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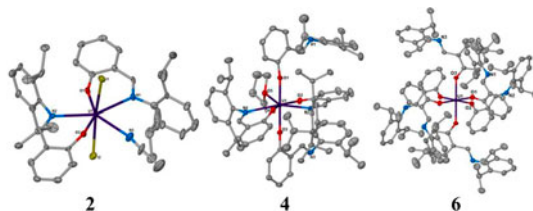
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Even and odd: uranium(IV) complexes with two, four, and six salicylaldimine ligands with an unusual κ^1 -coordination mode

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We report the synthesis and structural determination of three uranium(IV) complexes bearing two, four, and six salicylaldimine ligands. Reaction of $U_4(1,4\text{-dioxane})_2$ with two, four, and six equivalents of $K[OC_6H_4C(H)=N(2,6\text{-}i\text{-Pr}_2C_6H_3)]$, **1**, yielded $[(2,6\text{-}i\text{-Pr}_2C_6H_3)N=C(H)C_6H_4O\text{-}\kappa^2(O,N)]_2U_2(NCCH_3)$, **2**, $[(2,6\text{-}i\text{-Pr}_2C_6H_3)N=C(H)C_6H_4O\text{-}\kappa^1(O)]_2[(2,6\text{-}i\text{-Pr}_2C_6H_3)N=C(H)C_6H_4O\text{-}\kappa^2(O,N)]_2U(THF)$, **3**, and $\{[2,6\text{-}i\text{-Pr}_2C_6H_3)N=C(H)C_6H_4O\text{-}\kappa^1(O)]_6U\}^{2-}$, **4**. While **2** shows normal κ^2 -coordination through both oxygen and nitrogen donors, **3** has two salicylaldimine ligands bound only through oxygen and **4** has all six ligands bound only through oxygen. This is an exceedingly rare example of a chelating ligand not completing its chelation in f-element chemistry. In addition, **4** is the first report of a homoleptic octahedral actinide complex with a Schiff base ligand.

Keywords: Schiff base; Uranium; X-ray crystallography; Synthesis

1. Introduction

Schiff base ligands are well established in transition metal [1] and f-element chemistry [2, 3] and provide a rigid framework due to the presence of the imine bond. Schiff bases are traditionally dianionic, and therefore complexes with two ligands do not display much reactivity since the tetravalent oxidation state is quite stable for thorium and uranium. These ligands are popular due to their ease of preparation, facile variation of their steric and electronic properties, as well as their ability to chelate metal centers which enhance their stability. One subset of Schiff bases is salicylaldimine ligands which offer similar

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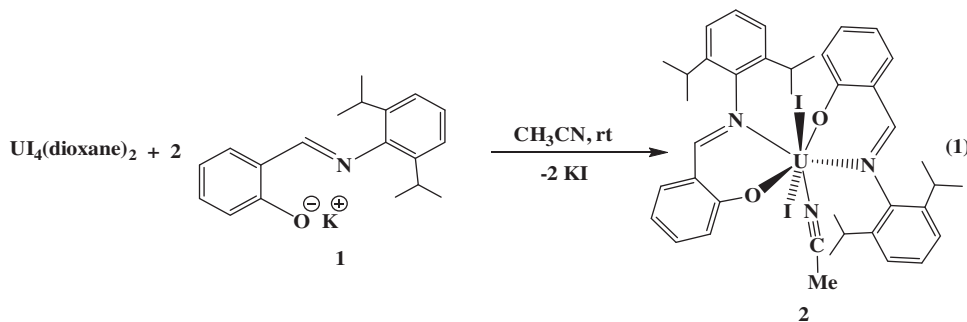
properties as Schiff base ligands but these are typically monoanionic and our objective was to synthesize a series of actinide salicylaldiminate complexes which could undergo further reactivity. Thus far we have reported metal complexes derived from 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde which, like most salicylaldiminate complexes previously synthesized, have been bi- or tridentate, depending on the aniline used[4, 5].

Steric, rather than electronic, properties tend to dictate f-element reactivity[6]. For example, sterically crowded molecules such as $(C_5Me_5)_3U$ have been synthesized through a variety of methods and shown to undergo redox chemistry through sterically induced reduction (SIR)[7]. In general, as long as the f element has sufficient electron density from coordinated ligands then various coordination modes can be obtained.

Schiff base ligands consistently coordinate to metals through the anionic oxygen and through the lone pair on nitrogen in a κ^2 -fashion. This is especially the case with f elements which require high coordination numbers and greater electron density to satisfy their electropositive nature and large ionic radii. However, we report herein the synthesis and structural determination of a series of uranium(IV) complexes with two, four, and six salicylaldiminate ligands which, in the latter two compounds, display κ^1 -coordination through the oxygen only.

2. Results and discussion

The ligand, $HOC_6H_4C(H)=N(2,6\text{-}^iPr_2C_6H_3)$, was deprotonated using potassium bis(trimethylsilyl)amide to form the potassium salt, $KOC_6H_4C(H)=N(2,6\text{-}^iPr_2C_6H_3)$, **1**. Reaction of two equivalents of **1** with $U_4(1,4\text{-dioxane})_2$ in acetonitrile, equation (1), yielded an orange solution. The structure was determined by X-ray crystallography and revealed, $[(2,6\text{-}^iPr_2C_6H_3)N=C(H)C_6H_4O\text{-}\kappa^2)]_2U_2(NCCH_3)_2$, **2**, a seven-coordinate complex with two κ^2 -salicylaldiminate and two iodide ligands, as well as an acetonitrile, figure 1. The iodides are nearly *trans* to each other with a I1–U1–I2 angle of $168.83(3)^\circ$, while the two salicylaldiminate ligands and acetonitrile form the equatorial plane of the molecule producing a pseudo-pentagonal bipyramidal structure. The distances for the U–O bond distances are unexceptional with respect to other U(IV) aryloxy complexes and are discussed later. The U–I bond distances of 3.0344(12) and 3.0531(13) Å are similar to those reported for other U(IV)–iodide bonds[8]. The U–N(acetonitrile) bond length of 2.758(11) Å is significantly longer than other adducts observed with U(IV) complexes. For example, the average U–N distance in $[(C_5Me_5)_2U(NCMe)_5]^{2+}$ is 2.547(8) Å [9] and 2.53(1) Å in $[U_2(NCMe)_7]^{2+}$ [10]. This elongation is most likely due to steric properties of the two salicylaldiminate ligands and two iodides.



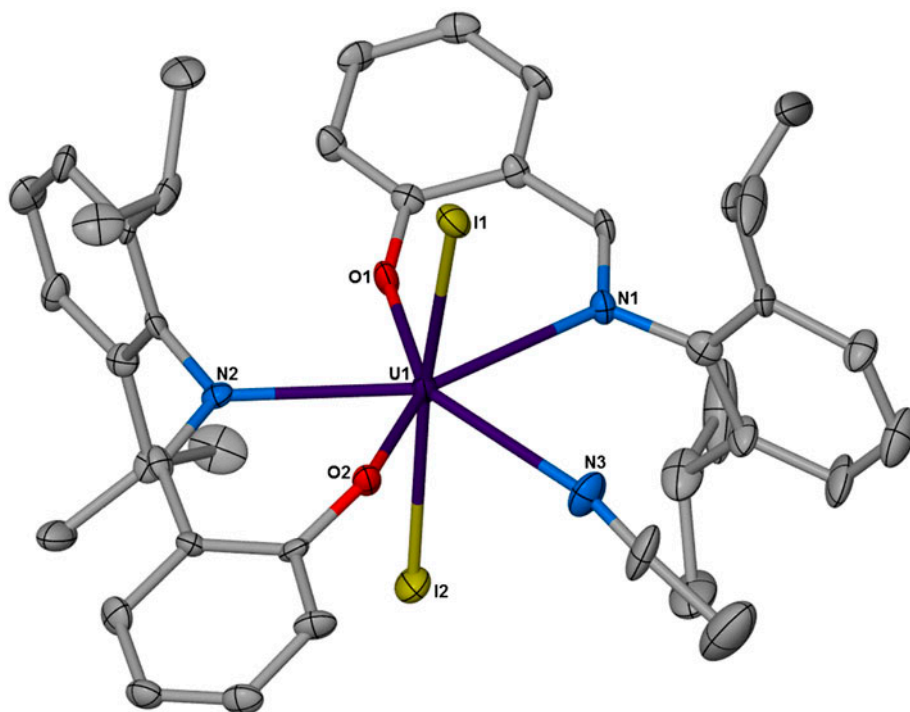


Figure 1. Thermal ellipsoid plot of $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{C}_6\text{H}_4)\text{O-}\kappa^2]_2\text{U}_12(\text{NCCH}_3)_2$, **2**, shown at the 30% probability level. The hydrogens have been omitted for clarity. Selected bond distances and angles: U1-O1, 2.106(12) Å; U1-O2, 2.111(11) Å; U1-N1, 2.759(11) Å; U1-N2, 2.648(12) Å; U1-N3, 2.616(14) Å; U1-I1, 3.0346(12) Å; U1-I2, 3.0531(13) Å; O1-U1-O2, 145.6(4)°; O1-U1-N1, 69.1(4)°; O1-U1-I1, 93.4(4)°; I1-U1-I2, 168.83(3)°.

Reaction of three or four equivalents of **1** with $\text{U}_4(1,4\text{-dioxane})_2$ formed the same product, $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O-}\kappa^2]_2[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O-}\kappa^1]_2\text{U}(\text{THF})$, **3**, equation (2). X-ray crystallographic analysis of the brown crystals obtained revealed a seven-coordinate complex with four salicylaldiminate ligands and one THF molecule, since THF was used for crystallization, coordinated to the uranium(IV) metal center, figure 2. Interestingly and quite unexpectedly, two of the salicylaldiminate ligands coordinate in a κ^1 -fashion through oxygen to uranium, while the other two with typical κ^2 -bidentate chelation. Our rationale for the two ligands bypassing the chelate effect is that uranium(IV), a hard Lewis acid, prefers the harder, anionic oxygen than the softer, neutral nitrogen donor. We know of no examples of this coordination mode in f-element chemistry; however, a $\kappa^1\text{-O}_2\text{CCH}_3$ has been observed[11]. This binding mode, and the binding mode in **3**, is presumably due to steric crowding around the metal center which forces the uranium between maintaining the iodide ligand or obtaining a more electronegative and better sigma bond donor oxygen and simply coordinating in an unusual manner.

It should be noted that the κ^1 -coordination via an oxygen has been observed with similar salicylaldiminate ligands for transition metal complexes. For example, reaction of CpTiCl_3 with $\text{Li}[\text{O}(2\text{-R}'\text{C}_6\text{H}_3)\text{C}=\text{NR}'']$, $\text{Cp}=\text{C}_5\text{H}_5$, C_5Me_5 , $1,2,4\text{-Me}_3\text{C}_5\text{H}_2$; $\text{R}'=\text{Me}$, ^tBu ; $\text{R}''=2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, ^tBu , produces the corresponding $\text{CpTiCl}_2[\text{O}(2\text{-R}'\text{C}_6\text{H}_3)\text{C}=\text{NR}'']$ [12].

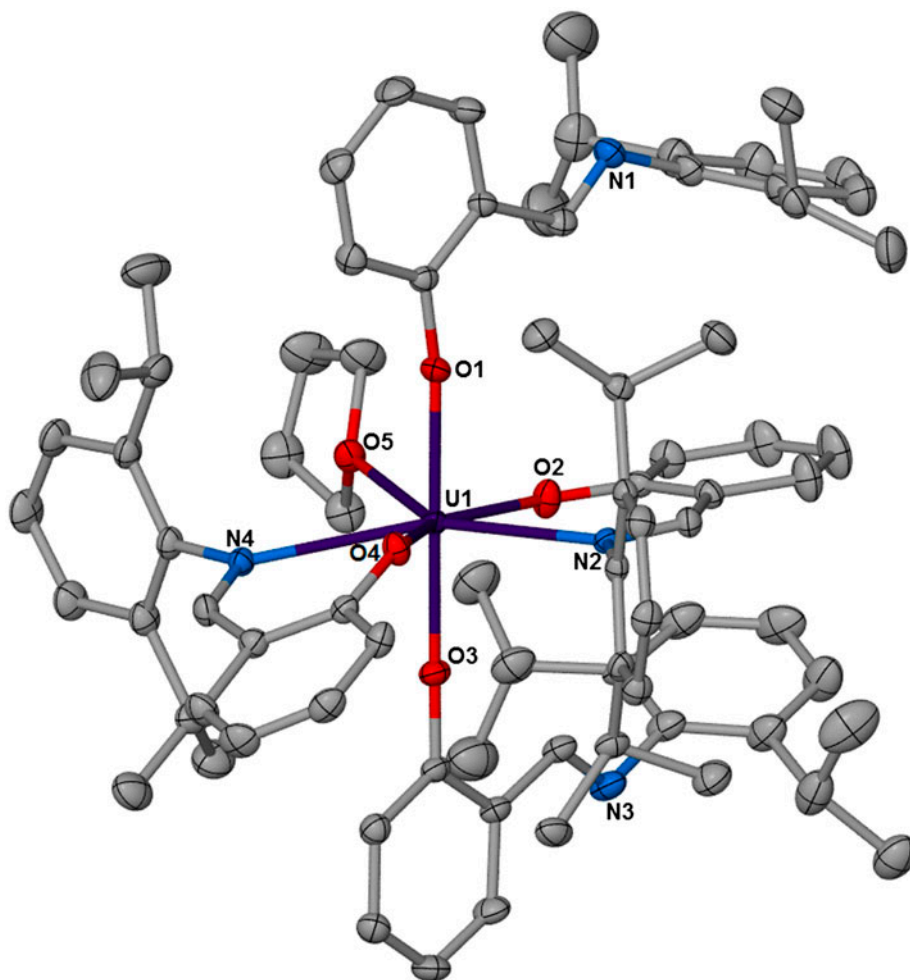
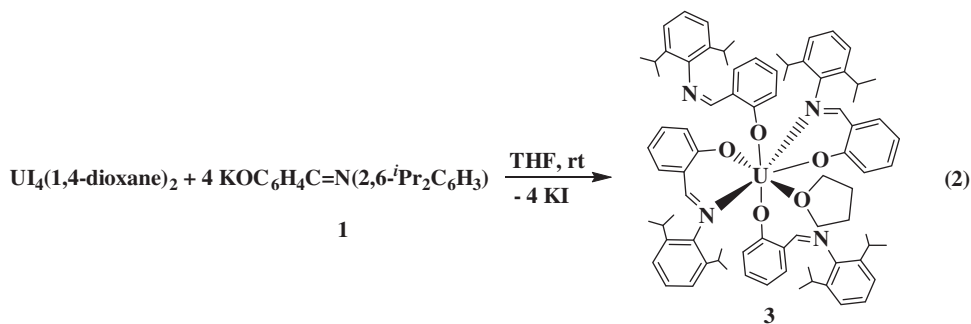


Figure 2. Thermal ellipsoid plot of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^2]_2[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^1]_2\text{U}$ (THF), **3**, shown at the 30% probability level. The hydrogens have been omitted for clarity. Selected bond distances and angles: U1-O1, 2.1523(18) Å; U1-O2, 2.2159(19) Å; U1-O3, 2.1534(18) Å; U1-O4, 2.1826(18) Å; U1-O5, 2.5204(19) Å; U1-N2, 2.625(2) Å; U1-N4, 2.729(2) Å; O1-U1-O2, 90.34(8)°; O1-U1-O3, 178.40(7)°; N2-U1-N4, 146.22(7)°.



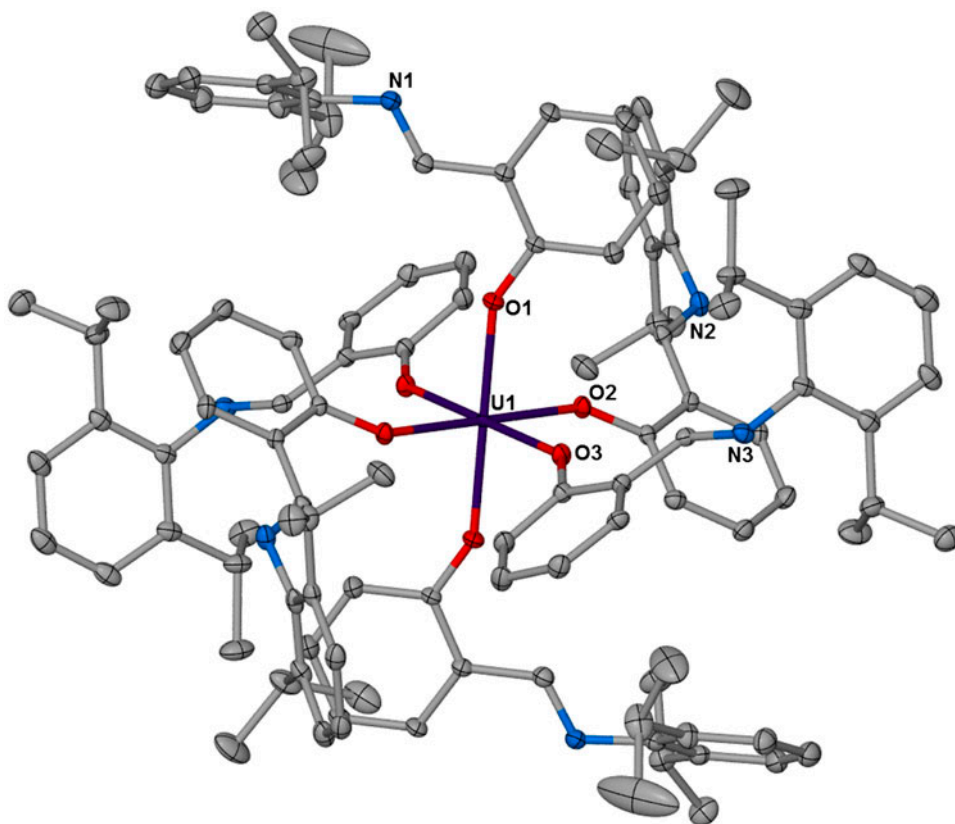


Figure 3. Thermal ellipsoid plot of $\{[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^1]_6\text{U}\}^{2-}$, **4**, shown at the 30% probability level. The hydrogens and two $[\text{K}(\text{NCCH}_3)_6]$ cations have been omitted for clarity. Selected bond distances and angles: U1-O1, 2.223(3) Å; U1-O2, 2.237(3) Å; U1-O3, 2.249(2) Å; O1-U1-O2, 90.36(10) $^\circ$; O1-U1-O3, 88.93(10) $^\circ$; O3-U1-O3*, 180.00(7) $^\circ$.

To test the limits of salicylaldimine coordination, six equivalents of **1** were reacted with $\text{U}(\text{I}_4(1,4\text{-dioxane})_2)_2$ in acetonitrile and a yellow product, **4**, was obtained, equation (3). The structure showed a six-coordinate, octahedral complex with six salicylaldimine ligands coordinated but only through oxygen of each ligand, figure 3. A few homoleptic U(IV) aryloxide species are known [13] but none involve a chelating ligand such as the one used here.

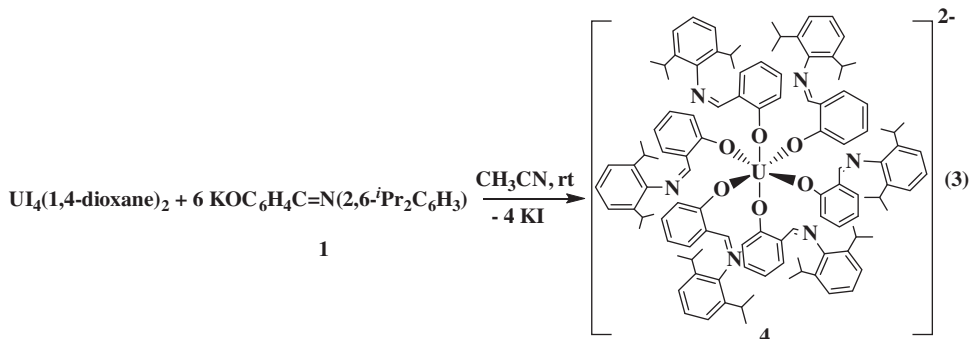


Table 1. X-ray crystallographic data for 2–4.

	2	3	4
CCDC deposit number	1042373	1042374	1042375
Empirical formula	$C_{43}H_{51.50}N_{4.50}O_{12}U$	$C_{84}H_{104}N_4O_6U$	$C_{138}H_{168}N_{18}O_6K_2U$
Formula weight (g/mol)	1155.21	1503.74	2491.12
Crystal habit, color	Orange, block	Brown, prism	Yellow, plate
Temperature (K)	173(2)	173(2)	173(2)
Space group	<i>Pn</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
Crystal system	<i>Monoclinic</i>	<i>Monoclinic</i>	<i>Monoclinic</i>
Volume (Å ³)	2306.5(7)	7603.2(13)	6776.6(16)
<i>a</i> (Å)	10.70(2)	16.0480(16)	16.666(2)
<i>b</i> (Å)	14.029(3)	19.1525(19)	27.251(2)
<i>c</i> (Å)	16.022(3)	25.131(3)	16.381(2)
α (°)	90	90	90
β (°)	106.584(2)	100.1500(10)	114.371(2)
γ (°)	90	90	90
<i>Z</i>	2	4	2
Calculated density (Mg/m ³)	1.663	1.314	1.221
Absorption coefficient (mm ⁻¹)	4.894	2.189	1.317
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0515, <i>wR</i> ₂ = 0.1340	<i>R</i> ₁ = 0.0286, <i>wR</i> ₂ = 0.0715	<i>R</i> ₁ = 0.0409, <i>wR</i> ₂ = 0.1088

The U–O bonds in **4** range from 2.223(3)–2.249(2) Å, longer than most terminal U–O bonds in U(IV) aryloxy complexes, presumably due to steric considerations. For example, most U–O bond distances in homoleptic U(IV) aryloxy complexes are 2.132(8)–2.19(2) Å [2, 14] and increase to 2.25–2.45 Å for bridging ligands [15]. Additionally, the U–O bond distances in **2** of 2.106(12) and 2.111(11) Å and in **3** of 2.1523(18), 2.2159(19), 2.1634(18), and 2.1826(18) Å support the idea that the elongation is due to steric crowding in **4**. Based on the bond angles, **4** adopts a nearly ideal octahedral geometry, another rarity for f-element complexes, especially tetravalent compounds.

Overall, these three complexes provide a rare opportunity to study the coordination chemistry of uranium with a chelating ligand that does not chelate. When only two ligands are present, then only κ^2 -coordination is observed. However, when four equivalents are added both κ^2 and κ^1 -modes are found. When six equivalents are used, all six ligands coordinate κ^1 . In each case, the more oxophilic uranium chooses the strongest possible donor. In the case of **2**, the chelate effect is best, however, in **3**, uranium would prefer the anionic oxygen and neutral oxygen from THF over nitrogen to complete chelation. In **4**, only the anionic oxygens are preferred but this comes at the price of increased uranium–oxygen bond distances.

3. Conclusions

The structures of three new uranium(IV) complexes with an even number (2, 4, or 6) of salicylaldiminate ligands are reported. With two salicylaldiminate ligands, only the κ^2 -chelate was observed but with four and six ligands, κ^1 -coordination was found. $\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}]_6\text{U}\}\{\text{K}(\text{NCCH}_3)_6\}_2$, **4**, is the first homoleptic octahedral complex with a Schiff base ligand. This is the first report of a Schiff base ligand coordinating to an f element in a κ^1 -fashion.

4. Experimental section

The syntheses and manipulations described below were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Anhydrous solvents (Aldrich) were used as received and kept over molecular sieves while handled in the glove box. Salicylaldehyde, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, potassium bis(trimethylsilyl)amide, and 2,6-di-isopropylaniline (Aldrich) were used as received. (2,6-*i*-Pr₂C₆H₃)N=C(H)C₆H₄OH [16] and U₄(1,4-dioxane)₂ [17] were made as previously described.

Caution! Depleted uranium (>99.5% ²³⁸U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years. All reactions were carried out in a fume hood or nitrogen atmosphere glove box in a radiation laboratory equipped with α - and β -counting equipment and inspected monthly for contamination.

4.1. Synthesis of $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^2(\text{O},\text{N})]_2\text{U}_2(\text{NCCH}_3)_2$, **2**.

In a 20-mL scintillation vial, potassium bis(trimethylsilyl)amide (70 mg, 0.351 mmol) was added to a stirred solution of (2,6-*i*-Pr₂C₆H₃)N=C(H)C₆H₄OH (100 mg, 0.330 mmol) in acetonitrile (10 mL). After 3 h, U₄(1,4-dioxane)₂ (150 mg, 0.163 mmol) was added.

The solution color immediately turned from orange to orange-brown. After 12 h, insoluble material, presumably potassium iodide, was removed by centrifugation and the volatiles removed under vacuum to yield an orange-brown solid. Orange crystals suitable for X-ray crystallographic analysis were grown from a saturated acetonitrile solution at $-25\text{ }^{\circ}\text{C}$.

4.2. Synthesis of $\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^2(\text{O},\text{N})]_2[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^1(\text{O})]_2\}(\text{THF})\text{U}$, 3

In a 20-mL scintillation vial, potassium bis(trimethylsilyl)amide (135 mg, 0.677 mmol) was added to a stirred solution of $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{OH}$ (200 mg, 0.659 mmol) in THF (10 mL). After 3 h, $\text{UI}_4(1,4\text{-dioxane})_2$ (150 mg, 0.163 mmol) was added. The solution color immediately turned from orange to red-brown. After 12 h, insoluble material, presumably potassium iodide, was removed by centrifugation and the volatiles removed under vacuum to yield a red-brown solid. Brown crystals suitable for X-ray crystallography analysis were grown from a saturated THF solution at $-25\text{ }^{\circ}\text{C}$.

4.3. Synthesis of $\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O}-\kappa^1(\text{O})]_6\text{U}\}\{\text{K}(\text{NCCH}_3)_6\}_2$, 4

In a 20-mL scintillation vial, potassium bis(trimethylsilyl)amide (200 mg, 1.00 mmol) was added to a stirred solution of $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{OH}$ (300 mg, 0.989 mmol) in acetonitrile (10 mL). After 3 h, $\text{UI}_4(1,4\text{-dioxane})_2$ (150 mg, 0.163 mmol) was added. The solution color immediately turned from yellow to red-brown. After 12 h, insoluble material, presumably potassium iodide, was removed by centrifugation and the volatiles removed under vacuum to yield a yellow-brown solid. Yellow crystals suitable for X-ray crystallography analysis were grown from a saturated acetonitrile solution at $-25\text{ }^{\circ}\text{C}$.

4.4. Crystallographic data collection and structure determination

The selected single crystal was mounted on a nylon cryoloop using viscous hydrocarbon oil. X-ray data collection was performed at 173(2) K. The X-ray data were collected on a Bruker CCD diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). The data collection and processing utilized Bruker Apex2 suite of programs. The structures were solved using direct methods and refined by full-matrix least-squares methods on F^2 using the Bruker SHELX-97 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were placed at calculated positions and included in the refinement using a riding model. Thermal ellipsoid plots were prepared using X-seed with 30% probability displacements for non-hydrogen atoms. Crystal data and detail for data collection for 2–4 are provided in table 1.

Acknowledgments

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

Disclosure statement

No potential conflict of interest was reported by the authors.

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