Computer Chemistry

Theoretical Search for Very Short Metal–Actinide Bonds: NUIr and Isoelectronic Systems**

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It was recently discovered[1] that platinum can act, in discrete molecular groups, as a chemical analogue to oxygen. For instance the discrete molecular groups CPt, CPt_2, and CPt_3^{2-} were then found to have analogous bonding systems as CO, CO_2, and CO_3^{2-}, respectively. These analogues provide an example of the isolobal principle, now without any outside ligands on the Pt atom, a situation described as its "autogenic isolobality". These systems have multiple C–Pt bonds. The isolobal principle of Hoffmann refers to the similar chemical behavior of an sp hybrid and a metal atom with ligands, -ML_n. In "autogenic isolobality" a similar behavior occurs without the ligands, L.

Granted the extreme oxophilicity of the early actinides it is interesting to ask whether Pt or its neighbors could act as an oxygen analogue in uranyl, UO_2^{2+}. The isoelectronic neighbors, such as IrUIr as an analogue to the known NUN, immediately present themselves. It turned out that at least in the half-substituted case, the idea works. The suggestion is remotely favored by the existence of UPt_n ($n = 1$–3, 5) in the solid phase.[2] In general, the early-d–late-d metallic alloys, such as $CePt_2$ or $HfPt_3$, are astonishingly stable. This was described as Lewis acid–base interactions.[3] These suggested

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molecules would have multiple bonds. The molecule UAu$_4$ with a calculated single U^{IV}–Au bond of about 270 pm was recently predicted.[4] While Au is a pseudohalogen, Au$^+$ is for the present purpose a pseudochalcogen.

A further aspect is the conspicuous absence of strong actinide–actinide bonds in molecules. While a D_0 of 2.25(22) eV has been measured for diatomic U$_2$,[5] the only example on such a bond in singlet systems is the acetylene-like molecule predicted to be HTh≡ThH.[6] A theoretical treatment of U$_2$,[7,8] or even the possibly closed-shell and quintuply-bonded U$_2^{2+}$ still presents daunting difficulties.[9] That would also make an An–M(5d) bond an interesting halfway achievement.

The only previous structurally characterized molecular actinide–M(nd) bonds that we are aware of, are the unbridged Th–Ru bond of 302.77(6) pm in (Cp′)$_2$Th^{I}Ru(Cp)(CO)$_2$, (Cp′ = C$_5$Me$_5$).[10,11] and the phosphido-bridged Th–Pt bond of 298.4(1) pm in the molecule (C$_5$Me$_5$)$_2$Th(μ-PPh$_2$)$_2$Pt(PMe$_3$), reported by Hay et al. [12] Theoretical calculations suggested a normal σ bond between Th and Pt.

Herein we report the results of a study of a series of new molecules with general formula EUM, E = C,N,O, or F. U is the uranium atom, and M = Re,Os,Ir, or Pt. These molecules turned out to be stable according to our quantum-chemical calculations and the bond between the uranium and the 5d metal is very short.

Table 1: Trends of the DFT-level singlet-state E–U and U–M bond lengths (in pm) for the EUM^q isoelectronic series.[a]

	Re	Os	Ir	Pt	Au
F	FURe 200, **207** +0.31				
O	OURe$^-$ 184, 209 +0.17	OUOs 179, 210 +0.38	OUIr$^+$ 175, 215 −0.27	OUPt^{2+} 172, 226 −0.83	
N		NUOs$^-$ 176, 213 +1.16	NUIr 172, 218 +1.07	NUPt$^+$ **169**, 230 +0.17	NUAu^{2+} 168, 256 −0.34
C				CUPt 175, 236 −0.21	

[a] Shortest bond lengths in boldface. NUAu^{2+} is exceptionally a triplet state. The singlet-triplet splitting (in eV) is given below the bond lengths. Positive values indicate a singlet ground state.

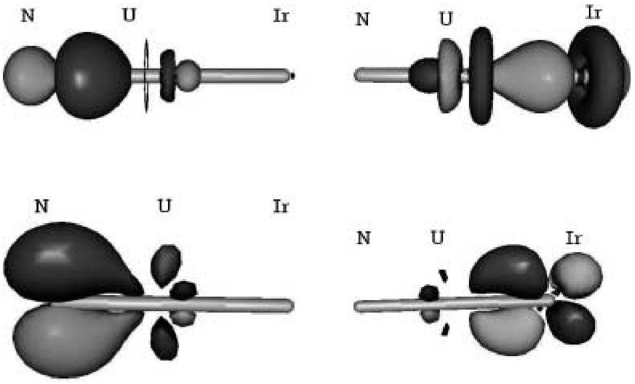

Figure 1. CASSCF molecular orbitals of NUIr.

We have first carried out a quasirelativistic density functional theory (DFT) mapping of the trends of the E–U and U–M bond lengths and the singlet–triplet splittings in the EUM^q isoelectronic series. The results are shown in Table 1, where q is the charge chosen to obtain closed shells, isoelectronic with uranyl. Among the neutral species, a singlet ground state is most clearly favored at NUIr. The shortest N–U bond occurs at NUPt$^+$ and the shortest DFT singlet-state U–M bond of 207 pm occurs in FURe. Such a predicted bond length is extremely short. The four bonding orbitals are shown in Figure 1 for NUIr and also strongly suggest a N≡U≡Ir system with two well-developed triple bonds, as previously found for uranyl, NUN, and isoelectronic systems.[13–17] The calculated dipole moment for NUIr is 0.24 Debye. with direction N(+) Ir(−). Both the smallness of the electric dipole moment of NUIr and the similarity of the CASSCF orbitals in Figure 1 suggest that the two bonds to the central uranium atom have a very similar character.

Table 2: Predicted species and bond distances (pm) in their ground state.

XUM	El. state	R(UX)	R(UM)	ΔE(Trip-Sing) [eV]
NUIr	$^1\Sigma^+$	172.2	218.4	+1.07
	$^3\Phi$	175.2	220.9	
NUIr[a]	$^1\Sigma^+$	174.9	216.7	+1.49[b]
NUIr[c]	$^1\Sigma^+$	174.1	214.5	
OUOs	$^1\Sigma^+$	179.2	210.2	+0.38
	$^3\Phi$	182.6	211.6	
FURe	$^1\Sigma^+$	200.1	206.7	+0.31
	$^3\Phi$	202.4	207.6	
CUPt	$^1\Sigma^+$	174.6	235.6	−0.21[b]
NUOs$^-$	$^1\Sigma^+$	213.2	176.2	+1.16
	$^3\Phi$	216.6	180.2	
OURe$^-$	$^1\Sigma^+$	184.1	209.1	+0.17
	$^3\Phi$	186.1	220.0	
NUPt$^+$	$^1\Sigma^+$	169.3	229.6	+0.17
	$^3\Phi$	173.0	236.7	
NUAu^{2+}	$^1\Sigma^+$	168.1	256.4	−0.34
	$^3\Phi$	173.2	279.1	
OUIr$^+$	$^1\Sigma^+$	174.6	215.0	−0.27
	$^3\Phi$	177.2	218.3	
OUPt^{2+}	$^1\Sigma^+$	171.6	226.3	−0.83
	$^3\Phi$	172.2	236.0	

[a] CASPT2 BS2. [b] Vertical. [c] CASPT2 BS3.

The DFT results can be compared with the CASPT2 results in Table 2, and are not found to change much. The CASPT2 electronic spectrum of NUIr up to 5 eV is reported in Table 3. The ground state of NUIr is of $^1\Sigma^+$ type. The first excited state, $^1\Pi$, lies 1.33 eV above the ground state. The first triplet excited state, $^3\Phi$, lies 1.49 eV above the ground state. The spectrum has been recalculated with the inclusion of spin–orbit coupling between all the spin-free singlet and triplet states reported in Table 3 and the first spin–orbit excited state is found to lie (vertically) 1.07 eV above the Ω_0 ground state. The inclusion of spin–orbit coupling does not have any effect on the structure of NUIr in its ground state.

Table 3: CASPT2 vertical electronic spectrum for NUIr with BS2.

XUM	El. state	*E* [eV]	*E* [cm^{-1}]
	$^1\Sigma^+$	0.00	0.00
	$^1\Phi$	1.33	10727.7
	$^3\Phi$	1.49	12005.6
	$^1\Phi$	2.35	19015.0
	$^3\Phi$	2.61	21043.9
	$^3\Sigma^-$	3.11	25073.1
	$^3\Sigma^-$	3.14	25291.2
	$^1\Sigma^-$	3.41	27503.9
	$^1\Sigma^-$	3.54	28601.8
	$^3\Sigma^+$	4.51	36353.9
	$^3\Sigma^+$	5.08	40985.0

The bond along the molecule involves essentially σ- and π-bonding orbitals (see also below the discussion about the active space). The *δ* orbitals are strongly localized at Ir and only weakly bonding to U. As a simple test, a Mulliken population analysis for NUIr is shown in Table 4. The end atoms are only slightly negative. The U populations amount to 6d$^{2.41}$5f$^{2.76}$. If the 7p is neglected, only a very slight 6p hole of −0.03 is assigned to U.

Table 4: CASPT2-BS2 Mulliken population analysis for NUIr.[a]

	N	U	Ir
δ	−0.24	+0.46	−0.22
s	3.65	12.28	11.37
p	3.49	29.97	24.15
d	0.20	32.41	27.58
f		16.76	14.10
g		0.12	

[a] *δ* is the partial charge on each atom, followed by the number of electrons in each type of orbitals.

The calculated vibrational frequencies are reported in Table 5. The U–M stretching vibrations are calculated to occur in the range from 300 to 400 cm^{-1}. All the systems are clearly linear.

In view of the potentially helpful 4d^{10}5s^0 electron configuration of Pd, one attempt was made on NUPd$^+$. The U–Pd bond length was 231.5 pm and the triplet was clearly below the singlet. Other less promising tests were those on the symmetric, doubly substituted systems IrUIr and PtUPt^{2+}, analogous to the known NUN and OUO^{2+}. They both turned out to be linear. IrUIr has a triplet ground state, with a Ir–U bond length of 220.7 pm and harmonic frequencies in the range 56–367 cm^{-1}. PtUPt^{2+} in its singlet state has a Pt–U bond length of 222.6 pm, and harmonic frequencies in the range 46–333 cm^{-1}. The triplet lies lower in energy than the singlet, but a full triplet optimization could not be carried out. The asymmetric OsUPt was also investigated and it has a triplet ground state with Os–U and U–Pt bond lengths of 211 and 239 pm, respectively, and harmonic frequencies in the range 53–385 cm^{-1}.

One possible way to create the present species might be by "brute force", which would involve the simultaneous evaporation of the three elements. Another possibility would be to start with the experimentally known diatomics IrN or UN. The exothermic reaction energies with a U or Ir atom are −460 and −510 kJ mol^{-1}, respectively.

Table 5: Harmonic B3LYP frequencies (cm^{-1}) and their IR intensities (km mol^{-1}) in parentheses with the BS1 basis set.

States	π	σ	σ
		NUIr	
$^1\Sigma^+$	100.63	320.35	1119.51
	(36.5)	(3.1)	(282.5)
$^3\Phi$	117.56	300.75	991.37
	(38.5)	(4.1)	(49.8)
		OUOs	
$^1\Sigma^+$	102.67	372.83	943.61
	(16.5)	(0.9)	(274.5)
$^3\Phi$	119.80	363.00	888.54
	(21.7)	(2.0)	(297.3)
		FURe	
$^1\Sigma^+$	39.30	390.96	628.81
	(3.8)	(1.1)	(96.7)
$^3\Phi$	62.80	368.86	594.64
	(6.2)	(0.0)	(113.5)
		NUOs$^-$	
$^1\Sigma^+$	105.11	344.48	1034.96
	(34.4)	(0.0)	(525.2)
$^3\Phi$	120.14	320.93	928.34
	(41.0)	(3.7)	(273.8)
		OURe$^-$	
$^1\Sigma^+$	89.76	377.50	857.09
	(9.2)	(0.2)	(325.2)
$^3\Phi$	87.76	309.61	828.46
	(15.4)	(0.4)	(333.1)

IrN has a calculated bond length of 160.4 pm and a harmonic frequency of 1231 cm^{-1} in the $^1\Sigma^+$ ground state, compared to the experimental values of 160.68 pm and 1126 cm^{-1}.[18] UN has a calculated bond length of 174.4 and a harmonic frequency of 1052 cm^{-1} pm in the $^4\Sigma$ ground state, compared to the experimental value of 996 cm^{-1}.[19,20] In a previous study[17] the formation of NUN from U and N$_2$ was investigated, and NUN was found to lie about −230 kJ mol^{-1} lower in energy than U and N$_2$. The present results thus indicate that the energy balance would be even more favorable for NUIr. In conclusion, we are predicting the existence of a very short triple Ir$\equiv$U bond of about 215 pm in a closed-shell NUIr molecule.

Experimental Section

Computational methods: The calculations were performed at the B3LYP density functional level of theory. Some of the species were also studied by using the complete active space (CAS) SCF (SCF = self-consistent field) method[21] with dynamic correlation added by second-order perturbation theory (CASPT2).[22]

A 3s2p1d basis set of 6-31g* type was used for the light atoms, namely N and O. For the heavy atoms the core electrons were replaced with quasirelativistic pseudopotentials[23] resulting in 16, 17, 18, and 32 valence electrons for Os, Ir, Pt, and U, respectively. The corresponding valence basis sets were of 6s5p3d quality for Os, Ir, Pt, and 8s7p6d4f quality for U. We labeled such basis sets as BS1 basis sets. The CASSCF/CASPT2 calculations were performed with all electron basis sets of ANO type for all atoms. The exponents were optimized by using the Douglas–Kroll (DK) Hamiltonian. The contracted basis set was 4s3p2d for N, 8s7p5d3f for Ir, and 9s8p7d5f for U, indicated as BS2. The BS2 basis was further extended by one f function for N, one g function for Ir, and two g function for U, indicated as BS3.

In the CASPT2 calculations scalar relativistic effects were included with a DK Hamiltonian.[24,25] The effects of spin–orbit coupling were introduced by using a method based on the CASSCF state interaction approach (CASSI).[26,27] Here, the CASSCF wave function generated for a number of electronic states are allowed to mix under the influence of a spin–orbit Hamiltonian. The method has recently been described,[28] and we refer to this article for details.

In our recent study of the NUN system,[17] we found that it was important to include in the active space the nitrogen 2p orbitals and the corresponding UN antibonding orbitals of σ and π type. They are hybrid orbitals mixing 5f, 6d, and 7s. This gives an active space of 12 electrons in 12 orbitals (12/12). In the NUIr case, the 2p orbitals of one nitrogen atom have been replaced with the 4d orbitals of appropriate symmetry, namely 4d σ and π. Preliminary calculations, including also the unoccupied Ir 4d δ, indicated that the antibonding orbitals did not affect the results, so they have not been included in most of the calculations. The CASPT2 geometry optimization of NUIr was carried out numerically.

The DFT calculations have been performed with the Gaussian 98 package and the CASSCF/CASPT2 calculations with the MOLCAS 6.0 program.[29]

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