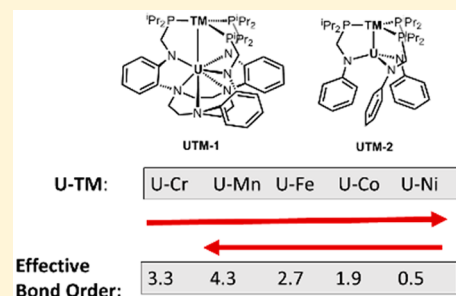


Multiple Bonds in Uranium–Transition Metal Complexes

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S Supporting Information

ABSTRACT: Novel heterobimetallic complexes featuring a uranium atom paired with a first-row transition metal have been computationally predicted and analyzed using density functional theory and multireference wave function based methods. The synthetically inspired metalloligands $U\{(^iPr_2PCH_2NAr)_3tacn\}$ (1) and $U(^iPr_2PCH_2NPh)_3$ (2) are explored in this study. We report the presence of multiple bonds between uranium and chromium, uranium and manganese, and uranium and iron. The calculations predict a 5-fold bonding between uranium and manganese in the $UMn(^iPr_2PCH_2NPh)_3$ complex, which is unprecedented in the literature.



1. INTRODUCTION

Metal–metal bonding is a fundamental concept in chemistry that affects the properties of the systems of interest and is instrumental to understanding structure and reactivity, metal–surface chemistry, and metal-based catalysis.¹ Compared to transition metals, the nature of metal–metal bonds involving f-block metals, especially the actinide series, has been less explored.² The 5f orbitals of the actinides, such as uranium, have suitable spatial extension to participate in bonding, which makes the d–f heterobimetallic bond an interesting target to improve our understanding of the interplay of the d and f orbitals.

A review of both theoretical and experimental data in the literature shows that very few examples have been reported for bonding between an actinide, such as uranium, and a transition metal to date. The first attempt to synthesize a uranium–transition metal (U–TM) compound was made by Stone in 1971.³ He reported the synthesis of a uranium–manganese complex with carbonyl ligands; however, the complex, being highly air sensitive, decomposed before it could be analyzed. In 1987, Sternal and Marks⁴ reported the successful synthesis of uranium–ruthenium and uranium–iron complexes, although the X-ray diffraction was not reported for these complexes. Although U–TM complexes are promising, the research in the field had been dormant for more than a decade. Later in 2000, Ephritikhine and co-workers⁵ reported the successful synthesis and characterization of urana[1]ferrocenophane compounds with Fe–U–Fe bonds, where the average U–Fe bond length is 3.14 Å, which is shorter than the covalent U–Fe distance of 3.28 Å.⁶ Since then, several bimetallic U–TM complexes have been reported in the literature, including experimental⁷ and predominantly theoretical studies.⁸

The bonding interactions in these previously reported U–TM compounds are predominantly dative;^{7d,f,h,j,m,o} however, minor σ and π contributions were also predicted in some complexes by computational calculations.^{7a,c,k}

Bimetallic complexes generally contain numerous low-lying states, and therefore, it is important to use a multireference method to accurately predict the nature of chemical bonding.¹⁴ Multireference methods, such as complete active-space self-consistent field method (CASSCF),⁹ have been employed to explore the bonding of f-block metals, particularly in uranium chemistry.^{8a,c,e,10} Multireference calculations have predicted the existence of high bond orders in the uranium–uranium bond of U_2 .^{10d,f} Furthermore, multiple computational studies have been used to explore uranium–ligand bonding,^{10a,b,11} and uranium–transition metal chemistry.⁸

In this article, we explore the chemical bonding between a first-row transition metal and a uranium atom in UTM-[(iPr_2PCH_2NAr)₃tacn] (UTM-1) and UTM-(iPr_2PCH_2NPh)₃ (UTM-2) species, where TM = Cr, Mn, Fe, Co, Ni. UTM-1 and UTM-2 are comprised of nonadentate (iPr_2PCH_2NAr)₃tacn and bidentate iPr_2PCH_2NPh ligands, respectively; both contain hard amido and soft phosphine groups. We focus on first-row transition metals because the 5f–3d interactions are less explored compared to f-block and second-row transition metals and, because of the unique electronic structures and greater spin-flexibility

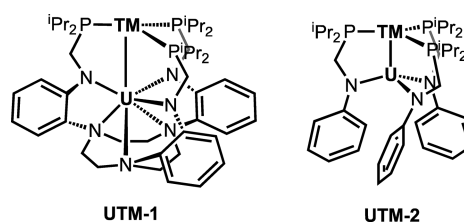


Figure 1. Schematic representation of (left) UTM-[(iPr_2PCH_2NAr)₃tacn] (UTM-1) and (right) UTM-(iPr_2PCH_2NPh)₃ (UTM-2), where TM = {Cr, Mn, Fe, Co, Ni}.

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Table 1. Geometrical Parameters, Including Bond Lengths (Å) and Angles (deg) for UTM-1 Obtained from DFT Calculations^a

UTM	UCr				UMn			UFe			UCo			UNi	
spin (2S + 1)	2	4	6	8	1	3	5	2	4	6	1	3	5	2	4
Cal. S ²	0.75	3.75	8.75	15.75	0.00	2.00	6.00	0.75	3.75	8.75	0.02	2.00	6.00	0.77	3.75
U–TM	1.99	2.07	2.28	3.00	1.94	2.03	2.17	2.02	2.20	2.75	2.25	2.26	2.63	2.68	2.72
avg TM–P	2.40	2.39	2.38	2.37	2.35	2.32	2.34	2.28	2.27	2.24	2.22	2.22	2.22	2.20	2.21
avg U–N _{facn}	2.80	2.78	2.78	2.73	2.79	2.80	2.79	2.80	2.81	2.75	2.80	2.80	2.78	2.76	2.76
avg U–N _{amide}	2.41	2.45	2.44	2.41	2.40	2.44	2.45	2.42	2.43	2.41	2.40	2.40	2.41	2.38	2.40
E ^{DFT} (kcal/mol)	0.0	11.6	27.6	41.6	0.0	13.3	37.1	0.0	20.1	47.2	7.5	0.0	28.8	10.2	0.0
FSR ^b	0.68	0.71	0.78	1.03	0.67	0.70	0.84	0.71	0.77	0.96	0.80	0.80	0.94	0.96	0.97

^aBond lengths in angstroms (Å). The most stable spin states are shown in bold text. ^bFSR: Formal shortness ratio; defined as the ratio between the calculated bond length and the sum of covalent radii of the two metals.

Table 2. Geometrical Parameters, Including Bond Lengths (Å) and Angles (deg) for UTM-2 Obtained from DFT Calculations^a

UTM	UCr				UMn			UFe			UCo			UNi	
spin (2S + 1)	2	4	6	8	1	3	5	2	4	6	1	3	5	2	4
Cal. S ²	0.75	3.75	8.75	15.75	1.00	2.00	6.00	0.75	3.75	8.75	0.03	2.00	6.00	0.79	3.75
U–TM	1.99	2.07	2.29	2.75	1.94	2.03	2.20	2.02	2.21	2.62	2.23	2.25	2.47	2.64	2.62
avg TM–P	2.39	2.41	2.39	2.36	2.35	2.33	2.35	2.30	2.28	2.27	2.24	2.23	2.24	2.21	2.24
avg U–N _{amide}	2.38	2.38	2.37	2.41	2.36	2.37	2.37	2.35	2.36	2.32	2.33	2.34	2.34	2.30	2.33
E ^{DFT} (kcal/mol)	0.0	13.0	26.9	41.9	0.0	19.6	45.3	0.0	19.6	45.3	6.8	0.0	28.0	4.7	0.0
E ^{CASSCF} (kcal/mol)	0.0	5.2	−0.4	14.2	0.0	15.2	21.4	0.0	6.9	38.8	21.3	0.0	57.7	10.7	0.0
E ^{CASPT2} (kcal/mol)	0.0	22.7	29.1	47.6	0.0	38.5	73.1	0.0	26.5	83.8	14.4	0.0	64.3	22.3	0.0
FSR ^b	0.68	0.71	0.78	0.94	0.67	0.70	0.76	0.70	0.77	0.91	0.80	0.80	0.88	0.94	0.94

^aBond lengths in angstroms (Å). The most stable spin states are shown in bold text. Relative energies with respect to the most stable spin-state are calculated at DFT, CASSCF, and CASPT2 levels of theory. ^bFSR: Formal shortness ratio; defined as the ratio between the calculated bond length and the sum of covalent radii of the two metals.

Table 3. Mayer Bond Order (BO) Calculated at DFT Level for Ground Spin State for UTM-1 and UTM-2 Complexes

	UCr	UMn	UFe	UCo	UNi
Mayer BO UTM-1	3.3	3.6	2.8	1.5	0.5
Mayer BO UTM-2	3.3	3.6	2.9	1.5	0.7

of first-row transition metals, these interactions might have unique features. The structures of the potential U-TM complexes are shown in Figure 1. The complexes hypothesized

here are inspired by previous work by Ramirez et al.,¹² in which the same ligands were employed to make 4f–3d Lu–Ni bimetallic species. In this study, we employ density functional theory (DFT) and multireference methods to predict the stability and nature of the bonding in these novel complexes.

2. COMPUTATIONS

The structures of UTM-1 and UTM-2 (TM = Cr, Mn, Fe, Co, and Ni) were optimized with the PBE¹³ functional with D3 dispersion

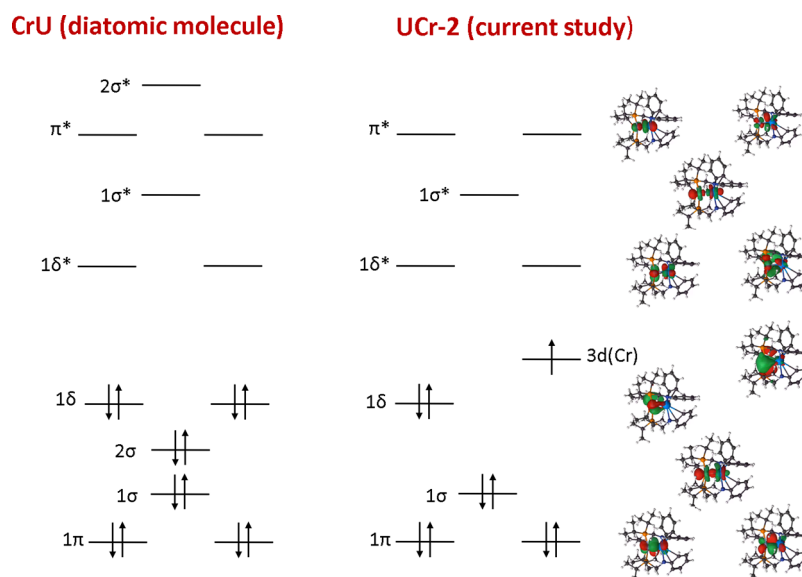
**Figure 2.** Comparison between the MO diagrams of CrU diatomic molecule reported in ref 8e and UCr-2 complexes.

Table 4. Detailed CASSCF Orbital Analysis of UTM-2 Species^a

complex	orbital	%TM	%U	total electrons	EBO	percent of main configuration (%)
UCr-2	σ	48.5 (4s:3.9; 3d:92.4)	51.5 (5f:88.2; 7p:4.1)	1.78	3.3	80
	π	63.2 (3d:99.9)	36.8 (6d: 60.9; 5f: 39.1)	1.91		
	π	66.5 (3d: 99.9)	33.6 (6d: 65.5; 5f:34.5)	1.91		
	δ	52.2 (3d: 96.9; 4s: 2.9)	47.8 (5f: 99.9)	1.67		
	δ	60.2 (3d:97.2; 4p: 2.8)	39.8 (5f: 96.0; 6d:4.0)	1.85		
UMn-2	π	69.7(3d: 99.9)	30.3(6d: 60.4; 5f: 34.9)	1.91	4.3	69
	π	68.7 (3d: 99.9)	31.3 (6d:57.8; 5f:38.1)	1.91		
	δ	75.7 (3d: 96.3; 4p: 3.7)	24.3 (5f:95.8; 6d:4.2)	1.81		
	δ	71.3 (3d:96.3; 4s:3.7)	28.7 (6d:4.8; 5f:95.1)	1.77		
	δ	65.3 (3d: 99.9)	34.7 (6d:9.2; 5f:90.7)	1.82		
UFe-2	π	77.7 (3d:98.3; 4p:1.7)	22.3 (6d:59.2; 5f:34.5)	1.91	2.7	78
	π	75.4 (3d: 99.9)	24.6 (6d:58.9; 5f:34.9)	1.91		
	3d(Fe)-5f/6d(U)	95.7 (3d:95.8; 4p:4.1)	4.3 (6d:32.5; 5f:67.4)	1.92		
	3d(Fe)-5f/6d(U)	97.2 (3d:95.9; 4p:3.9)	2.8 (6d:46.4; 5f:53.5)	1.93		
	3d(Fe)-5f/6d(U)	97.2 (3d:95.9; 4p:3.9)	2.8 (6d:46.4; 5f:53.5)	1.93		
UCo-2	3d/4p(Co)-6d(U)	88.2 (3d:98.3; 4p:1.6)	10.3 (6d:99.9)	1.93	1.9	86
	3d/4p(Co)-5f/6d(U)	88.3 (3d:97.9; 4p:2.0)	10.0 (6d:85.0; 5f:1.5)	1.93		
	3d(Co)-5f/6d(U)	91.8(3d:95.4; 4p:3.7)	8.2(7s:20.7; 6d:79.3)	1.94		
	3d(Co)-5f/6d(U)	95.9 (3d:97.7; 4p:2.3)	4.2 (7s:33.3; 6d:66.7)	1.94		
	3d/4s(Ni)-5f/6d(U)	34.5 (3d:31.6; 4p:37.1; 4s:28.4)	57.7 (7s:41.8; 6d:38.8; 5f:13.5)	1.01		
UNi-2	3d/4s(Ni)-7s/6d(U)	88.6 (3d:97.4; 4s:2.6)	11.4 (6d:66.7; 7s:33.3)	1.95	0.5	91

^aFor each orbital, we report the % contribution on the TM and on U and its composition in terms of atomic orbitals. Only natural MOs with an overlap percentage higher than 10% from either metal are considered as bonding MOs.

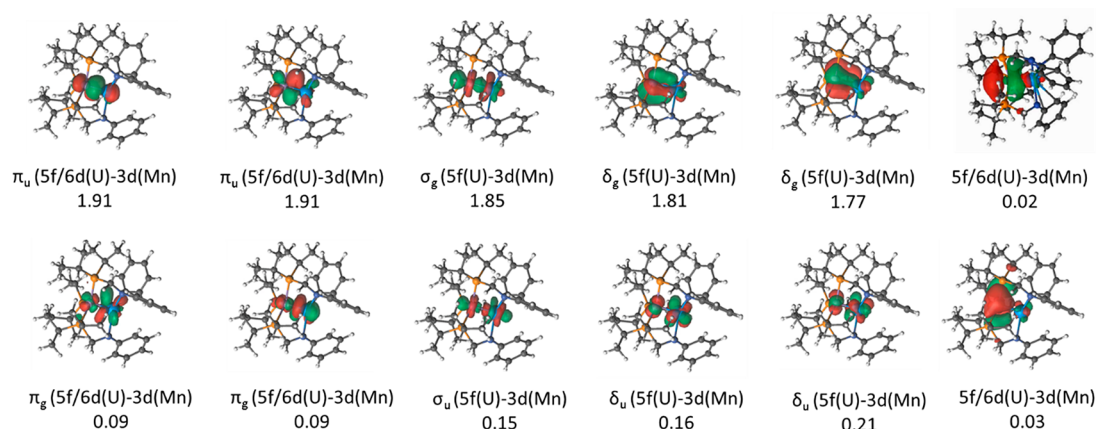


Figure 3. UMn-2 orbitals predicted by CASSCF (10, 12) for the singlet state along with the occupation number of the orbitals.

correction,¹⁴ using the unrestricted formalism, UPBE-D3. UPBE-D3 gave satisfactory results for related bimetallic systems featuring the

same ligand.¹² The def2-TZVP basis set¹⁵ was used for the transition metals, N and P, while the Stuttgart/Dresden pseudopotential¹⁶ was

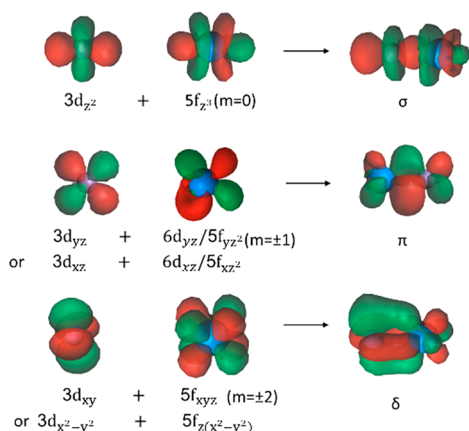


Figure 4. Combinations of the metal 3d, 5f, and 6d atomic orbitals that participate in metal–metal bonding in UMn-2 complex.

Table 5. MS-CASPT2 Excitation Energies from S_0 in eV and nm for the Lowest Singlet and Triplet States and Their Electronic Configurations for UMn-2

state	E (eV)	λ (nm)	configuration
S_0	0.0	0	45.2% $(\sigma)^2(\pi)^4(\delta)^4$ 33.0% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_1	1.48	837	79.7% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_2	1.65	750	71.1% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_3	1.74	712	79.4% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_2	1.76	705	80.6% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_4	1.82	682	75.9% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_3	1.84	673	79.4% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_4	1.98	626	79.6% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$

used for uranium. All the other atoms (C and H) were treated using the def2-SVP basis set. All the DFT calculations were performed with the Gaussian 09 software.¹⁷ Single-point calculations were performed at the PBE-D3 optimized geometries using the complete active space, CASSCF method,⁹ to gain insight into the electronic structure of the UTM-2 complexes. The ANO-RCC-vtzip basis set¹⁸ was employed for U and TM, while a double- ζ quality ANO-RCC-vdzip basis set was used for N and P atoms. A minimal basis set of ANO-RCC type was used for C and H. Douglas–Kroll–Hess Hamiltonian was used to include scalar relativistic effects.¹⁹ The active space employed in the CASSCF calculations consists of the valence 5f and 6d orbitals of U and the 3d and 4s orbitals of TM. Larger active-spaces were also explored; however, there were no changes in the final results (see Supporting Information (SI)). The electronic excitation energies were calculated at multistate complete active space second-order perturbation theory (MS-CASPT2) level of theory.²⁰ We used the default ionization-potential-electron-affinity (IPEA) shift of 0.25 au, which is an empirical correction applied to the zero-order Hamiltonian.²¹ We also applied an imaginary shift of 0.2 au to avoid possible intruder states. The Molcas 8.0 software package²² was used for the CASSCF calculations.

The effective bond order (EBO) was calculated using the formula^{1e}

$$\text{EBO} = \frac{\sum_i (B_i - AB_i)}{2}$$

where B_i and AB_i are the occupation numbers of bonding and antibonding natural orbital in an orbital pair, respectively, and the sum runs over all the orbital pairs.

3. RESULTS

Unrestricted DFT (UPBE-D3) calculations were performed for UTM-1 and UTM-2 (TM = Cr, Mn, Fe, Co, Ni) complexes for various possible spin states. Table 1 summarizes the results for different spin states for the UTM-1 complexes. The most stable spin state results are highlighted. DFT optimized geometries show that the shortest U–TM bond occurs between U and Mn atoms.

The most stable spin states for UCr-1, UMn-1, UFe-1, UCo-1, and UNi-1 complexes as determined from UPBE-D3 calculations are the doublet, singlet, doublet, triplet, and quartet state, respectively. The formal shortness ratio (FSR) is defined herein as the ratio of metal–metal bond distance to the sum of the metals' covalent radii.²³ A FSR value of 1 suggests the presence of single bond, while a smaller value indicates multiple bonds. According to their FSR values, UCr-1, UMn-1, UFe-1, and UCo-1 complexes should have multiple bonds between the two metals, while the UNi-1 complex shows a weaker interaction.

The DFT results along with CASSCF and CASPT2 relative energies for UTM-2 are summarized in Table 2. The U–TM bond distance does not change significantly between UTM-1 and UTM-2. CASSCF and CASPT2 relative energies follow the same trend as DFT for all UTM-2 complexes with minor caveat for UCr-2. In UCr-2, CASSCF predicts a sextet ground spin state 0.4 kcal/mol lower in energy than the doublet; however, after application of the perturbative correction to the CASSCF energies (i.e., CASPT2), the doublet spin state appears as the ground state. The Mayer bond order for UTM-1 and UTM-2 at the ground spin state are reported in Table 3. For UCr and UMn complexes, the Mayer bond order is the same for the two ligands; however, UTM-2 favors shorter bond lengths for UFe, UCo, and UNi, which is in line with the trend seen in LuNi complexes with the two ligands.¹² To understand the nature of uranium and first-row transition metals, UTM-2 were further studied with multiconfigurational methods as they are smaller calculations and thus require fewer computational resources such as time and memory.

3.1. UCr Complex. In 2013, Infante and co-workers proposed a 6-fold bonding for a theoretical CrU diatomic molecule with an EBO of 5.3.^{8e} However, this diatomic molecule could be experimentally synthesized only in extreme conditions. In this article, we investigate the nature of the bonding in synthetically motivated $\text{UCr}[(^i\text{Pr}_2\text{PCH}_2\text{NAr})_3\text{tacn}]$ (UCr-1)

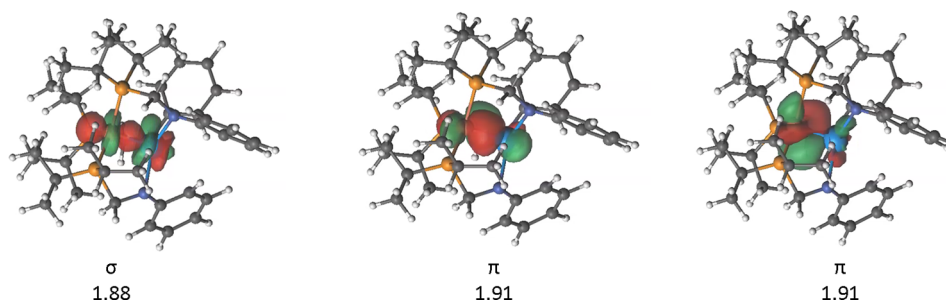


Figure 5. Bonding orbitals of UFe-2 complex along with the occupation number of the orbitals.

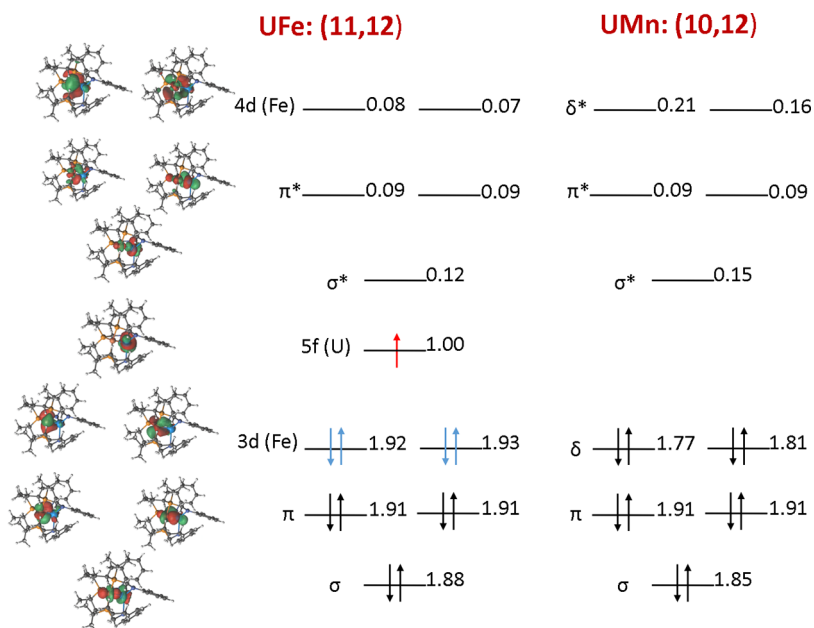


Figure 6. Comparison between the MO diagrams of UFe-2 and UMn-2 complexes. The blue and red colors represent electrons localized on Fe and U, respectively. The occupation numbers of the orbitals are listed above them.

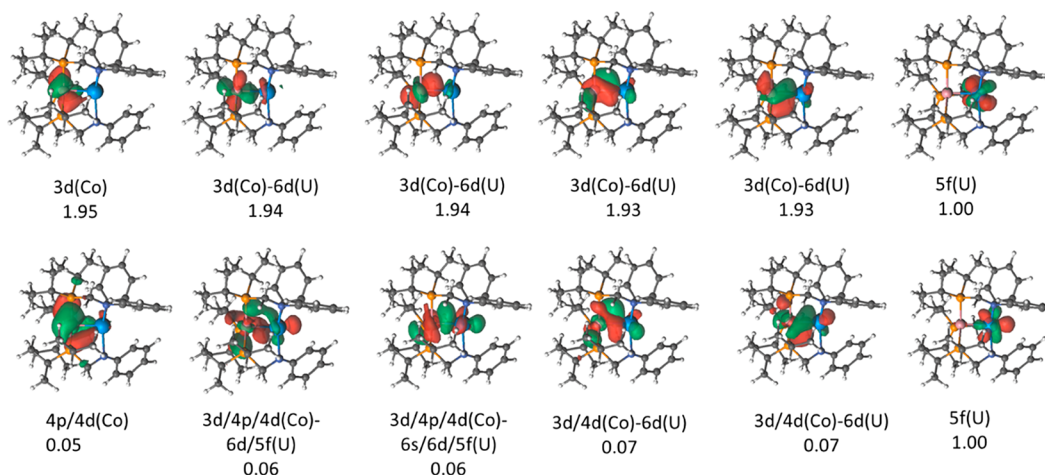


Figure 7. UCo-2 orbitals predicted by CASSCF(13, 12) for the triplet state along with their occupation numbers.

and $\text{UCr}(\text{Pr}_2\text{PCH}_2\text{NAr})_3$ (UCr-2) complexes. Since the bond distance between Cr and U and other geometric parameters are similar between the UCr-1 and UCr-2 complexes, we further investigated UCr-2 complex using multiconfigurational methods. Figure 2 shows a comparison between the previously reported electronic structure of the diatomic molecule CrU,^{8e} and the complex UCr-2 proposed in this study. The dominant electronic configuration of CrU is $(1\sigma)^2(1\sigma)^2(1\pi)^4(1\delta)^4$. The second σ bond in CrU has contributions from 7s and 6d of U. Since the U atom is formally U^{3+} in UCr-2 while it is U^0 in CrU, we do not observe a second sigma (2σ) bond in UCr-2. The occupation numbers for CASSCF orbitals for UCr-2 are reported in Table 4. The EBO is calculated to be 3.3.

3.2. UMn-2 Complex. Inspection of the CASSCF wave function shows that UMn-2 is highly multiconfigurational, with a dominant configuration- $((\sigma)^2(\pi)^4(\delta)^4)$ with a weight of 70% and a second configuration- $((\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2)$ with a weight of 7% and 7% weight for the configuration- $((\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2)$. A formal quintuple bond between

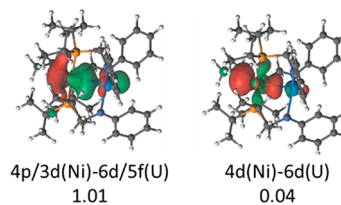


Figure 8. Bonding and antibonding orbitals in UNi-2 complexes along with their occupation numbers.

uranium and manganese with an EBO of 4.3 is predicted. Such a high bond order between uranium and manganese is unprecedented. Figure 3 shows the UMn-2 bonding and antibonding orbitals present in the active space. The atomic orbitals on Mn and U along with the resulting bonding orbitals are shown in Figure 4. The UMn-2 σ and δ bonding molecular orbitals contain minor contributions ($\sim 5\%$) from uranium 6d atomic orbitals. The σ -type orbital contains major contributions from the U $5f_z$ and the Mn $3d_z^2$ orbitals, while the two δ

Table 6. Detailed DFT Natural Bond Orbital Analysis of UTM-2 Species

complex	orbital	%TM	%U	total electrons
UCr-2	σ (alpha)	63.0	37.0	0.89
		(3d: 84.4; 4p: 13.4)	(6d:7.8; 5f:90.2)	
	π (alpha)	65.3	34.7	0.89
		(3d: 91.3; 4p: 8.7)	(5f:58.3; 6d:40.3)	
	π (alpha)	66.0	34.0	0.90
		(3d:82.4; 4p:17.6)	(6d:34.6; 5f:63.6)	
	δ (alpha)	63.8	36.23	0.88
		(3d: 79.6; 4p: 20.4)	(6d; 6.6; 5f: 92.8)	
	δ (alpha)	68.8	31.2	0.87
		(3d:85.4; 4p: 13.9)	(5f:90.0; 6d:9.4)	
UMn-2	σ (beta)	59.6	40.4	0.89
		(3d: 82.9; 4p: 15.1)	(6d:7.7; 5f:90.5)	
	π (beta)	64.5	35.5	0.92
		(3d: 91.3; 4p: 8.7)	(5f:60.9; 6d:37.9)	
	π (beta)	63.0	37.0	0.90
		(3d:81.3; 4p:18.6)	(6d:35.0; 5f:63.4)	
	δ (beta)	61.9	38.1	0.87
		(3d: 86.5; 4p: 12.9)	(6d; 8.0; 5f: 91.6)	
	σ	66.6	33.4	1.77
		(3d: 87.8; 4p: 9.04)	(6d:8.9; 5f:89.9)	
UFe-2	π	71.8	21.2	1.78
		(3d: 79.1; 4p: 20.9)	(6d; 67.7; 5f: 30.8)	
	π	70.5	29.5	1.74
		(3d:73.9; 4p: 26.1)	(5f:65.7; 6d:33.0)	
	δ	70.2	29.8	1.78
		(3d: 85.4; 4p: 14.6)	(5f:93.1; 6d:6.3)	
	δ	70.7	29.8	1.77
		(3d:85.8; 4p:14. CAS1_C2_1.52)	(6d:8.0; 5f:91.5)	
	σ (alpha)	73.6	26.4	0.90
		(3d: 89.2; 4p: 10.2)	(6d:16.2; 5f:82.6)	
UFe-2	δ (alpha)	76.2	23.8	0.87
		(3d: 79.5; 4p: 16.3)	(6d; 16.8; 5f: 80.3)	
	δ (alpha)	80.4	19.6	0.92
		(3d: 97.5)	(6d:12.5; 5f: 86.3)	

orbitals are mainly composed of the U $5f_{z(x^2-y^2)}$ and $5f_{xyz}$ and Mn $3d_{x^2-y^2}$ and $3d_{xy}$. The two π -orbitals also have major contributions from U 6d orbitals in addition to U $5f_{yz^2}$, Mn $3d_{yz}$, U $5f_{xz^2}$ and Mn $3d_{xz}$.

To study the electronic spectra of UMn-2 complex, MS-CASPT2 was employed. The major configurations for all the low-lying excited states consist of $\delta \rightarrow \delta^*$ transitions (Table 5). The MS-CASPT2 data show the first excited state to be a triplet state (T_1).

The infrared-spectra were calculated at the UPBE-D3 level (SI). The U–Mn stretching is predicted at 474 cm^{-1} , which

Table 7. Mulliken and LoProp Charges for U and TM in UTM-2 Complexes for the Most Stable Spin States

UCr-2(S = 2)	U		Cr	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.333	2.247	−0.476	−0.235
DFT	0.458	N/A	−0.276	N/A
UMn-2(S = 0)	U		Mn	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.329	2.160	−0.692	−0.069
DFT	0.471	N/A	0.056	N/A
UFe-2(S = 2)	U		Fe	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.355	2.291	−0.516	−0.154
DFT	0.640	N/A	−0.161	N/A
UCo-2(S = 3)	U		Co	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.148	2.345	0.107	−0.171
DFT	0.799	N/A	−0.339	N/A
UNi-2(S = 4)	U		Ni	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.037	2.136	−0.259	−0.166
DFT	0.678	N/A	−0.206	N/A

is comparable to the IR-frequency reported for a nearly isostructural dichromium complex that is also quintuply bonded (434 cm^{-1});²⁴ P–Mn–P stretch are observed at 277 and 269 cm^{-1} , respectively.

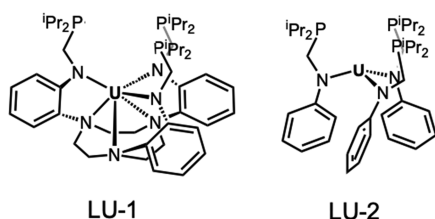
3.3. UFe-2 Complex. The UFe-2 complex shows a formal triple bond between U and Fe, with an effective bond order of 2.7. The three bonding orbitals are shown in Figure 5. A comparison of UFe-2 molecular orbital (MO) diagram shows that the Fe $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ orbitals overlap with U $5f_z^3$, $5f_{xz^2}$, and $5f_{yz^2}$. One would expect a higher bond order for UFe-2 based on the electronic configuration of Fe; however, $3d_{x^2-y^2}$ and $3d_{xy}$ are localized on the Fe center and, thus, do not participate in bonding. We compare the frontier molecular orbitals of UFe-2 and UMn-2 complexes in Figure 6. The unpaired electron of UFe-2 is localized on the uranium $5f_{x(x^2-3y^2)}$ orbital.

3.4. UCo-2 and UNi-2 Complexes. The interaction between U and TM in UCo-2 is different from those in UMn-2 and UFe-2. Their bonding is more dative in nature, directed from the occupied Co 3d orbitals toward the U 6d orbitals while the U 5f orbitals do not participate in the bonding. Since the most stable spin state of the UCo-2 complex is the triplet state, the two unoccupied electrons are localized on U 5f orbitals. Although there are four orbitals with nonzero contributions from the uranium atom (Figure 7), only two orbitals show an effective overlap between U and Co where the contribution of uranium atom is more than 10% (Table 4). In contrast, in the UNi-2 complex with a quintet spin ground state, we observe the presence of half-a-bond (Figure 8) and a singly occupied orbital containing significant contributions from the U $5f_z^3$ and Ni $3d_{z^2}$ orbitals. Interestingly, the trends for bond order and bond length observed for UTM-2 are similar to observations made in the previously reported family of complexes $\text{TMCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)$ (TM = Mn, Fe, Co, Ni).^{1b}

3.5. Natural Bond Orbital Analysis. The density functional natural bond orbital (NBO)²⁵ analysis studies

Table 8. Spin Densities for U and TM in UTM-2 Complexes for the Most Stable Spin States

UCr-2		UMn-2		UFe-2		UCo-2		UNi-2	
U	Cr	U	Mn	U	Fe	U	Co	U	Ni
0.266	0.620	0.000	0.000	1.368	−0.337	2.226	−0.157	3.003	−0.060

Figure 9. Schematic representation of (left) [(*i*Pr₂PCH₂NAr)₃tacn]U (LU-1) and (right) (*i*Pr₂PCH₂NPh)₃U (LU-2).Table 9. Binding Energies (kcal/mol) for UTM-1 and UTM-2^a

	UCr	UMn	UFe	UCo	UNi
UTM-1	−84.7	−111.6	−136.5	−135.6	−123.9
UTM-2	−78.5	−105.4	−130.2	−129.5	−116.2

^aLU = [(*i*Ph₂PCH₂N)C₆H₅]₃U.

predict quadruple bonds in UCr-2 and 5-fold bonding in UMn-2 (Table 6). In case of UCr-2, DFT NBO calculation also predicts the presence of a half delta bond in addition to the four bonding MOs predicted by CASSCF studies. For the UMn-2 complex, CASSCF and NBO agree well where both methods predict the presence of a quintuple bond between U and Mn. Strangely, for the UFe-2 molecule, only alpha spin orbitals show the presence of molecular bonds between U and Fe, while no bonding MOs are found among beta spin orbitals. It should be noted that these bimetallic complexes are highly multireference and DFT NBO calculations are not always reliable.

3.6. Charge and Spin Density Analysis. The Mulliken²⁶ and LoProp²⁷ charge densities are shown in Table 7. While the CASSCF LoProp charge density on U remains almost constant along the series, for TM, it increases from Cr to Mn and then decreases again for Fe and does not change significantly thereafter. DFT and CASSCF Mulliken charge densities present different trends for U and TM. The spin densities obtained from unrestricted DFT calculations show that the unpaired electron is located on Cr in UCr-2, while it is located on U rather than on TM in UFe-2, UCo-2, and UNi-2 (Table 8). These results are in agreement with the picture that emerges from the CASSCF MOs analysis (Figures 2, 6, and 7).

3.7. Binding Energies. We also calculated the binding energies by subdividing UTM-1 and UTM-2 into the following fragments: UTM-1 is divided up into [(*i*Pr₂PCH₂NAr)₃tacn]U (which we name LU-1) and TM, and UTM-2 is divided up into (*i*Pr₂PCH₂NPh)₃U (which we name LU-2) and TM (Figure 9). The binding energies were calculated at the DFT level for the most stable spin state of each species (Table 9). The optimized LU-1 and LU-2 species have a quartet ground state. The binding energies do not follow the same trend as the bond-orders since these are not diatomic molecules and the ligand also plays a role. The binding energies increase from UCr-1 to UFe-1 then decrease from UFe-1 to UNi-1; a similar trend is observed for the UTM-2 complexes. Although, the U-TM bond lengths are shorter in UTM-2 than in UTM-1, the binding energies are higher for UTM-1 suggesting that TM is

bound more strongly to the phosphine ligands in UTM-1 than in UTM-2.

4. CONCLUSIONS

In summary, we presented a study of the bonding of uranium with the first-row transition metals Cr, Mn, Fe, Co, and Ni, in the UTM[(*i*Pr₂PCH₂NAr)₃tacn] (UTM-1) and UTM-(*i*Pr₂PCH₂NAr)₃ (UTM-2) species. Higher bond orders have yet to be obtained (or predicted) between a transition metal and uranium, and our predictions point to which specific metal–metal pairing will ultimately lead to these higher order TM-U bonds. A systematic study of the uranium–first-row transition metal interaction demonstrates the wide tunability of bond orders across the period, ranging from formally quintuple to single by replacing the transition metal in UTM-2. The periodic trend shows an increase in bond order from Cr to Mn and then a decrease across the period. We predict for the first time 5-fold bonding between U and Mn in the synthetically inspired complexes: UMn-2. The electronic spectra of UMn-2 complex shows low-lying $\delta \rightarrow \delta^*$ singlet and triplet transitions. We observed the presence of dative bonds in UCo-2, which are directed from the 3d orbitals of Co to the unoccupied 6d orbital of uranium, while UNi contains a half bond between U and Ni. Our study will help the future design of novel uranium–transition metal compounds with multiple bonds.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01264.

Orbitals and active spaces, partial atomic charges and spin populations, structures, computed infrared spectra, binding energies, CASSCF and MS-CASPT2 absolute energies (PDF)

CASSCF optimized natural orbitals in the Molcas format (RasOrb, plain text) (ZIP)

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Notes

The authors declare no competing financial interest.

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