Uranium–Metal Bonds

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# σ and π Donation in an Unsupported Uranium–Gallium Bond**

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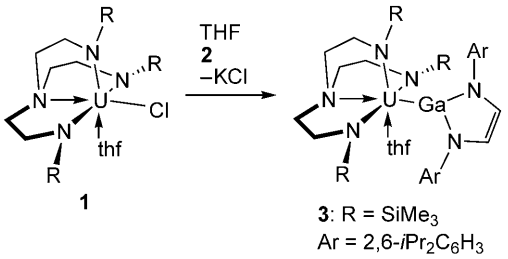
The majority of the elements in the Periodic Table are metals. Therefore, the study of molecular compounds that exhibit metal–metal bonds is fundamental to furthering our understanding of structure and bonding, catalysis, metal surface chemistry, and magnetism.[1] The recognition of $Re^{III}$–$Re^{III}$ quadruple bonding[2] showed that the study of metal–metal bonds is fertile territory for the identification of novel types of bonding. This is exemplified by landmark results such as a $Zn^{I}$–$Zn^{I}$ bond,[3] $Cr^{I}$–$Cr^{I}$ quintuple bonds,[4] and $Mg^{I}$–$Mg^{I}$ bonds.[5]

The study of the actinides is a challenging yet essential frontier; its development requires a fundamental understanding of the roles played by the valence region orbitals in chemical bonding since there is continued debate over the extent of covalency in f-element bonding. For example, structurally authenticated complexes between uranium and carbon dioxide,[6] carbon monoxide,[7] dinitrogen,[8] arenes,[9] and alkanes[10] are known, most of which exhibit f-orbital/ligand interactions. This is relevant to nuclear waste separation because ligands that engage in covalent bonding have been shown to be selective in the extraction of actinides over lanthanides in solution.[11] However, despite the propensity of molecular metal–metal complexes to demonstrate novel bonding, complexes that contain unsupported uranium–metal bonds are rare even though novel bonding manifolds have been predicted.[12] Only two examples of molecular uranium–metal bonds have been structurally authenticated,[13] namely the heavy-alkyl complex $[(C_5H_5)_3U\text{–}SnPh_3]$,[14] and the donor–acceptor complex $[(C_5H_4SiMe_3)_3U\text{–}Al(C_5Me_5)]$.[15] Motivated by recent reports of lanthanide–gallium bonds by some of us,[16] we targeted a U–Ga bond because Group 13 diyl species have the potential to engage in π-donor and π-acceptor bonding depending on the Group 13 substituents. However, π bonding has not yet been observed in any Group 13/f element bonds.[15–17] Herein, we report the first molecular compound to feature a U–Ga bond which, in addition to the expected σ donation, exhibits the first example of Group 13/f element π donation (Scheme 1).




***Scheme 1.*** Synthesis of **3**.

The new uranium(IV) complex [(tren–TMS)UCl(thf)] (**1**, tren–TMS = $[N(CH_2CH_2NSiMe_3)_3]$)[18] was prepared as a precursor to a U–Ga bond.[19] In some reactions, insertion of gallyl species into metal–halide bonds is followed by reductive elimination to afford gallium(II)–halide species.[20] Therefore, the tren ligand scaffold was chosen for uranium because it has been shown to be effective for supporting tetravalent uranium[21] and tetravalent cerium.[22] Reaction of **1** with $[\{Ga(NArCH)_2\}K(tmeda)]$ (**2**; Ar = 2,6-*i*$Pr_2C_6H_3$, tmeda = $Me_2NCH_2CH_2NMe_2$)[23] affords, after workup and recrystallization, orange crystals of [(tren–TMS)U{$Ga(NArCH)_2$}(thf)] (**3**) in high yield (Scheme 1).[19]

The elemental analysis and $^1$H NMR spectrum of **3** supports the proposed formulation (although the carbon analysis was consistently low by ca. 3%, which we attribute to partial desolvation); the latter exhibits paramagnetically shifted resonances in the range from +20 to −45 ppm, which is typical of tetravalent uranium–tren compounds.[18,21] Resonances attributable to hydrides were not observed and treatment of a solution of **3** in $C_6D_6$ with 1–5 equivalents of $CCl_4$ did not result in the formation of $CHCl_3$. In the IR spectrum of **3**, the region where bridging hydrides would be expected[24] is silent, except for an absorption at 1587 $cm^{-1}$ which is characteristic of the gallyl heterocycle. Whilst the molecular ion of **3** was not seen in the EI mass spectrum, $[M^+]$-THF was observed at $m/z$ 1043 (10%).

The X-ray single-crystal structure of **3**,[19,25] shows a distorted octahedral uranium center; the three amido centers of the tren ligand adopt a mer conformation, and the Ga center resides trans to the tertiary amine; a molecule of THF completes the coordination sphere of uranium (Figure 1). Two molecules are present in the asymmetric unit of the

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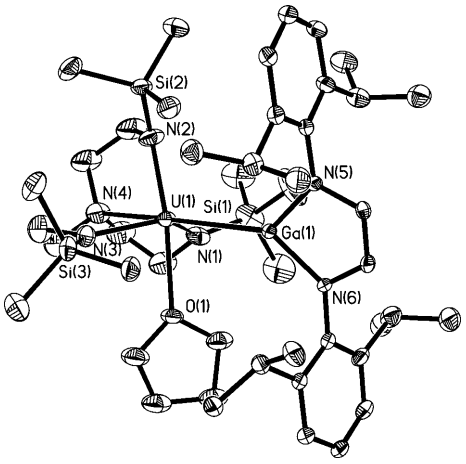


***Figure 1.*** Molecular structure of **3**. Thermal ellipsoids are set at 30% probability and hydrogen atoms are omitted for clarity.

crystal. The data were carefully checked to confirm the absence of a crystallographic relationship. The metrical parameters of each molecule are very similar except, interestingly, the U–Ga bond lengths are significantly different, at 3.2115(8) and 3.2983(9) Å for U(1)–Ga(1) and U(2)–Ga(2), respectively. These values are without precedent, but the lower value compares well to the sum of covalent radii (U–Ga=3.18 Å).[26] The difference between the two observed U–Ga bond lengths is 0.0868(8) Å, but it is now well established that post-second-row elements do not always obey classic bond length–strength relationships.[27] The recognition of "long-bond" organometallic species[28] exemplifies an "elastic" quality for f-element bonds, and we propose that the "soft" U–Ga bond is easily disturbed by crystal packing forces. Unfortunately, we have been unable to obtain X-ray quality crystals of **3** in a different habit from other solvents. The average $U–N_{amido}$ and $U–N_{amine}$ bond lengths of 2.245(7) and 2.648(7) Å, respectively, are indicative of $U–N_{amido}$ and $U–N_{amine}$ bonds.[29] The $U–O_{thf}$ bond lengths are unexceptional. The metrical, geometrical, and spectroscopic evidence essentially rules out the possibility of bridging hydrides.

Variable-temperature magnetic moment measurements on a powdered sample of **3** showed it to have a magnetic moment of 0.38 $\mu_B$ at 1.8 K, which increases smoothly to 2.46 $\mu_B$ at 300 K (Figure 2). This is significantly below the

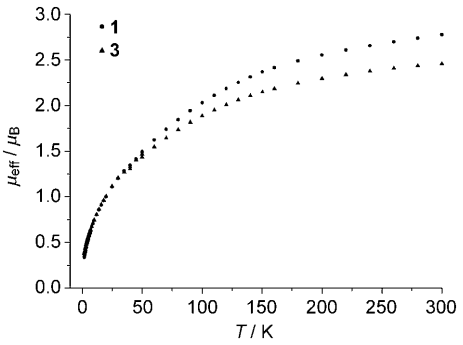


***Figure 2.*** Variable-temperature magnetic moment measurements for **1** and **3**.

theoretical free-ion value of 3.58 $\mu_B$ expected for the $^3H_4$ ground state of $f^2$ uranium,[30] which indicates a quenching of spin–orbit coupling by low symmetry and/or significant covalency at the uranium center. Uranium(IV) compounds typically exhibit magnetic moments in the range 2.5–2.9 $\mu_B$ at 300 K.[31] We therefore carried out calculations on a model of **3** (**3a**), which has some peripheral groups necessarily pruned for computational efficacy.[19]

The principal features of the molecule in the crystal structure of **3**, which exhibits the shorter U–Ga bond, are reproduced well in **3a**. Thus, we conclude that the calculations provide a qualitative description of the electronic structure of **3**. Mulliken population analysis shows that the spin density on U(1) (+2.4795) is above that for a formal $5f^2$ $U^{IV}$ center and this, together with the small negative spin densities across the O (−0.0145) and N atoms (average −0.0541 amide; −0.0176 amine) centers in **3a**, is consistent with charge donation from the ligands. A spin density less than +2 for U(1) would indicate metal-to-ligand charge transfer so we can effectively rule out π-type back donation in **3a**. The Mulliken charge of +1.5948 for U(1) is considerably less than the charge of +4 expected for a $U^{IV}$ center, which indicates significant charge donation from the ligands.

The Mayer bond orders reveal a U–Ga bond order (0.722) that is similar in magnitude to that of the $U–N_{amide}$ bonds (average 0.712) and which is significantly greater than the dative $U–N_{amine}$ bond (0.278) that lies trans to the U–Ga bond. We examined the U–Ga bond in **3a** by using an energy decomposition analysis, which gave a calculated U–Ga bond energy of −408.47 kJ mol$^{-1}$; whilst there is a strong electrostatic contribution to the U–Ga bond, there is also a significant orbital contribution; these interactions contribute 72 and 28%, respectively, to the total attractive interaction.

The four highest occupied α-spin frontier orbitals of **3a** are shown in Figure 3. The highest occupied molecular orbitals (HOMO; 210*a*) and HOMO-1 (209*a*) are localized on uranium and these two singly occupied molecular orbitals (SOMO) possess essentially 5f orbital character consistent with a $^3H_4$ $U^{IV}$ center.[30] The α-spin Kohn–Sham HOMO-2 (208*a*) and HOMO-3 (207*a*) orbitals, together with their β-spin counterparts, are the principal molecular orbitals involved in the U–Ga bond. HOMO-3 contains Ga 4s (13%), Ga $4p_z$ (10%), U $6d_{z^2}$ (3%), U $7p_z$ (2%), U 7s (2%), and U $5f_{z^3}$ (2%) character, and can be considered as σ donation from a sp lone pair of electrons on Ga into vacant valence orbitals of U. Of greater significance is HOMO-2, which contains Ga $4p_y$ (17%), C $2p_y$ (24%), N $2p_y$ (22%), U $5f_{z^2y}$ (20%), and U $6d_{yz}$ (2%) character and involves π donation from a filled π orbital from the Ga heterocycle principally into the empty U $5f_{z^2y}$ orbital.

N-heterocyclic carbenes (NHCs) are valence isoelectronic and isolobal to **2**. NHCs do not require π backbonding, but it has been observed.[32] Recently, the capacity of NHCs to engage in π donation has been recognized,[33] and **3** suggests that carbene π donation might be more widespread than previously recognized, but this contrasts with calculations on lanthanide–NHCs,[34] which do not exhibit π-donor character. However, this raises the possibility that the selectivity of NHCs for uranium over lanthanides could originate from a

  

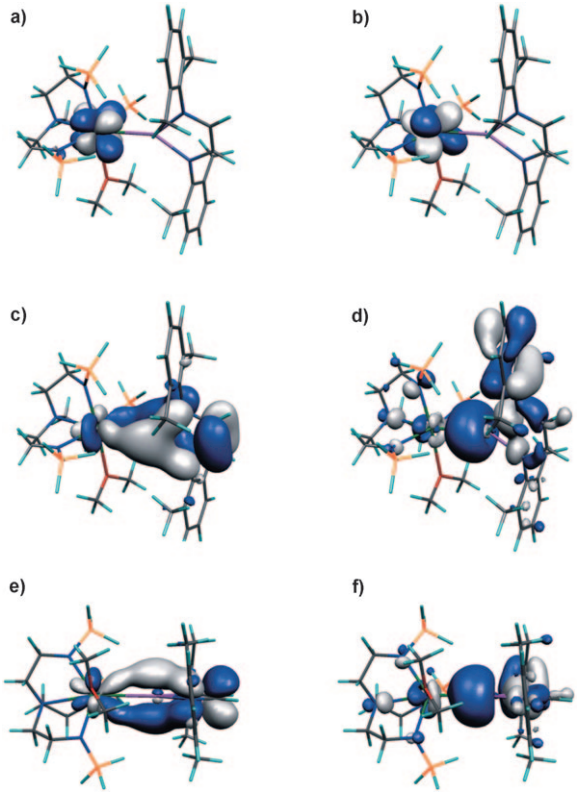


***Figure 3.*** Kohn–Sham α-spin frontier orbitals of **3a**: a) HOMO (−2.891 eV), b) HOMO-1 (−2.945 eV), c) HOMO-2 (−3.118 eV), d) HOMO-3 (−4.913 eV), e) side view of HOMO-2, and f) side view of HOMO-3.

selective π-donor phenomenon.[11] The π-donor character present in the U–Ga bond in **3** contrasts with previously reported U–Al[15] and Nd–Ga[16] bonds which do not exhibit π acceptor or π donor components, respectively. This underscores the differences between dative donor–acceptor and polar-covalent uranium/Group 13 bonds, and neodymium (4f)/Group 13 versus uranium (5f)/Group 13 bonds. The fact that the U–Ga bond in **3a** is mainly electrostatic in nature and therefore perturbable[28] may explain the presence of two different U–Ga bond lengths in the crystal structure of **3**. Finally, **2** is isolobal to CO and **3** can tentatively be regarded as an analogue of the $U^{IV}$–$CO^{-\bullet}$ unit which, in contrast to $U^{III}$–CO[7b,c] and $U^{IV}$–$OCO^{-\bullet}$,[6] is yet to be isolated, although it has been reported to be present in a CO-bridged mixed-valence $U^{III}/U^{IV}$ dimer,[7a] and is strongly implicated in the reductive oligomerization of CO by $U^{III}$.[35]

To conclude, we have reported the first polar, covalent uranium/Group 13 bond (**3**) which exhibits the first example of Group 13/f element π donation in addition to σ donation. **3** may be regarded as a model for the unknown $U^{IV}$–$CO^{-\bullet}$ unit, and suggests that π donation by carbene-type fragments may be more widespread than previously recognized.

## Experimental Section

THF (20 mL) was added to a mixture of **1** (1.06 g, 1.5 mmol) and **2** (0.91 g, 1.5 mmol) at −78 °C with stirring. The mixture was allowed to warm to room temperature and stirred for 20 h. The volatile components were removed and the red residue was extracted into toluene, filtered, and the volatile components removed. The red solid was extracted into hexane (10 mL), filtered, and concentrated. Storage at −30 °C overnight afforded **3** as orange blocks. Yield: 1.19 g, 71 %. m.p. 120–122 °C (decomp); $^1$H NMR ($C_6D_6$, 295 K): $\delta$ = 19.82 (4H, s, br, thf), 15.96 (6H, s, br, $CH_2$), 9.96 (27H, s, br, $SiMe_3$), 7.06 (2H, s, *para*-CH), 5.98 (4H, s, CH), 3.66 (2H, s, CH), 2.10 (4H, s, br, CH), −1.44 (12H, s, Me), −3.05 (12H, s, Me), −10.45 (6H, s, $CH_2$), −43.51 ppm (4H, s, br, THF); FTIR (Nujol): $\tilde{\nu}$ = 678.7 (m), 722.1 (m), 744.1 (m), 758.8 (m), 772.0 (m), 801.25 (m), 836.5 (s), 900.9 (s), 929.3 (s), 1021.7 (m), 1059.2 (m), 1142.9 (m), 1179.4 (w), 1210.9 (w), 1259.0 (s), 1587.9 (w); (MS/EI): *m*/*z* (%) 378 (61) [$DABH_2^+$], 379 (25) [$DABH_3^+$], 445 (79)[$DABGa^+$], 446 (40) [$DABGaH^+$], 447 (64) [$DABGaH_2^+$], 892 (25) [$(DABGa)_2^+$], 895 (5) [$M^+$−3$SiMe_3$−H], 1043 (10) [$M^+$−THF]; elemental analysis calcd (%) for $C_{45}H_{83}GaN_6OSi_3U$: C 48.42, H 7.50, N 7.53; found: C 45.89, H 7.23, N 7.22.

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[25] Crystal data for **3**: $C_{46.75}H_{85}GaN_6OSi_3U$, $M = 1139.23$, monoclinic space group $P2_1/c$, $a = 19.9862(14)$, $b = 13.0182(9)$, $c = 44.033(3)$ Å, $\beta = 97.329(2)°$, $V = 11363.0(14)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.332$ g cm$^{-3}$; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 3.420$ mm$^{-1}$, $T = 150$ K. 46118 reflections (14816 unique reflections, $R_{int} = 0.0555$, $\theta < 22.50°$) were collected on a Bruker SMART APEX CCD diffractometer using narrow frames (0.3° in ω) and were corrected semiempirically for absorption (transmission 0.47–0.66). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ values of all data (G. M. Sheldrick, SHELXTL manual, Bruker AXS, Madison, WI, USA, **1997**) to give $wR2 = 0.1139$ and $R = 0.0466$ for $F$ values of 11774 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.04$ for 1068 parameters. Residual electron density extremes were 1.181 and −1.324 e Å$^{-3}$. CCDC 693901 **1** and 693900 **3** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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