1070 *J. Am. Chem. Soc.* **1998,** *120,* 1070−1071

Communications to the Editor

Complex of Dinitrogen with Trivalent Uranium

Paul Roussel and Peter Scott*

Department of Chemistry, University of Warwick
Coventry CV4 7AL, U.K.

Received August 18, 1997

Metal complexes of dinitrogen are usually formed from low-valent precursors. For example, the two known lanthanide complexes of this highly discriminating ligand are derived from Sm(II) starting materials.[1] For the actinide elements, no dinitrogen complexes have been detected despite the availability of coordinatively unsaturated trivalent uranium compounds such as [U{N(SiMe$_3$)$_2$}$_3$][2] and the cyclopentadienyls [U{η^5-C$_5$H$_4$(SiMe$_3$)}$_3$] and [U(η^5-C$_5$Me$_4$H)$_3$] which form adducts with carbon monoxide.[3]

We have reported that reduction of tetravalent [U(NN′$_3$)Cl] (**1**) [NN′$_3$ = N(CH$_2$CH$_2$NSiBu^{t}Me$_2$)$_3$] gives the mixed valence species [{U(NN′$_3$)}$_2$-μ-Cl] (**2**) (Scheme 1).[4] This latter complex can be used as a source of the trivalent U(NN′$_3$) fragment giving, for example, the pentavalent imido complex [U(NN′$_3$)(NSiMe$_3$)] on reaction with trimethylsilyl azide. We had also noticed that exposure of purple pentane solutions of **2** to dinitrogen causes a color change to dark red. Unfortunately we could not separate the red material from the tetravalent coproduct **1**. Encouraged by recent reports of remarkable new dinitrogen chemistry,[5] and in particular the success of amido(metal) complexes in this area,[6] we set out to find a synthesis of "base-free" [U(NN′$_3$)].

Careful sublimation of **2** at 120 °C and 10^{-6} mbar affords a deep purple solid which we have characterized[7] as the trivalent complex [U(NN′$_3$)] (**3**).[8] When a sample of pure **3** in benzene-d_6 is placed under ca. 1 atm of dinitrogen, a color change from purple to red occurs and new peaks appear in the ^{1}H NMR spectrum corresponding to a species with 3-fold symmetry on this time scale. Increasing the pressure to slightly above 1 atm leads to essentially complete conversion to this new species. When the sample is freeze−thaw degassed, the intense purple color is regenerated and the ^{1}H NMR spectrum of **3** is again observed. So long as rigorously pure dinitrogen is used, this process may be carried out several times on the same sample with little or no decomposition of either **3** or the new complex. Exposure of a saturated pentane solution of **3** to dinitrogen and cooling to −20 °C gave dark red crystals of analytically pure [{U(NN′$_3$)}$_2$(μ^2-η^2:η^2-N$_2$)] (**4**), the first complex of dinitrogen with an actinide element.[9] In the solid state, crystalline samples of **4** are stable for at least 3 months when stored under an atmosphere of dinitrogen or argon.

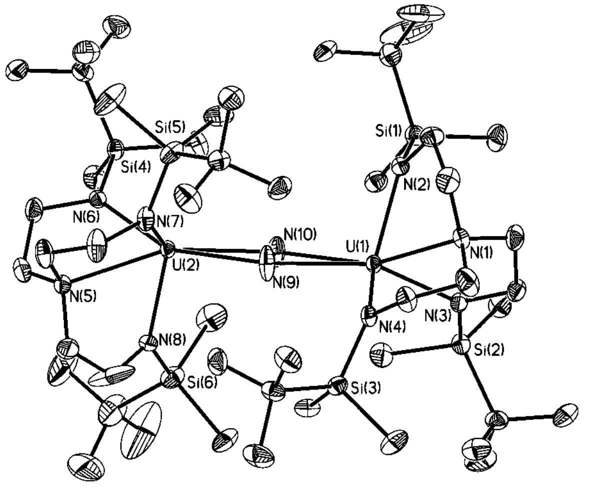
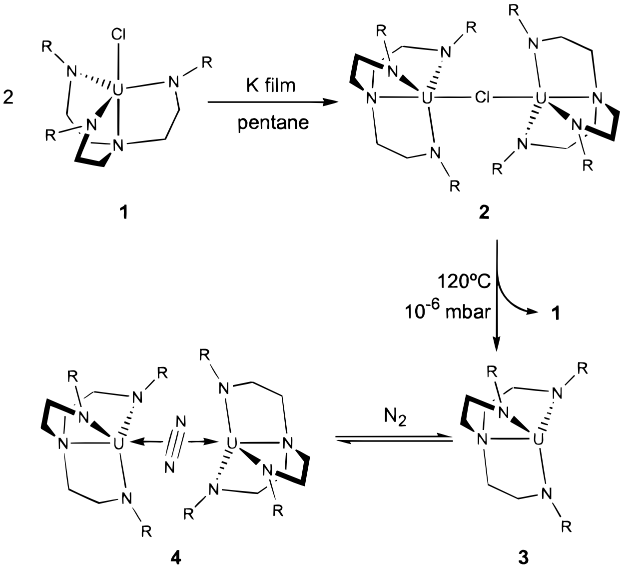


Figure 1. Thermal ellipsoid plot of the molecular structure of **4** (hydrogen atoms omitted).

Scheme 1. Synthetic Route to **4** (R = SiBu^{t}Me$_2$)



The molecular structure of **4** (Figure 1) shows that the dinitrogen ligand is bound in a side-on bridging mode between

---

[1] (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877−6879. (b) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477−4478.

[2] Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507.

[3] (a) Brennen, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335−336. (b) Parry, J.; Camona, E.; Coles, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649−2650.

[4] Roussel, P.; Hitchcock, P. B.; Tinker, N. D.; Scott, P. *Chem. Commun.* **1996**, 2053.

[5] (a) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445−1447. (b) Shan, H.; Young, Y.; James, A. J.; Sharp P. R. *Science* **1997**, *275*, 1460.

[6] (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861−863. (b) O'Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 2753−2754.

[7] Characterizing data for **3**. Anal. Calcd for C$_{24}$H$_{57}$N$_4$Si$_3$U: C, 39.81; H, 7.93; N, 7.73. Found C, 39.14; H, 7.73; N, 7.44. ^{1}H NMR (benzene-d_6, $w_{1/2}$ = ca. 30 Hz): δ 26.6 (s, 6H, CH$_2$), 9.9 (s, 27H, Bu^t), −5.6 (s, 18H, Me$_2$Si), −38.5 (s, CH$_2$, 6H) MS (EI): *m/z* 723 (100%, M$^+$), 685 (15, M$^+$ − Bu^t) IR (Nujol): 1377 (w), 1345 (w), 1247 (m), 1123 (m), 1077 (w), 1038 (w), 1005 (w), 957 (w), 936 (s), 915 (s), 823 (s), 807 (s), 771 (s), 722 (s), 649 (w) UV λ_{max} (ϵ M^{-1} cm^{-1}) (pentane): 337 (2254), 538 (1390), 680 (843), 775 (573), 832 (302), 855 (260) nm. We cannot exclude the possibility that **3** exhibits an agostic interaction at the apical coordination site.

[8] At 180 °C, pale green **1** can be recovered.

[9] Characterizing data for **4**. Anal. Calcd for C$_{48}$H$_{114}$N$_{10}$Si$_6$U$_2$: C, 39.06; H, 7.78; N, 9.49. Found C, 39.14; H, 7.82; N, 9.62. ^{1}H NMR (benzene-d_6, $w_{1/2}$ = ca. 30 Hz): δ 10.8 (s, 6H, CH$_2$), 7.76 (s, CH$_2$, 6H), 3.79 (s, 27H, Bu^t), −20.81 (s, 18H, Me$_2$Si) MS (EI): *m/z* 723 (100%, M$^+$), 685 (15, M$^+$ − Bu^t) IR (Nujol): 1378 (s), 1345 (s), 1287 (w), 1247 (s), 1122 (s), 1077 (s), 1038 (m), 1005 (m), 957 (s), 937 (s), 826 (s), 736 (m), 649 (m) UV λ_{max} (ϵ M^{-1} cm^{-1}) (pentane): 535 (1034), 680 (608), 775 (415), 832 (230), 856 (201).

S0002-7863(97)02933-8 CCC: $15.00

two uranium centers.[10] The (triamidoammine)uranium fragments are of approximate trigonal monopyramidal geometry and are arranged in a mutually staggered conformation as found for **2**.[4] The uranium atoms sit out of the planes defined by the three respective amido nitrogen atoms by ca. 0.84 and 0.85 Å. The apical amino N−U bond lengths of 2.555(5) and 2.601(5) Å are unexpectedly short compared to those in tetravalent $U(NN'_3)$ complexes (ca. 2.7 Å)[11] and in **2** [2.78(2) Å]. The U−N(dinitrogen) bonds of between 2.39 and 2.44 Å, are slightly longer than typical U−N(amido) distances of ca. 2.28 Å. In contrast, the Sm−N bond lengths in $[\{Cp^*_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ are similar to those observed in $Sm(III){-}NR_2$ compounds. The N−N bond length in **4** of 1.109(7) Å is essentially the same as that found in dinitrogen gas (1.0975 Å).[12]

As is expected for this symmetric complex, $^{14}N_2$-**4** and $^{15}N_2$-**4** gave superimposable IR spectra. We have thus far been unable to obtain reliable Raman spectra of these isotopomers. The UV/visible spectrum of **4** is virtually indistinguishable from that of **3**, with intense broad bands typical of trivalent uranium complexes.[13] Similarly, the solution magnetic susceptibility of **4** measured by the Evans method is 3.22 μ_B *per* uranium atom between 218 and 293 K compared to the value for **3** of 3.06 μ_B in the same temperature range.

From these data it does not appear that coordination of dinitrogen to **3** leads to an increase in the valence number (formal oxidation state) of the uranium centers. In contrast, ^{13}C NMR spectroscopic data for $[\{Cp^*_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ are consistent with the presence of Sm(III).[1a] Similarly, $[\{Mo(NN'_3)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)]$ contains a diazenido (N_2^{2-}) ligand and tetravalent molybdenum.[14]

In the end-on coordination mode of dinitrogen at transition metals, two filled metal π-orbitals are utilized in M→N back-bonding. The less commonly observed side-on mode occurs where only one metal π- and one δ-orbital are available.[15] The end-on mode is favored where possible over side-on by virtue of the fact that π-overlap is considerably more efficient than δ. Although there does not appear to be significant M−L π-donation in lanthanide complexes such as $[Cp^*_2Yb(\eta^2\text{-}MeCCMe)]$,[16] Bursten has argued that, for trivalent uranium, increased 5f-orbital extension can lead to significant covalent bonding character.[17] The short N−N bond length in **4** suggests that it contains what are essentially $N_2 \rightarrow U$ σ-bonds and that $[U(NN'_3)]$ is acting as an extremely potent Lewis acid. However, since **4** is a 1:2 complex, the dinitrogen ligand in the unobserved 1:1 intermediate $[U(NN'_3)(N_2)]$ is clearly more basic than free dinitrogen, arguing for some degree of $U \rightarrow N_2$ back-bonding. Nevertheless, this interaction is evidently small. We suggest that the preference for side-on over end-on bonding may be explained on the basis that the dinitrogen π_p orbital is a better σ-donor than the σ_p to trivalent uranium.

Acknowledgment. P.S. thanks the Royal Society for a Research Grant, the Nuffield foundation for a Newly Appointed Science Lecturers Award, EPSRC for a Project Studentship, and BNFL for a CASE award (to P.R.).

Supporting Information Available: Tables of crystal data, structural refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **4** (10 pages). See any current masthead page for ordering and Internet access instructions.

JA972933+

---

(10) Crystal data for **4**: $C_{48}H_{114}N_{10}Si_6U_2$, $M = 1476.09$, monoclinic, space group $P2_1/n$, $a = 19.549(2)$ Å, $b = 16.2751(14)$ Å, $c = 21.517(2)$, $\beta = 105.611(3)°$, $U = 6593.2(5)$ Å^3, $Z = 4$, $D_c = 1487$ Mg/m^{-3}, $F(000) = 2960$, dark red air-sensitive block 0.24 × 0.20 × 0.12 mm, final $R1$, $wR2$, and S were 0.0494, 0.0756, and 1.023.

(11) Roussel, P.; Scott, P. Unpublished results.

(12) Wilkinson, P. G.; Houk, N. B. *J. Chem. Phys.* **1956**, *24*, 528.

(13) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248−2256.

(14) Shih, K. Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804−8805.

(15) Fryzuk, M. D.; Haddad, T. S.; Mylvaganan, M.; McConville, D. H.; Rettig, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 2782−2792.

(16) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941−942.

(17) Bursten, B. E.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6606−6608.