Isolation of U(II) Compounds Using Strong Donor Ligands, C5Me4H and N(SiMe3)2, Including a Three-Coordinate U(II) Complex

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Isolation of U(II) Compounds Using Strong Donor Ligands, C_5Me_4H and $N(SiMe_3)_2$, Including a Three-Coordinate U(II) Complex

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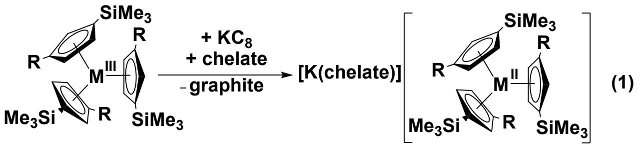
New examples of uranium in the formal +2 oxidation state have been isolated by reduction of Cp^{tet}_3U ($Cp^{tet} = C_5Me_4H$) and $U(NR_2)_3$ (R = $SiMe_3$) in the presence of 2.2.2-cryptand (crypt) to produce $[K(crypt)][Cp^{tet}_3U]$ and $[K(crypt)][U(NR_2)_3]$, respectively. Both complexes have properties consistent with $5f^36d^1$ electron configurations and demonstrate that the U(II) ion can be isolated with electron donating ligands.

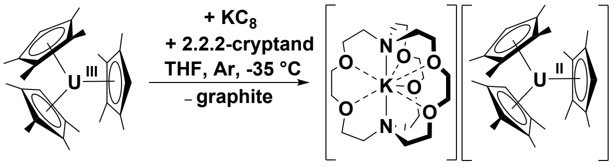
The initial discoveries of crystallographically-characterizable complexes of the new +2 ions of the rare-earth metals and the actinides involved complexes of three silyl-substituted cyclopentadienyl ligands like $C_5H_3(SiMe_3)_2$ (Cp″)[1-5] and $C_5H_4SiMe_3$ (Cp′),[6, 7] eq 1.[8, 9] Complexes of +2 ions were also isolated with the tris(aryloxide) mesitylene ligand, $[(^{Ad,Me}ArO)_3mes]^{3-}$,[10-12] and with complexes containing two alkyl-substituted cyclopentadienyl ligands, $C_5H_3(CMe_3)_2$ (Cp^{tt})[13, 14] and $C_5H_2(CMe_3)_3$ (Cp^{ttt}).[15, 16]



R = H, M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu, and U
R = $SiMe_3$, M = La, Ce, Pr, Th, U, Pu, and Np
chelate = 2.2.2-cryptand or 18-crown-6$(THF)_n$

A comparison of Cp″ vs Cp^{tt}, showed the more electron-donating ligand, Cp^{tt}, to be less effective in stabilizing the ions in the formal +2 oxidation state.[13, 14, 17] Consequently, it was surprising that crystallographically-characterizable rare-earth metal complexes of Ln(II) ions incorporating the electron donating ligands, $N(SiMe_3)_2$[18] and C_5Me_4H,[19] were recently obtained. It was therefore of interest to determine if these ligands would also form isolable complexes with U(II). This would demonstrate new targets for the isolation of complexes of +2 ions of the transuranic elements, Np,[5, 20-22] Pu,[4] Am, etc.

Reaction of a green-brown solution of Cp^{tet}_3U (Cp^{tet} = C_5Me_4H) in THF with a potassium smear generates a black solution from which $[K(crypt)][Cp^{tet}_3U]$, **1**, can be isolated in 38% crystalline yield, eq 2. The complex was definitively identified by X-ray crystallography, Figure 1.



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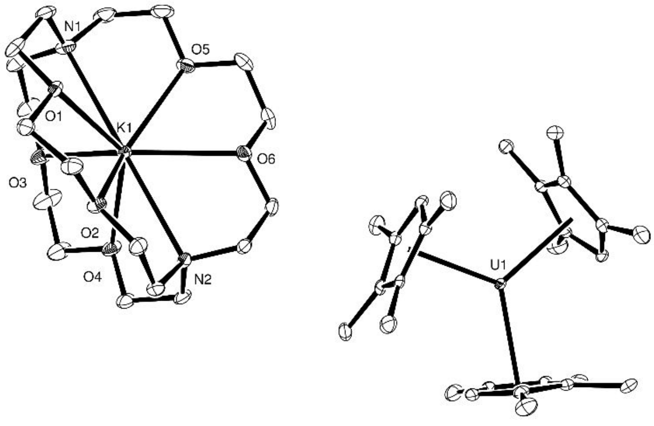

Figure 1. ORTEP representation of $[K(crypt)][Cp^{tet}_3U]$, **1**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Complex **1** crystallizes in the *C*2/*c* space group and is isomorphous with the rare-earth complex, $[K(crypt)][Cp^{tet}_3Sm]$.[19] The other members of the $[K(crypt)][Cp^{tet}_3Ln]$ series crystallize in different space groups,

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$P2_12_12_1$ (Ln = La, Ce), $P2_1/c$ (Ln = Pr, Nd, Gd, Tb), and R-3c (Ln = Dy).[19] The 2.564 Å average U–(Cp^{tet} ring centroid) distance in **1** is closer to the 2.563 Å analog in [K(crypt)][Cp$^{tet}_3$Nd], than to the 2.63 Å distance in the isomorphous [K(crypt)][Cp$^{tet}_3$Sm]. The ionic radius of uranium is usually considered to be in between those of La and Ce based on Shannon ionic radii for +3 ions, the lowest oxidation state available in the Shannon compilation.[23] Only the six-coordinate radius is published for U(III), 1.025 Å.[23] In comparison, the six coordinate radii for La(III), Ce(III), and Nd(III) are 1.032, 1.01, and 0.983 Å, respectively.[23] The metrical data for **1** raise the possibility that the lanthanide of closest size to uranium in the +2 ion series is not the same as in other oxidation states.

The 2.564 Å average U–(Cp^{tet} ring centroid) distance in **1** is 0.041 Å larger than that of Cp$^{tet}_3$U.[24] This difference is similar to the 0.045–0.058 Å differences observed between the 4f^{n}5d^1 [K(crypt)][Cp$^{tet}_3$Ln] complexes and Cp$^{tet}_3$Ln for Ln = La, Ce, Pr, Nd, Gd, and Tb. The 0.041 Å difference is smaller than the 0.147 and 0.099 Å differences for Ln = Sm and Dy, respectively, which have 4f^{n+1} configurations for the Ln(II) ions.[19] The small increase in size for **1** is consistent with a 5f^{3}6d^1 electron configuration[8, 9] as was found for [K(crypt)][Cp′$_3$U].[7]

The UV-visible spectrum of **1** is compared with those of [K(crypt)][Cp'$_3$U][7] [λ_{max}, nm (ε, M^{-1}cm^{-1}) 306(6200), 412(5000)] and [K(crypt)][Cp″$_3$U][25] [315(7500), 470(6000)] in Figure 2. The spectrum of **1** contains broadened absorption bands with less intensity and an absorption at lower energy, [λ_{max} = 790 nm with ε = 1800 M^{-1}cm^{-1}) that is not present in the spectra of the other U(II) complexes. The spectra of the [K(crypt)][Cp$^{tet}_3$Ln] complexes differ similarly compared to the [K(crypt)][Cp'$_3$Ln] complexes.[19] In contrast, the 5f^4 complex, [K(crypt)][((^{Ad,Me}ArO)$_3$mes)U],[10] has a single absorption at λ_{max} = 400 with ε = 750 M^{-1}cm^{-1}. Complex **1** is stable at −35 °C for weeks, but its dark color persists for only 4-5 h at room temperature. It therefore has intermediate stability compared to [K(crypt)][Cp′$_3$U][7] and [K(crypt)][Cp″$_3$U],[25] which have half-lives of 1.5 and 20 h, respectively, at room temperature in THF.

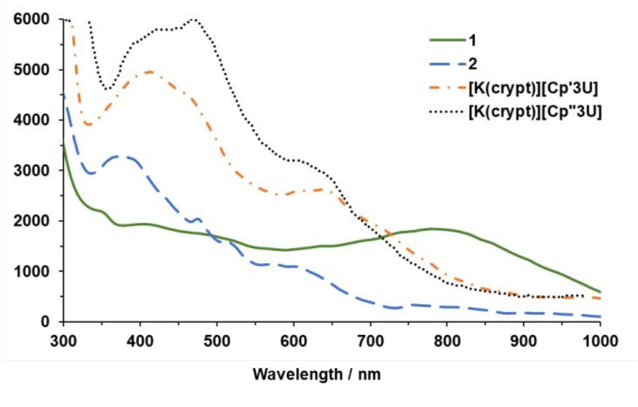
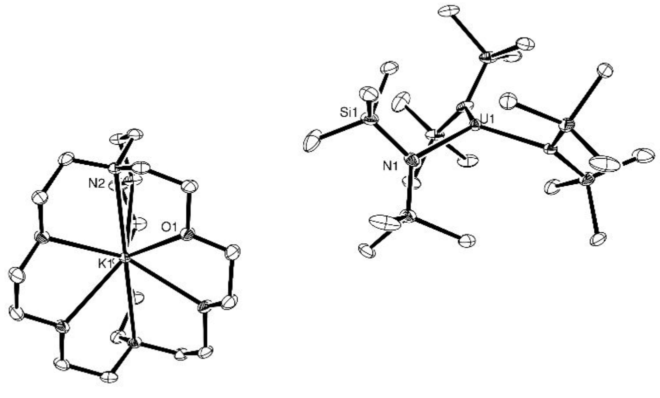


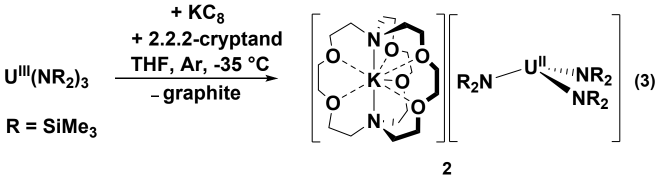
Figure 2. Experimental UV-Vis spectra of **1**,**2**, [K(crypt)][Cp′$_3$U],[7] and [K(crypt)][Cp″$_3$U][25] in THF at 293 K.

Reaction of a dark purple solution of U(NR$_2$)$_3$ (R = SiMe$_3$) with potassium graphite in the presence of crypt caused a color change to black. Crystals of [K(crypt)][U(NR$_2$)$_3$], **2**, were isolated in 47% yield and identified by X-ray crystallography, eq 3, Figure 3. Complex **2** crystallizes in the R32 space group and is not isomorphous with any [K(crypt)][Ln(NR$_2$)$_3$] complexes (Ln = Gd, Tb, Dy) or [Rb(crypt)][Ln(NR$_2$)$_3$] (Ln = Er, Ho, Tm) which crystallize in the P-1 space group and are all isomorphous with each other.[18] Complex **2** crystallizes with disorder in the position of the uranium atom above and below the N$_3$ plane similar to that observed in the [M(crypt)][Ln(NR$_2$)$_3$] analogs, Figure S1.[18]

The 2.373 Å average U–N distance in **2** is 0.052 Å longer than that in the U(III) analog, U(NR$_2$)$_3$,[26] 2.320 Å, which is consistent with a 5f^{3}6d^1 electron configuration.[8, 9] Complex **2** has a pyramidal structure with the metal 0.411 Å above the plane of the three nitrogen donors. This is similar to the structure of U(NR$_2$)$_3$ in which the metal is 0.456 Å above the N$_3$ donor atom plane.[26] The U(II) and U(III) amides are also similar in that the closest approach of a methyl carbon of the ligands to uranium in **2** is 3.029 Å for C(2). In comparison, the smallest U…C(Me) in U(NR$_2$)$_3$ is 3.046 Å.[26]

The UV-visible spectrum of **2**, Figure 2, shows multiple features on an absorption starting in the near IR region including peaks with λ_{max}, nm (ε, M^{-1}cm^{-1}) of 290 (4300), 380 (3700), and 600 nm (1100). In contrast, the [Ln(NR$_2$)$_3$]$^{1-}$ (Ln = Gd, Tb, Dy) anions display a single peak at 597-607 nm with ε = 1100–3500 M^{-1}cm^{-1}.[18] The differences between the spectra of **1** and **2** are similar to the differences observed in the Ln(II) complexes utilizing NR$_2$ and Cp^{tet} ligands.[18,19] The complicated nature of the spectra apparently arises from multiple absorptions of varying intensity depending on the specific system. As a result, the data may serve more as fingerprint than an indicator of electronic structure. . Compound **2** is stable for 2-4 hours at room temperature in THF.





$$\mathrm{U^{III}(NR_2)_3} \xrightarrow[\text{– graphite}]{\text{+ KC}_8,\ \text{+ 2.2.2-cryptand},\ \text{THF, Ar, -35 °C}} [\mathrm{K(crypt)}][\mathrm{U^{II}(NR_2)_3}] \quad (3)$$

R = SiMe$_3$

Figure 3. Thermal ellipsoids plot of [K(crypt)][U(NR$_2$)$_3$], **2**, drawn at the 50% probability level. Hydrogen atoms, disordered methyl groups, and the disorder in the uranium position are omitted for clarity.

Conclusions

In summary, crystallographically-characterizable complexes of +2 actinide ions are not limited to only $(Cp'_3)^{3-}$, $(Cp''_3)^{3-}$, and $[(^{Ad,Me}ArO)_3mes]^{3-}$ ligand sets: the electron-donating ligand sets $(Cp^{tet}_3)^{3-}$ and $[(NR_2)_3]^{3-}$ also form isolable complexes of U(II). The large size of the Cp^{tet} ligand leads to a longer U–(Cp^{tet} ring centroid) average distance, 2.564 Å, compared to the 2.521 Å U–(Cp′ ring centroid) analog in $[K(crypt)][Cp'_3U]$.[7] This can counteract the electron donating nature of the tetramethyl-substitution pattern as discussed previously for the $[K(crypt)][Cp^{tet}_3Ln]$ complexes.[19] However, in the three coordinate **2**, no analogous crowding is evident and it is clear that ligands with strong field donor atoms can form U(II) complexes.

Acknowledgments

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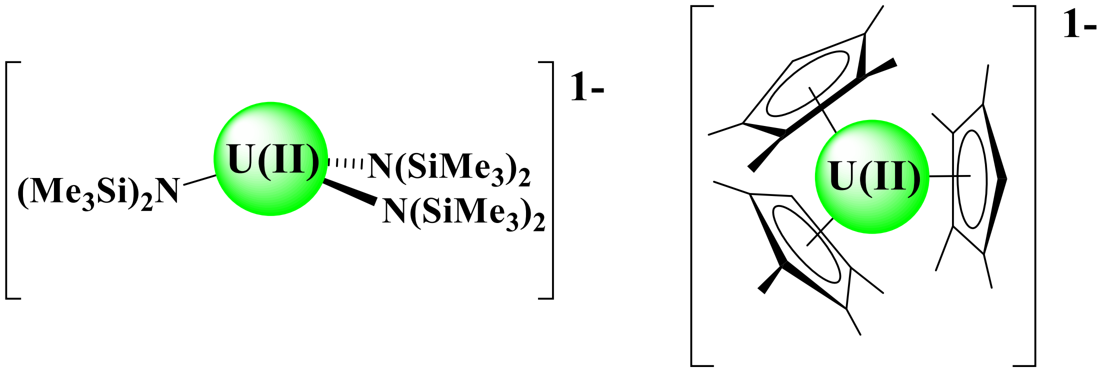
Conflicts of interest

There are no conflicts to declare

Notes and references

1. P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem. Int. Ed.*, 2008, **47**, 1488-1491.
2. R. R. Langeslay, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *Chem. Sci.*, 2015, **6**, 517-521.
3. C. J. Windorff, M. R. MacDonald, K. R. Meihaus, J. W. Ziller, J. R. Long and W. J. Evans, *Chem. Eur. J.*, 2016, **22**, 772-782.
4. C. J. Windorff, G. P. Chen, J. N. Cross, W. J. Evans, F. Furche, A. J. Gaunt, M. T. Janicke, S. A. Kozimor and B. L. Scott, *J. Am. Chem. Soc.*, 2017, **139**, 3970-3973.
5. J. Su, C. J. Windorff, E. R. Batista, W. J. Evans, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, D. H. Woen and P. Yang, *J. Am. Chem. Soc.*, 2018.
6. M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857-9868.
7. M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 13310-13313.
8. D. H. Woen and W. J. Evans, *Handbook on the Physics and Chemistry of Rare Earths*, 2016, **50**, 337-394.
9. W. J. Evans, *Organometallics*, 2016, **35**, 3088-3100.
10. H. S. La Pierre, A. Scheurer, F. W. Heinemann, W. Hieringer and K. Meyer, *Angew. Chem. Int. Ed.*, 2014, **53**, 7158-7162.
11. M. E. Fieser, C. T. Palumbo, H. S. La Pierre, D. P. Halter, V. K. Voora, J. W. Ziller, F. Furche, K. Meyer and W. J. Evans, *Chemical science*, 2017, **8**, 7424-7433.
12. C. T. Palumbo, D. P. Halter, V. K. Voora, G. P. Chen, A. K. Chan, M. E. Fieser, J. W. Ziller, W. Hieringer, F. Furche and K. Meyer, *Inorg. Chem.*, 2018, **57**, 2823-2833.
13. Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Organomet. Chem.*, 1995, **499**, 213-219.
14. M. C. Cassani, D. J. Duncalf and M. F. Lappert, *J. Am. Chem. Soc.*, 1998, **120**, 12958-12959.
15. F. Jaroschik, F. Nief, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, **26**, 1123-1125.
16. F. Jaroschik, A. Momin, F. Nief, X.-F. Le Goff, G. B. Deacon and P. C. Junk, *Angew. Chem.*, 2009, **121**, 1137-1141.
17. C. E. Zachmanoglou, A. Docrat, B. M. Bridgewater, G. Parkin, C. G. Brandow, J. E. Bercaw, C. N. Jardine, M. Lyall, J. C. Green and J. B. Keister, *J. Am. Chem. Soc.*, 2002, **124**, 9525-9546.
18. A. J. Ryan, L. E. Darago, S. G. Balasubramani, G. P. Chen, J. W. Ziller, F. Furche, J. R. Long and W. J. Evans, *Chem. Eur. J.*, 2018, **24**, 7702-7709.
19. T. F. Jenkins, D. H. Woen, L. N. Mohanam, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2018, DOI: 10.1021/acs.organomet.8b00557.
20. P. L. Arnold, M. S. Dutkiewicz and O. Walter, *Chem. Rev.*, 2017, **117**, 11460-11475.
21. M. S. Dutkiewicz, C. Apostolidis, O. Walter and P. L. Arnold, *Chem. Sci.*, 2017, **8**, 2553-2561.
22. M. S. Dutkiewicz, J. H. Farnaby, C. Apostolidis, E. Colineau, O. Walter, N. Magnani, M. G. Gardiner, J. B. Love, N. Kaltsoyannis and R. Caciuffo, *Nature chemistry*, 2016, **8**, 797-802.
23. R. Shannon, *Acta Cryst. A*, 1976, **32**, 751-767.
24. M. del Mar Conejo, J. S. Parry, E. Carmona, M. Schultz, J. G. Brennann, S. M. Beshouri, R. A. Andersen, R. D. Rogers, S. Coles and M. B. Hursthouse, *Chem. Eur. J.*, 1999, **5**, 3000-3009.
25. C. J. Windorff, M. R. MacDonald, K. R. Meihaus, J. W. Ziller, J. R. Long and W. J. Evans, *Chem. Eur. J.*, 2016, **22**, 772-782.
26. J. L. Stewart and R. A. Andersen, *Polyhedron*, 1998, **17**, 953-958.

Table of Contents Graphic:



Summary of Importance:

New examples of uranium in the +2 oxidation state have been isolated by reduction of $Cp^{tet}{}_3U$ (Cp^{tet} = C_5Me_4H) and $U(NR_2)_3$ (R = $SiMe_3$) , these results show that more donating ligands as well as lower coordination number complexes are viable for U(II) and suggest new targets for other An(II) complexes involving Np, Pu, and Am.