Dinuclear Trivalent and Mixed-Valence Uranium $[(-CH_2-)_5]_4$-calix[4]tetrapyrrole Complexes with Short Intermetallic Distances

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A dinuclear trivalent uranium complex (**1**) and a mixed-valence U(III)/U(IV) complex (**2**) have been prepared by using the $[(-CH_2-)_5]_4$-calix[4]tetrapyrrole tetraanion. Both compounds display unusually short U−U distances with two metals held together by the bridging tetraanion, where each pyrrole ring adopts the η^1:η^5 bonding mode. Both magnetic measurements at variable temperature and DFT calculations carried out on the trivalent **1** indicate the existence of antiferromagnetic coupling between the two metal centers as the only significant U−U interaction.

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Introduction

Tremendous reactivity featuring the most disparate performances in terms of molecular activation is a distinctive characteristic of the chemistry of low-valent lanthanides and actinides.[1] The strong reducing power of these species enables a broad spectrum of reactivity targeting solvents,[2] nitrogen gas,[3] and a large variety of chemical functions.[4] This high level of reactivity is closely reminiscent of the behavior of low-valent early transition metals.[5] However, in the case of these species, and particularly with second- and third-row derivatives, the stabilization of the low state may be also achieved via direct M−M interaction[6] (either M−M bonds or magnetic couplings) rather than via oxidative addition to a substrate. This behavior is not observed in the chemistry of lanthanides and actinides, presumably because of the inefficient overlap of the f orbitals. Accordingly, lanthanides and actinides only seldom display short intermetallic distances[7,8] while aggregated in dinuclear or cluster structures.

Following our interest for the reactivity of f-block metals with dinitrogen,[3d−h] we have recently embarked on a study of the chemical reactivity of trivalent uranium supported by polypyrrolide polyanions. In fact, these particular ligands have allowed us to gain some understanding of the behavior of divalent samarium with dinitrogen[3d,e,g] and have shown the ability not only to stabilize the low-valent state but also to significantly enhance the reactivity of the metal center.

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In this paper we describe the results of our attempts to prepare a trivalent uranium complex of the $[(-CH_2-)_5]_4$-calix[4]tetrapyrrole ligand.[9] Rather than affording the expected dinitrogen fixation, the reaction afforded an unusual dinuclear compound where the ligand system holds together two trivalent uranium centers at short proximity. Given the size of trivalent uranium, these intermetallic contacts might be considered in the M−M bonding range. Herein we describe our findings.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenk type techniques. $UI_3(THF)_4$,[11] UCl_4,[12] and $\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}[Li(THF)]_4$[1c,3d] were prepared according to published procedures. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox.

Samples for magnetic susceptibility measurements were preweighed inside a drybox equipped with an analytical balance and flame-sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out using a Quantum Design MPMS5S SQUID magnetometer at 1.0 T, in the temperature range 2−300 K. The accurate sample mass was determined by difference by breaking the tube after data collection. Background data on the cleaned, empty tube were obtained under identical experimental conditions. Standard corrections for underlying diamagnetism were applied to the data.[13] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Electronic structure calculations employing density functional theory (DFT) were performed on the model anionic U dimer complex $[(TP)U_2I_4]^{2-}$ compound, in which the bridging $C(CH_2)_5$ cyclohexyl substituents were replaced by CH_2 units. Relativistic effective core potentials (RECP) on the U atoms[14,15] replaced the 78 inner core electrons, leaving the 6s, 6p, 6d, 5f, and higher shells as valence electrons represented by a [3s3p2d2f] basis. For **1** the RECP replaced all but the outer 5s and 5p electrons described by the LANL2DZ basis.[16] A 6-31G basis was used on the remaining atoms. Hybrid DFT calculations employing the B3LYP functional[17,18] were carried out using the Gaussian98 program.[19]

Preparation of $[Li(THF)_4]_2\{U_2[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}[\mu$-I$]_4$ (1). A solution of $UI_3(THF)_4$ (5.6 g, 6.2 mmol) in THF (70 mL) was reacted with $[Li(THF)]_4\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$ (1.9 g, 3.1 mmol). Upon mixing, the solution immediately turned dark emerald green. Stirring was continued for 10 h, after which a small mount of light-colored material was removed by centrifugation. The solution was concentrated to small volume (35 mL) and allowed to stand overnight at −36 °C, upon which dark green crystals of **1** separated (4.4 g, 2.0 mmol, 66%). Anal. Calcd. (found) for $Li_2U_2C_{72}H_{112}N_4O_8I_4$: C, 40.05 (39.88); H, 5.23 (5.19); N, 2.59 (2.43). IR (Nujol mull, cm^{-1}): ν 1286 (m), 1264 (w), 1233 (w), 1182 (w), 1134 (w), 1043 (s), 985 (w), 890 (s), 874 (m), 833 (w), 773 (s), 722 (w), 669 (w), 589 (w).

Preparation of $[Li(THF)_2](\mu$-Cl$)_2\{U_2[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}Cl_2\cdot$THF (2). A solution of potassium naphthalenide was prepared by stirring metallic potassium (0.3 g, 7.1 mmol) in a solution of naphthalene (0.9 g, 7.1 mmol) in THF (50 mL). The resulting dark green solution was combined with a green solution of UCl_4 (5.3 g, 14.0 mmol) in THF (50 mL). The resulting mixture immediately turned dark red upon mixing while a dark precipitate separated. The suspension was stirred for an additional 3 h and then treated with a solution of $[Li(THF)]_4\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$ (6.16 g, 7.0 mmol) also in THF (60 mL). The color of the reaction mixture changed through dark rose to dark green, and stirring was continued overnight. The resulting mixture was centrifuged to eliminate some colorless material, and the resulting solution was concentrated (40 mL) and allowed to stand in the freezer (−37 °C) overnight, upon which dark green crystals of **2** separated (8.4 g, 5.9 mmol, 84%). Anal. Calcd (found) for $LiU_2C_{52}H_{72}N_4O_3Cl_4$: C, 43.80 (43.54); H, 5.09 (5.00); N, 3.93

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Table 1. Summary of Crystallographic Data for Compounds 1 and 2

	1	2
formula	$Li_2U_2I_4C_{72}H_{112}N_4O_8$	$LiU_2Cl_4C_{52}H_{72}N_4O_3$
fw	2159.3	1425.9
cryst syst	tetragonal	monoclinic
space group	$I4_1/acd$	$P2_1/n$
a, Å	18.344(2)	12.115(1)
b, Å	18.344(2)	16.211(1)
c, Å	47.367(7)	27.406(2)
α, deg	90	90
β, deg	90	99.415(2)
γ, deg	90	90
Z	16	4
V, Å^3	15 938(3)	5309.6(8)
density (calcd), Mg/m^3	1.800	1.784
abs coeff, mm^{-1}	5.660	6.338
F(000)	8304	2764
no. of rflns collected	126 426	40 895
no. of indep rflns	3405	12 527
GOF	1.001	1.043
R1	0.0414	0.0473
wR2	0.0986	0.1147

(3.87). IR (Nujol mull, cm^{-1}): ν 1343 (m), 1294 (m), 1248 (m), 1178 (m), 1038 (s), 1000 (s), 95 (w), 917 (s), 887 (s), 837 (s), 782 (w), 721 (m), 675 (s).

X-ray Crystallography. Suitable crystals were selected, mounted on thin glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[20] Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library.[21] It is worth mentioning that, in the structure of **1**, the anion is located on a crystallographic site of $\bar{4}$ symmetry while the two uranium atoms are on the 2-fold axis. This provides a rare case of the S_4 point group. The space group No. 142 is also rare. Crystal data and relevant bond distances and angles are given in Tables 1 and 2, respectively.

Results and Discussion

Synthesis and Structures. The reaction of $UI_3(THF)_4$ with $[Li(THF)]_4\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole} afforded air-sensitive, dark green crystals of the dinuclear $[Li(THF)_4]_2[U_2I_4\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole}] (**1**) in 66% yield. While the NMR spectra were uninformative, combustion analysis data in agreement with the proposed formulation were obtained.

The molecular structure of **1**, as determined by X-ray diffraction, consists of two trivalent uranium atoms held together by the $[(-CH_2-)_5]_4$-calix[4]tetrapyrrole ligand and is similar to those of the divalent, trivalent, and mixed-valence Sm analogues (Figure 1).[22] The ligand is centered on the U−U vector (U1−U1A = 3.4515(5) Å) and adopts a conformation in which each pair of pyrrole rings at opposite positions of the macrocycle coordinates one of the two U atoms in a η^5 mode (U1−N1A = 2.735(7) Å, U1−C1A = 2.873(8) Å, U1−C2A = 2.953(8) Å, U1−C3A = 2.937 Å(8) Å, U1−C4A = 2.834(8) Å). Thus, each uranium atom displays a bent, metallocene-like coordination geometry (centroid−U−centroid = 99.1(1)°). The two N atoms of each pair of pyrrole rings π-bonded to one uranium are also σ-bonded to the second one (U1−N1 = 2.695(7) Å). Thus, by adopting a η^1:η^5 bonding mode, each uranium is overall connected to the four pyrrole rings. Two iodine atoms are terminally bonded to each uranium atom, pointing away from the molecular core (U1−I1 = 3.199(1) Å). The coordination geometry around the two identical uranium atoms may be viewed as tetragonally distorted octahedral with the two σ-bonded nitrogen atoms (N1−U1−N1C = 102.0(3)°) and the bridging iodines defining the equatorial plane (I1−U1−I1C = 86.6(2)°, I1−U1−

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1 and 2

Compound **1**			
U1−U1A	3.4560(8)	U1−C1A	2.872(8)
U1−I1	3.1988(8)	U1−C3A	2.937(9)
U1−N1	2.695(7)	U1−C2A1	2.953(8)
U1−N1A	2.735(7)	Li−O2	1.896(15)
U1−C4A	2.834(8)	Li−O1	1.907(15)
N1B−U1−N1	102.0(3)	I1−U1−U1A	136.72(10)
N1A−U1−N1A	66.11(10)	I1−U1−N1A	172.18(19)
N1A−U1−N1C	100.0(3)	O2−Li−O2A	109.8(13)
U1−N1−U1A	79.05(19)	O2−Li−O1	110.5(4)
I1−U1−I1C	86.56(10)		
Compound **2**			
U1−U2	3.365(6)	U2−Cl3	2.701(2)
U1−N1	2.626(7)	U2−Cl4	2.710(2)
U1−N3	2.610(5)	U2−N3	2.662(5)
U1−Cl1	2.640(2)	U2−C21	2.829(7)
U1−Cl2	2.655(2)	U2−C22	2.931(7)
U1−N2	2.684(5)	U2−C23	2.932(7)
U1−C11	2.854(8)	U2−C24	2.799(7)
U1−C12	2.868(8)	U2−N1	2.680(6)
U1−C13	2.861(7)	U2−C1	2.841(7)
U1−C14	2.779(7)	U2−C2	2.931(7)
U1−N4	2.682(5)	U2−C3	2.911(8)
U1−C31	2.825(8)	U2−C4	2.797(7)
U1−C32	2.877(8)	Li−O2	1.80(3)
U1−C33	2.853(7)	Li−O1	2.11(3)
U1−C34	2.792(7)	Li−Cl4	2.43(4)
U2−N4	2.674(6)	Li−Cl3	2.57(5)
U2−N2	2.684(6)		
N3−U1−N1	102.37(17)	N1−U2−Cl3	119.82(16)
N3−U1−Cl1	170.93(13)	N2−U2−Cl3	170.58(13)
N1−U1−Cl1	86.70(14)	N3−U2−Cl4	119.52(12)
N3−U1−Cl2	84.01(13)	N4−U2−Cl4	170.04(13)
N1−U1−Cl2	173.57(14)	N1−U2−Cl4	117.81(15)
Cl1−U1−Cl2	86.92(8)	N2−U2−Cl4	87.53(14)
N3−U1−N4	67.09(16)	Cl3−U2−Cl4	83.08(9)
N1−U1−N4	67.3(2)	O2−Li−O1	114.1(15)
Cl1−U1−N4	117.47(12)	O2−Li−Cl4	110.8(17)
Cl2−U1−N4	116.66(14)	O1−Li−Cl4	121.6(19)
N3−U1−N2	66.67(17)	O2−Li−Cl3	118(2)
N1−U1−N2	66.22(19)	O1−Li−Cl3	97.9(15)
Cl1−U1−N2	117.96(13)	Cl4−Li−Cl3	91.9(10)
Cl2−U1−N2	116.42(15)	O2−Li−C45	25.8(6)
N4−U1−N2	102.16(18)	O1−Li−C45	133.7(14)
N3−U2−N4	66.47(16)	Cl4−Li−C45	85.0(11)
N3−U2−N1	99.56(18)	Cl3−Li−C45	120.0(15)
N4−U2−N1	66.61(18)	O2−Li−U2	120.5(14)
N3−U2−N2	65.96(18)	O1−Li−U2	124.1(11)
N4−U2−N2	102.39(17)	Cl4−Li−U2	46.3(5)
N1−U2−N2	65.49(19)	Cl3−Li−U2	46.2(5)
N3−U2−Cl3	118.46(13)	Li−Cl3−U2	90.5(9)
N4−U2−Cl3	87.02(13)	Li−Cl4−U2	93.4(9)

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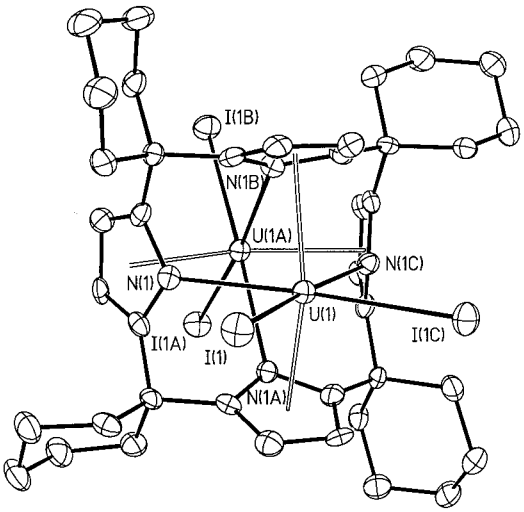

Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level.

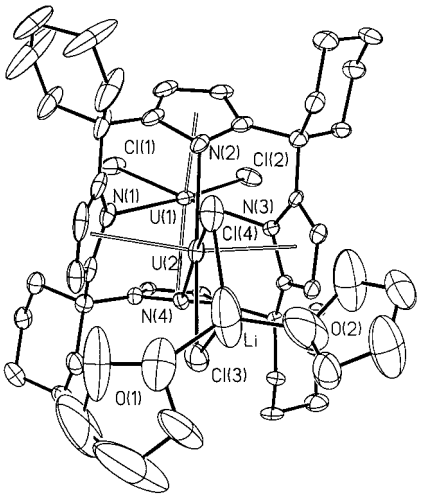

Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level.

N1C = 172.2(2)°), while the two centroids of the two η^5-bonded rings occupy the axial positions. Two lithium cations, each solvated by four molecules of THF and unconnected to the diuranium dianion, complete the structure.

The nearly isostructural U(IV)/U(III) mixed-valence $[Li(THF)_2](\mu\text{-}Cl)_2\{U_2[(-CH_2-)_5]_4\text{-calix[4]tetrapyrrole}\}\text{-}Cl_2\cdot THF$ (**2**) was readily prepared by partial in situ reduction of UCl_4 and subsequent addition of the appropriate amount of ligand.

The X-ray crystal structure of the compound shows an arrangement very similar to that observed in **1** (Figure 2). Even in this case the ligand adopts the η^1:η^5 bonding mode by bridging the two uranium atoms. The coordination geometry around each uranium atom is pseudo-octahedral and is defined by two centroids of two π-bonded pyrrolyl rings (U1-centroid = 2.552(7), 2.547(7) Å, centroid−U1−centroid = 153.9(2)°; U2−centroid = 2.576(7), 2.574(7) Å, centroid−U2−centroid = 152.3(2)°) and two N atoms of the other two σ-bonded rings (U1−N1 = 2.626(7) Å, U1−N3 = 2.610(7) Å, N1−U1−N3 = 102.4(2)°, centroid−U1−N1 = 80.4(2)°; U2−N2 = 2.684(7) Å, U2−N4 = 2.674(7) Å, N2−U2−N4 = 102.4(2)°, centroid−U2−N2 = 81.6(2)°). Two chlorine atoms (U1−Cl1 = 2.640(5) Å, U1−Cl2 = 2.655(5) Å, U2−Cl3 = 2.701(5) Å, U2−Cl4 = 2.710(5) Å) in cis positions (Cl1−U1−Cl2 = 86.9(2)°, Cl3−U2−Cl4 = 83.1(2)°) complete the coordination octahedron around each uranium. The two uranium atoms are held at short proximity (U1−U2 = 3.365(3) Å) and are nonequivalent in the sense that the two chlorine atoms attached to one of the two metals also bridge a $Li(THF)_2$ unit (Cl3−Li = 2.57(5) Å, Cl4−Li = 2.43(4) Å, Cl3−Li−Cl4 = 91.9(2)°, U−Cl3−Li = 93.4(2)°).

To the best of our knowledge complex **2** is the first example of a mixed-valence U(III)/U(IV) compound. From the bonding parameters, it seems that the U1−N distances are consistently slightly shorter than those for U2, suggesting that the two uranium atoms are respectively U(IV) and U(III). According to this hypothesis complex **2** would be a class 2 mixed-valence species. Also, the presence of Li near U2 might actually be taken as another indication for U2 being trivalent, as one would expect on electrostatic grounds.

Magnetism. The short intermetallic distances in complexes **1** and **2** are intriguing. They appear to be among the shortest in uranium chemistry, and that observed in **1** is the shortest ever reported among trivalent uranium atoms.[8] Given the low oxidation state and the large dimensions of the U^{3+} atom, it is reasonable to expect a substantial overlap of electronic charge with consequent magnetic coupling. Accordingly, the magnetic moment of complex **1** at room temperature is quite low (Figure 3), decreasing from 1.99 μ_B (per U) at 300 K to 0.55 μ_B at 2 K. A theoretical exchange model properly fitting the experimental data could not be elaborated because of the inherent difficulties of dealing with the magnetic properties of actinide systems (large spin−orbit effects, etc.). By assuming that no direct metal−metal bonding interactions are present in **1**, the drop in moment on lowering the temperature can be interpreted to indicate the presence of intramolecular antiferromagnetic coupling. Low-temperature moments for mononuclear U(III) systems would be expected to be somewhat higher (e.g. $U(Cp)_3THF$ ~1.3 μ_B at 5 K).[23]

The magnetic behavior of the mixed-valence **2,** which possesses one electron less than **1** and has an even shorter U···U distance, is interesting. The room-temperature magnetic moment at 300 K (3.04 μ_B (per mole)) was found to be higher than **1** and drops to 1.03 μ_B (per mole) at 2 K, which again does point to possible antiferromagnetic coupling (Figure 4). Monomeric U(IV) compounds typically display room-temperature magnetic moments in the range 2.5−3 μ_B but have moments approaching a temperature-independent value at low temperatures due to coupling between a nonmagnetic ground state and low-lying excited states through a Zeeman perturbation.[24,25] The magnetic moment shown by the few known monomeric trivalent uranium compounds is usually larger than 3.4 μ_B and is also expected to drop to around 1.7 μ_B at 2 K.[23,24] Combining all this in the context of possible M−M bonding or antiferromagnetic exchange, the actual value obtained is very

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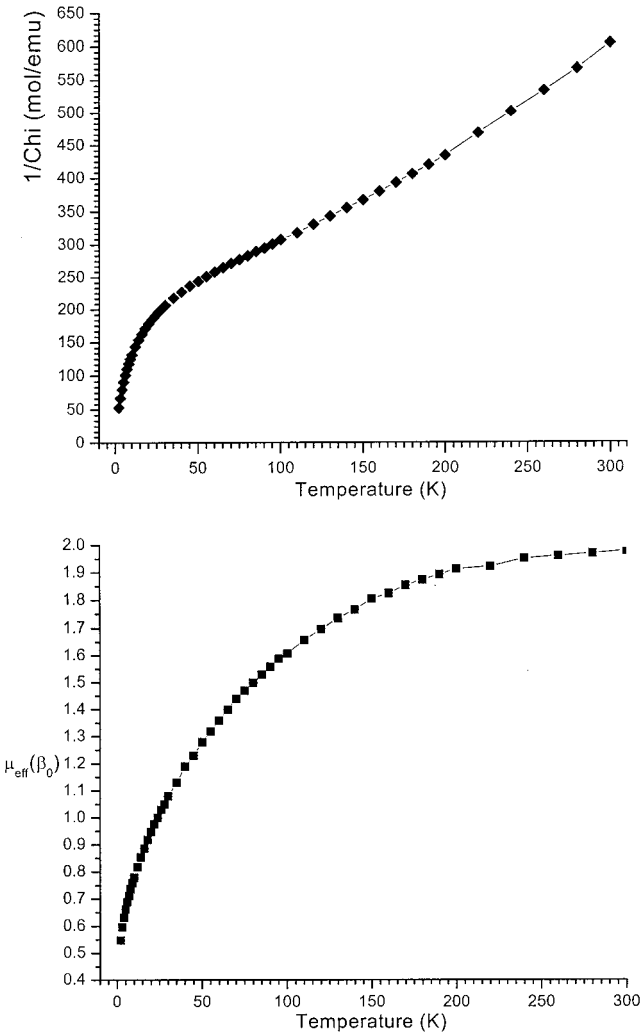

Figure 3. Plots of $1/\chi$ and of μ_{eff} vs T for **1**.

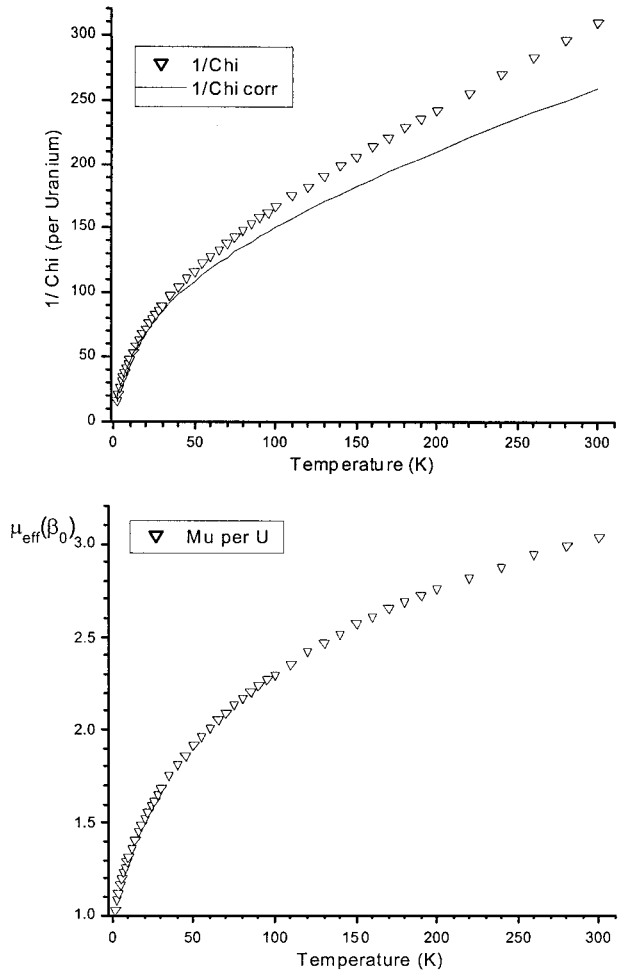

Figure 4. Plots of $1/\chi$ and of μ_{eff} vs T for **2**.

close to what one would calculate for a noncoupled combination of the two ions (e.g. ~1.2 μ_B at 2 K and ~3.1 at 300 K). This might indicate that not much exchange occurs between the two ions and is in agreement with a suggestion provided by the crystallographic data of complex **2** as a type 2 mixed-valence compound.

Electronic Structure. Electronic structure calculations employing density functional theory (DFT) were performed on the model anionic U dimer complex $[(TP)U_2I_4]^{2-}$, in which the bridging $C(CH_2)_5$ cyclohexyl substituents were replaced by CH_2 units. Relativistic effective core potentials (RECP) were employed on the U atoms,s[14] in which the 78 inner core electrons were replaced, leaving the 6s, 6p, 6d, 5f, and higher shells as valence electrons in a [3s3p2d2f] basis. For the I atom**s** the RECP replaced all but the outer 5s and 5p electrons described by the LANL2DZ basis.[15] A 6-31G basis was used on the remaining atoms. Hybrid DFT calculations employing the B3LYP functional[16−18] were carried out using the Gaussian98 program.[19]

Spin-unrestricted (or "spin-polarized") calculations were performed for the "high-spin" state ($S = 3$) corresponding to two U(III) f^3 ions, each with $S = 3/2$. There was very little spin contamination in the spin-unrestricted calculations, as $\langle S^2 \rangle = 12.02$ (compared to $\langle S^2 \rangle = 12.00$ for $S = 3$) and the net electron spin on each U was +3.02 e.

For the "low-spin" state, "broken-symmetry" spin-unrestricted calculations were performed corresponding to $S_A = 3/2$ and $M_{SA} = +3/2$ on the first uranium atom (U_A) and $S_B = 3/2$ and $M_{SB} = -3/2$ on the second (U_B). For this antiferromagnetic case the overall spin is not well defined but the total $M_S = 0$. From the population analysis the net electron spin on U_A and U_B was +3.04 and −3.04 e, respectively. The SCF energy of the low-spin state was found to be 0.000 45 au, or 99 cm^{-1}, lower than the spin-unrestricted high-spin result.

The above high-spin results were also compared with the spin-restricted calculations where the open-shell electrons are more clearly identified. The spin-unrestricted SCF result was 0.012 68 au lower than the spin-restricted case.

The above results thus predict the ground state of the dimer complex to be low spin by a small amount (99 cm^{-1}). For both high- and low-spin cases the orbitals describing the three unpaired electrons on each U(III) are similar in the DFT results. If one chooses the z axis to lie along the line between the U atoms, the three 5f orbitals correspond to 5fσ (z^3), 5fδ ($z(x^2 - y^2)$), and 5fϕ ($3x^2y - x^3$) on each U atom. Despite the relatively short U−U distance there is little indication of any net bonding between the centers, as evident from the small energy difference between high- and low-spin states. The unpaired electrons are nearly pure 5f in character, with little admixture of ligand character. In the high-spin state the 5fσ orbitals, for example, form bonding

and antibonding combinations, both of which are singly occupied and are similar for the remaining unpaired electrons.

For $5f^5$ states of U(III) one would expect substantial mixing arising from configuration interaction with other $5f^5$ configurations. In addition, spin−orbit coupling effects will be very important for describing the low-lying excited states. Therefore, the above "single configuration" DFT results can provide only some guidance to interpret experimental results and give some support to the possibility suggested by the magnetic measurement of an antiferromagnetically coupled uranium dimer. Simply, the complexity of both the magnetic and theoretical treatment of such a unique atom does not allow, at this time, a detailed interpretation.

Conclusion

In conclusion, two new low-valent uranium complexes have been synthesized. For the U(III)/U(III) dimer the magnetic properties and electronic structure results consistently suggest a weakly coupled antiferromagnetic interaction between the metal centers. The magnetic behavior of the mixed-valence **2** suggests a complete absence of magnetic exchange between the two metals and is in agreement with the suggestion that this species might be a type 2 mixed-valence compound.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, thermal parameters. and hydrogen atom positional parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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