	3783(4)	37(3)
C(9)	10067(5)	2870(6)	5022(4)	34(3)
O(4)	7106(3)	251(4)	5956(3)	26(2)
C(10)	6407(5)	468(6)	6385(5)	44(3)
C(11)	6624(7)	368(13)	7127(6)	103(7)
C(12)	5749(5)	−211(8)	6172(6)	53(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La (**1**), Ce (**2**))

	Ln = La	Ln = Ce
Ln(1)−I(1)	3.216(1)	3.191(1)
Ln(1)−I(2)	3.179(1)	3.157(1)
Ln(1)−I(3)	3.224(1)	3.187(1)
Ln(1)−O(1)	2.508(8)	2.488(6)
Ln(1)−O(2)	2.525(6)	2.489(5)
Ln(1)−O(3)	2.492(7)	2.479(5)
Ln(1)−O(4)	2.506(7)	2.495(5)
O(1)−C(1)	1.495(13)	1.480(11)
O(2)−C(4)	1.457(12)	1.484(9)
O(3)−C(7)	1.478(11)	1.462(8)
O(4)−C(10)	1.478(13)	1.487(11)
I(1)−Ln(1)−I(2)	80.9(1)	81.2(1)
I(1)−Ln(1)−I(3)	124.6(1)	123.5(1)
I(2)−Ln(1)−I(3)	154.6(1)	155.3(1)
I(1)−Ln(1)−O(1)	80.9(2)	79.7(1)
I(2)−Ln(1)−O(1)	117.4(2)	115.1(1)
I(3)−Ln(1)−O(1)	72.2(2)	73.7(1)
I(1)−Ln(1)−O(2)	133.6(2)	133.4(1)
I(2)−Ln(1)−O(2)	76.0(1)	75.9(1)
I(3)−Ln(1)−O(2)	84.0(2)	85.1(1)
O(1)−Ln(1)−O(2)	145.5(2)	147.0(2)
I(1)−Ln(1)−O(3)	136.2(2)	136.2(1)
I(2)−Ln(1)−O(3)	80.4(2)	80.3(1)
I(3)−Ln(1)−O(3)	80.3(2)	80.6(1)
O(1)−Ln(1)−O(3)	73.4(2)	72.9(2)
O(2)−Ln(1)−O(3)	78.4(2)	78.9(2)
I(1)−Ln(1)−O(4)	76.6(2)	76.5(1)
I(2)−Ln(1)−O(4)	111.2(2)	111.4(1)
I(3)−Ln(1)−O(4)	77.9(2)	77.9(1)
O(1)−Ln(1)−O(4)	121.5(2)	122.9(2)
O(2)−Ln(1)−O(4)	75.3(2)	75.0(2)
O(3)−Ln(1)−O(4)	147.3(2)	147.3(2)
Ln(1)−O(1)−C(1)	134.8(7)	131.7(7)
Ln(1)−O(2)−C(4)	128.9(6)	130.0(4)
Ln(1)−O(3)−C(7)	135.9(6)	134.9(4)
Ln(1)−O(4)−C(10)	136.5(6)	136.3(5)

differs considerably from that of a number of structurally characterized adducts of the type $MX_3(THF)_4$ (X = Cl, M = Sm,[15] Eu,[16] Nd;[17] X = I, M = U[12]) and also the closely related 2-propanol adduct $SmBr_3(HO\text{-}i\text{-}Pr)_4$,[18] which all exhibit pentagonal bipyramidal geometry with halide ligands occupying axial sites. La−I distances of 3.216(1), 3.180(1), and 3.224(1) Å in **1** are directly comparable to that of 3.206(3) Å found in $(MeOCH_2CH_2C_5H_4)_2LaI$,[19] while Ce−I distances of 3.191(1), 3.157(1), and 3.187(1) Å in **2** are slightly shorter than those of 3.299(1), 3.231(2), and 3.200(9) (average) Å found in the organometallic complexes $(\eta\text{-}C_8H_8)CeI(THF)_3$,[20] $(\eta\text{-}C_5Me_5)_2CeI(NCCH_3)_2$,[21] and $(\eta\text{-}C_5Me_5)CeI_2(THF)_3$,[22] respectively. An average La−O distance of 2.509(7) Å to the four 2-propanol

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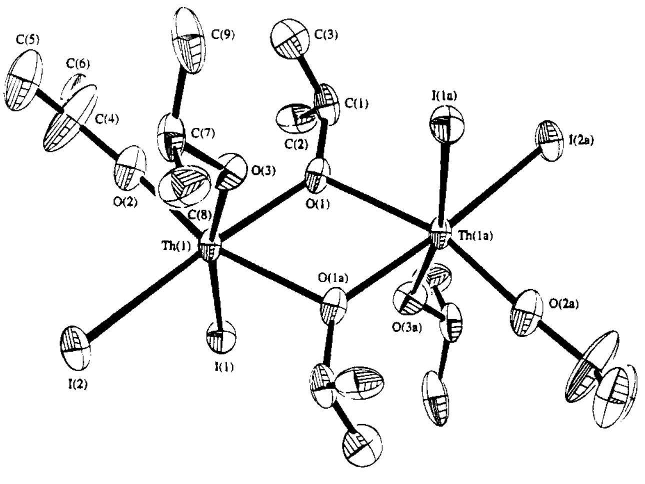

Figure 2. ORTEP plot (40% probability ellipsoids) of the solid-state structure of $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**) giving the atom-numbering scheme used in the tables.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$) for $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**)

	10^5x	10^5y	10^5z	$U(eq)^a$
Th(1)	9823(4)	6165(3)	17924(3)	262(2)
I(1)	−8604(8)	−32237(7)	12097(6)	417(3)
I(2)	43171(8)	16201(9)	33899(7)	468(3)
O(1)	−11661(62)	2194(57)	3604(49)	312(11)
C(1)	−25621(82)	4239(85)	4709(75)	386(12)
C(2)	−37143(84)	−9368(91)	8749(85)	515(13)
C(3)	−19791(93)	22095(85)	13652(82)	513(12)
O(2)	3083(71)	14579(68)	33946(56)	506(12)
C(4)	389(110)	21539(103)	45764(88)	1098(13)
C(5)	11829(104)	38725(100)	53691(83)	758(13)
C(6)	−14623(97)	11716(104)	47053(82)	695(13)
O(3)	23521(66)	34291(60)	17940(55)	411(12)
C(7)	35512(90)	51094(87)	27223(77)	431(13)
C(8)	51294(94)	57096(98)	23214(88)	675(13)
C(9)	29544(98)	63034(93)	28228(87)	660(13)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (**4**)

Th(1)−I(1)	3.104(1)	Th(1)−I(2)	3.094(1)
Th(1)−O(1)	2.327(6)	Th(1)−O(2)	2.056(7)
Th(1)−O(3)	2.437(6)	Th(1)−Th(1A)	3.924(1)
Th(1)−O(1A)	2.399(6)	O(1)−C(1)	1.461(11)
O(1)−Th(1A)	2.399(6)	O(2)−C(4)	1.416(12)
O(3)−C(7)	1.429(7)		

I(1)−Th(1)−I(2)	97.7(1)	I(1)−Th(1)−O(1)	91.3(1)
I(2)−Th(1)−O(1)	166.9(1)	I(1)−Th(1)−O(2)	97.8(2)
I(2)−Th(1)−O(2)	93.0(2)	O(1)−Th(1)−O(2)	95.1(3)
I(1)−Th(1)−O(3)	168.6(1)	I(2)−Th(1)−O(3)	87.0(2)
O(1)−Th(1)−O(3)	82.4(2)	O(2)−Th(1)−O(3)	92.2(2)
I(1)−Th(1)−Th(1A)	89.0(1)	I(2)−Th(1)−Th(1A)	135.8(1)
O(1)−Th(1)−Th(1A)	34.5(1)	O(2)−Th(1)−Th(1A)	129.5(2)
O(3)−Th(1)−Th(1A)	80.5(1)	I(1)−Th(1)−O(1A)	87.0(1)
I(2)−Th(1)−O(1A)	103.2(1)	O(1)−Th(1)−O(1A)	67.7(3)
O(2)−Th(1)−O(1A)	162.4(3)	O(3)−Th(1)−O(1A)	81.8(2)
Th(1A)−Th(1)−O(1A)	33.3(2)	Th(1)−O(1)−C(1)	135.1(5)
Th(1)−O(1)−Th(1A)	112.3(3)	C(1)−O(1)−Th(1A)	112.6(5)
Th(1)−O(2)−C(4)	173.4(5)	Th(1)−O(3)−C(7)	135.1(6)

ligands in **1** is comparable to the La−O distances found for the alcoholic end groups in the complexes $[LaCl(OH_2)(EO3)_2]Cl_2$,[23] $[LaCl_2(OH_2)_2(EO3)]_2Cl_2$,[23] and $[LaCl_3(EO4)]_2$[24] (EO3 = triethylene glycol, EO4 = tetraethylene glycol), which are 2.59(1), 2.556(5), and 2.57(1) Å, respectively. Ce−O distances to 2-propanol ligands in **2** average 2.488(5) Å. The differences in average Ln−I and Ln−O distances between **1** and **2** are directly in line with those expected for the decrease in atomic radius upon moving from lanthanum to cerium.[25]

$Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ (4). Crystals suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to −40 °C, and the structure determined from diffraction data collected at −48 °C. An ORTEP plot of the molecular structure of **4**, giving the atom-numbering scheme used in the tables, is depicted in Figure 2. Selected fractional coordinates and isotropic thermal parameters are given in Table 5, while selected bond lengths and angles are presented in Table 6. The overall molecular geometry of **4** is best described as an edge-shared bioctahedron with 2-propoxide ligands occupying bridging positions. The molecule is isostructural with the previously-described uranium analog[11] and is structurally very similar to a number of early transition metal and lanthanide alkoxide and halide−alkoxide species such as $M_2(O\text{-}i\text{-}Pr)_8(HO\text{-}i\text{-}Pr)_2$ (M = Zr, Ce)[26] and $Ti_2Cl_4(OR)_4(HOR)_2$ (R = CH_2CH_2Cl).[27] The 2-propoxide bridging ligands are somewhat asymmetric, with the Th(1)−O(1) distance of 2.327(6) Å being significantly shorter than the Th(1A)−O(1) distance of 2.399(6) Å. The short Th−O bond is trans to an iodide ligand while the longer Th−O bond is trans to a terminal alkoxide. An analogous asymmetric bridging unit was observed in the closely related titanium system $Ti_2Cl_4(OR)_4(HOR)_2$ (R = CH_2CH_2Cl).[27] The longer of these two Th−O bridging distances is comparable to those observed in other thorium alkoxide systems containing bridging alkoxide ligands, such as $Th_2(OCH\text{-}i\text{-}Pr_2)_8$ (2.436(11) Å (average)),[28] $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (2.420(10) Å (average)),[29] and $Th_2(OCHEt_2)_8(py)_2$ (2.427(5) Å (average)) (py = pyridine).[29] The Th−O distance to the terminal 2-propoxide ligand, however, appears to be the shortest yet documented for a thorium alkoxide at 2.056(7) Å. In the other reported examples of structurally characterized thorium alkoxide complexes,[13,28−30] terminal Th−O distances have been in the range 2.132(5)−2.204(6) Å, with an average value of 2.163 Å. There are two types of terminal iodide ligands, one set being trans to the bridging 2-propoxide ligands (Th(1)−I(2) = 3.094(1) Å) and the other set trans to the 2-propanol ligand (Th(1)−I(1) = 3.104(1) Å). These Th−I distances are similar to that found in $(\eta\text{-}C_5Me_5)_2ThI\text{−}Ru(CO)_2(\eta\text{-}C_5H_5)$ (3.045 Å)[31] but significantly shorter than the 3.226(1) Å observed in the thorium iodide−alkoxide complex $ThI(OCH\text{-}i\text{-}Pr_2)_3(py)_2$.[30] The proton of the 2-propanol ligand could not be located, but its presence is inferred by the long Th(1)−O(3) distance of 2.437(6) Å and the clear presence of hydrogen bonding across the dinuclear unit with a I(1)−Th(1)−O(3) angle of 168.6(1)°. The Th(1)−O(3)−C(7) angle of 135.1(6)° is also identical to the bridging alkoxide Th(1)−O(1)−C(1) angle of 135.1(5)°.

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Concluding Remarks

We have found that the direct oxidation of lanthanide metals (Ln = La, Ce, Nd) with iodine in 2-propanol solution provides a convenient synthetic route to tetrakis(2-propanol) adducts of the metal triiodides. In the case of uranium and thorium, however, an analogous reaction leads to the isolation of mixed iodide–alkoxide complexes [UI(O-*i*-Pr)$_2$(HO-*i*-Pr)$_4$]I[14] and M$_2$I$_4$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_2$ (M = Th, U[11]). We are currently extending this synthetic methodology to include the reaction of lanthanide and actinide metals with bromine and chlorine in an alcohol solvent and exploring the reactivity of the halide–alkoxide species toward halide metathesis reagents such as alkali-metal amides, alkoxides, and alkyls.[32]

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon, using standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres glovebox. Thorium metal turnings were obtained from Los Alamos National Laboratory stock, while lanthanum, cerium, and neodymium metals were purchased from Strem and used as received. 2-Propanol was distilled under nitrogen from sodium metal. Solvents were degassed and distilled from Na/K alloy under nitrogen. Dichloromethane-d_2 was degassed, dried over CaH$_2$ and then trap-to-trap distilled before use. Benzene-d_6 was degassed, dried over Na/K alloy, and then trap-to-trap distilled before use. Solvents were taken into a Vacuum Atmospheres glovebox, and small amounts were tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded on Brüker WM 300 and AF 250 spectrometers in benzene-d_6 and dichloromethane-d_2. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in benzene-d_6 and dichloromethane-d_2 set at δ 7.15 and 5.32, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 Central Processor or on a BioRad FTS-40 spectrophotometer as Nujol mulls between KBr salt plates. Elemental analyses were performed in-house on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Syntheses. LaI$_3$(HO-*i*-Pr)$_4$ (1). Lanthanum powder (40 mesh, 2.32 g, 16.7 mmol) was washed with hexanes and placed in a Schlenk vessel. Residual hexanes were removed from the metal powder *in vacuo*, and the vessel was refilled with argon before adding 125 mL of dry 2-propanol and a stir bar. Elemental iodine (6.36 g, 25.1 mmol) was added to the flask under an argon purge with stirring, and a cold water bath was used to maintain the reaction mixture at or below room temperature. The reaction vessel was then stoppered, and the mixture was left to stir at room temperature until metal powder could no longer be observed (typically 1–2 days), after which time it was taken into a drybox and filtered through Celite on a coarse frit. All solvent was removed from the filtrate under reduced pressure. The solid residue was washed with toluene to remove unreacted iodine, and the resulting off-white solids were dried *in vacuo*. Yield: 10.96 g (86%). Crystalline material was obtained by recrystallization at −40 °C from a minimum volume of 2-propanol. ^{1}H NMR (250 MHz, dichloromethane-d_2): δ 4.75 (septet, $^3J_{HH}$ = 6 Hz, 1 H, C*H*Me$_2$), 4.36 (s, 1 H, O*H*), 1.44 (d, 6 H, CH*Me*$_2$). IR (cm^{-1}): 3440 (sh, br), 3318 (br, s), 1394 (sh, s), 1287 (m), 1267 (m), 1156 (m), 1140 (m), 1119 (m), 1081 (s), 921 (s), 873 (sh, w), 819 (sh, m), 803 (s), 725 (m), 692 (w), 669 (w), 509 (m), 444 (m). Anal. Calcd for $C_{12}H_{32}I_3LaO_4$: C, 18.96; H, 4.25. Found: C, 19.27; H, 4.19.

CeI$_3$(HO-*i*-Pr)$_4$ (2). Cerium chips (1.00 g, 7.14 mmol) were allowed to react with elemental iodine (2.70 g, 10.6 mmol) in 50 mL of dry 2-propanol in an analogous manner to that described above for the preparation of LaI$_3$(HO-*i*-Pr)$_4$. Filtration of the reaction mixture through a medium-porosity frit yielded a pale yellow solution. The volume of the filtrate was reduced to *ca.* 20 mL *in vacuo*, and it was then placed in the freezer at −40 °C. Cream-colored crystals were isolated by removal of the mother liquor and drying under reduced pressure (10^{-4} Torr, 24 h). Yield: 4.6 g (85%). ^{1}H NMR (250 MHz, dichloromethane-d_2): δ 8.46 (br, 1 H, O*H*), 7.05 (br, 1 H, C*H*Me$_2$), 2.93 (s, 6 H, CH*Me*$_2$). IR (cm^{-1}): 3307 (br, m), 1082 (m), 947 (w), 808 (w). Anal. Calcd for $C_{12}H_{32}CeI_3O_4$: C, 18.93; H, 4.24. Found: C, 18.75; H, 3.42.

NdI$_3$(HO-*i*-Pr)$_4$ (3). Neodymium powder (4.60 g, 31.9 mmol) was allowed to react with elemental iodine (12.14 g, 47.8 mmol) in 125 mL of dry 2-propanol in a manner analogous to that described above for the preparation of LaI$_3$(HO-*i*-Pr)$_4$. Filtration of the reaction mixture through a medium-porosity frit yielded a burgundy-colored solution. 2-Propanol was removed from the filtrate *in vacuo*, and the residue was washed with toluene to remove unreacted iodine. The resulting pale blue solids were dried under reduced pressure. Yield: 14.14 g (58%). ^{1}H NMR (250 MHz, dichloromethane-d_2): δ 9.18 (br, 1 H, C*H*Me$_2$), 7.58 (v br, 1 H, O*H*), 4.48 (s, 6 H, CH*Me*$_2$). IR (cm^{-1}): 3435 (sh, br), 3228 (br, m), 1286 (m), 1265 (m), 1139 (m), 1082 (s), 915 (s), 795 (s), 727 (m), 690 (w). Anal. Calcd for $C_{12}H_{32}I_3NdO_4$: C, 18.83; H, 4.21. Found: C, 19.18; H, 4.41.

Th$_2$I$_4$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_2$ (4). In the drybox, 150 mL of dry 2-propanol was placed into a 250 mL Schlenk vessel. The flask was sealed, removed from the drybox, and attached to a Schlenk line. Under an argon purge, 12.56 g (54.13 mmol) of thorium turnings were placed into the flask and a stir bar was added. To the stirring thorium turnings was then added 13.74 g (54.14 mmol) of iodine in one batch. The flask was cooled in a water bath while the reaction took place. The deep brown/purple color of the iodine was slowly discharged to leave a gray suspension in the flask after 12 h of stirring. The flask was returned to the drybox, and the contents were filtered through a Celite pad to give a clear, pale yellow filtrate. The volume of the filtrate was reduced to 100 mL, and it was placed in the freezer at −40 °C. Overnight, a mass of white crystalline solid was deposited. This was filtered off onto a frit and allowed to dry in the box atmosphere. Yield: 19.5 g (50%). The solid was dissolved in 200 mL of toluene and the solution stirred for 30 min. All of the solvent was then removed in vacuo to leave an off-white solid. This solid was recrystallized from a minimum quantity of toluene at −40 °C to give a white microcrystalline solid. ^{1}H NMR (300 MHz, benzene-d_6): δ 5.03 (s, O*H*), 4.65 (br, C*H*Me$_2$), 1.21 (br, CH*Me*$_2$). Anal. Calcd. for $C_{18}H_{44}I_4O_6Th_2$: C, 16.28; H, 3.34. Found: C, 16.42; H, 3.40.

Crystallographic Studies. LaI$_3$(HO-*i*-Pr)$_4$. The crystals were examined in mineral oil under an argon stream. The chosen crystal, 0.3 × 0.18 × 0.13 mm, was affixed to a glass fiber using Apiezon grease and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation, where it was cooled to −70 °C in a nitrogen cold-stream. Unit cell parameters were determined from the least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were reduced using the Structure Determination Package provided by Enraf-Nonius and corrected for absorption empirically using high-χ ψ-scans. The intensities were corrected for Lorentz and polarization effects, equivalent reflections were merged ($R_{int} = 0.016$), and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods, using full-matrix least-squares refinement. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3447 unique observed $[F > 4\sigma(F)]$ reflections converged at $R = 0.044$, $R_w = 0.074$ {where $w = [\sigma^2(F) + 0.001F^2]^{-1}$}. The alcohol O-*H* protons were not located. All data refinement calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc, 1990).

CeI$_3$(HO-*i*-Pr)$_4$. The transparent, pale yellow crystals were examined in mineral oil under an argon stream, and a crystal measuring 0.325 × 0.40 × 0.425 mm was affixed to a glass fiber using Apiezon grease and transferred to the −70 °C nitrogen cold-stream of an Enraf-Nonius CAD4 diffractometer, with graphite-monochromated Mo Kα

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[32] Bryan, J. C.; Gordon, P. L.; Sauer, N. N.; Thompson, J. A. Manuscript in preparation.

radiation. Unit cell parameters were determined from the least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for absorption empirically using high-χ ψ-scans. The intensities were corrected for Lorentz and polarization effects, equivalent reflections were merged, and systematically absent reflections were rejected. The metal atom was located by direct methods, and the structure was solved by routine Fourier methods using full-matrix least-squares refinement. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3354 unique observed $[F > 4\sigma(F)]$ reflections converged at $R = 0.035$, $R_w = 0.062$ {where $w = [\sigma^2(F) + 0.003F^2]^{-1}$}. All calculations were performed using the SHELXTL PLUS suite of computer programs.

$Th_2I_4(O$-i-$Pr)_4(HO$-i-$Pr)_2$. The clear, well-formed crystals were examined in mineral oil under an argon stream. The chosen crystal, 0.15 × 0.2 × 0.25 mm, was affixed to a glass fiber using Apiezon grease and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer, with graphite-monochromated Mo Kα radiation, where it was cooled to −48 °C in a nitrogen cold-stream. Unit cell parameters were determined from the least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 24 accurately centered reflections (2θ range 27−32°). Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were reduced using the Structure Determination Package provided by Enraf-Nonius and corrected for absorption empirically using high-χ ψ-scans. The intensities were corrected for Lorentz and polarization effects, equivalent reflections were merged ($R_{int} = 0.015$), and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods, using full-matrix least-squares refinement. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 2467 unique observed $[F > 4\sigma(F)]$ reflections converged at $R = 0.032$, $R_w = 0.051$ {where $w = [\sigma^2(F) + 0.0008F^2]^{-1}$}. The alcohol O-*H* protons were not located. All data refinement calculations were performed using the SHELXTL PLUS suite of computer programs.

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Supporting Information Available: Complete tables of fractional coordinates, isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **1**, **2**, and **4** (11 pages). Ordering information is given on any current masthead page.

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