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Actinide-Transition Metal Heteronuclear Ions and Their Oxides: $\{IrUO\}^+$ as an Analogue to Uranyl

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Recent theoretical calculations have shown that Ir should behave as a chemical analogue to N, with the result that $IrUO^+$, like known NUO^+, is predicted to be a stable species isoelectronic with UO_2^{2+}, the uranyl dication. The target heterometallic analogue to uranyl has now been prepared by direct laser desorption/ionization of a U/Ir alloy, and by oxidation of UIr^+ with N_2O and C_2H_4O. Properties of UIr^+, UPt^+, and UAu^+ bimetallic ions have been studied. They demonstrate direct actinide–transition metal bonding, and support the concept of "autogenic isolobality".

Introduction

Despite that actinide–transition metal (An–M_{nd}) bonding has been an important goal in molecular actinide chemistry, remarkably few complexes have been characterized in which an An–M_{nd} bond has been clearly identified (An = Th, U).[1,2] In these complexes, the An–M_{nd} bonding is either mediated by phosphido bridges,[1] or is between the An and a M_{nd}-containing fragment, $M_{nd}Cp(CO)_2$ (Cp = *cyclo*-C_5H_5),[2] which can be considered an "organometallic pseudohalogen".[3] Accordingly, there to date seem to be no well-established molecular complexes with a direct, unsupported covalent An–M_{nd} bond.

Gaseous AnM_{nd} bimetallics are elementary molecular species incorporating distinct An–M_{nd} bonding. The ThRu, ThRh, ThIr, ThPt, and URh molecules, synthesized in high-temperature vapors, have bond energies of 500 to 600 kJ mol^{-1}.[4] Direct An–M_{5d} bonding was also demonstrated with the preparation of the $ThFe^+$ and UFe^+ ions by collision-induced dissociation (CID) of $AnFe(CO)_x^+$ (x = 2, 3).[5] In a recent theoretical study, Gagliardi and Pyykkö[6] predicted several stable triatomic species which would incorporate covalent bonds between uranium and 5d transition metals (M_{5d}), including $IrUO^+$. According to the concept of "autogenic isolobality",[6,7] Au can behave as a pseudohalogen, Pt as a pseudochalcogen, and Ir as a pseudopnictogen. Thus, $IrUO^+$ can be formally represented as $\{Ir{\equiv}U{=}O\}^+$, which is nominally isoelectronic with $\{N{\equiv}U{=}O\}^+$ and $\{O{=}U{=}O\}^{2+}$ (the uranyl dication);[6] both of the latter have been prepared in the gas phase.[8,9]

In view of recent theoretical predictions of strong U–M_{5d} covalent bonds and stable triatomic species incorporating such bonds, we employed laser desorption/ionization (LDI) of binary An/M_{5d} alloys to synthesize gaseous AnM_{5d}^+ bimetallic ions. The synthesis of these ions, and their reactions with nitrous oxide, ethylene oxide, and ethane, are interpreted in the context of "autogenic isolobality",[6,7] and the nature of An–M_{5d} bonds.[6]

Results and Discussion

In the initial experiments that employed dilute (≈ 2–5 wt.-%) An/Pt alloys (An = Th, Pa, U, Np, Pu, Am, Cm),[10] several diatomic and triatomic ions were produced. These included the bimetallics, $ThPt^+$, $PaPt^+$, UPt^+, $NpPt^+$, $PuPt^+$, $AmPt^+$ and $CmPt^+$, the trimetallics $ThPt_2^+$ and UPt_2^+, and the bimetallic oxides $OThPt^+$, $OPaPt^+$, $OUPt^+$ and $ONpPt^+$. The appearance of the $OAnPt^+$ (from O contamination in the alloys) only for Th through Np reflects the particularly strong O–An^+ bonds there;[10] the suggested atomic connectivities of the oxides are consistent with this strong bonding.

Generation of the $AnPt^+$ ions motivated a LDI study of U/M_{5d} alloys (M_{5d} = Os, Ir, Pt, Au; ≈ 20 wt.-% U). The following three bimetallics were produced in the indicated order of relative yields: $UAu^+ > UPt^+ > UIr^+$; UOs^+ was not observed. Illustrative LDI spectra are shown in Figure 1. For each U/M_{5d} (M_{5d} = Au, Pt, Ir) alloy, U^+ and M_{5d}^+ were produced by LDI, both in an abundance very roughly an order of magnitude greater than that of UM_{5d}^+.

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In analogy with high-temperature synthesis of AnM_{nd},[4] the UM_{5d}^{+} (and other AnM_{5d}^{+}) are presumably formed by coalescence of a neutral atom and monopositive ion in the laser-desorption plume. As the four IE[M_{5d}] are in the range of 8.7 eV (Os) to 9.2 eV (Au) and IE[U] = 6.2 eV,[11] electron transfer from U to M_{5d}^{+} is exothermic by ≥ 2.5 eV and should predominate over $\mathrm{U/M}_{5d}^{+}$ coalescence. A probable mechanism for generation of the UM_{5d}^{+} is instead association of U^{+} with M_{5d}. It is not possible to be conclusive regarding the bimetallic formation mechanism(s) or the relative yields. However, several atomic properties that might account for the relative UM_{5d}^{+} yields vary monotonically between Os and Au; for example, the electron affinities {EA/eV}[11] are: Os {1.1} < Ir {1.6} < Pt {2.1} < Au {2.3}. Another factor that likely affects the propensity for coalescence during alloy LDI is the relative volatilities of the transition-metal constituents, as indicated by their vapor pressures at 2500 K{P/Torr}:[12] Os {$3 \cdot 10^{-6}$} < Ir {$6 \cdot 10^{-4}$} < Pt {0.04} < Au {17}. In a general sense, the relative yields can be considered to be related to the different electronic structures of the M_{5d}. LDI also resulted in the formation of the trimetallics UAu_2^{+} and (minor) UPt_2^{+}, but not UIr_2^{+} or UOs_2^{+}. Bimetallic monoxides were also produced by LDI, with the following average relative abundances: $\mathrm{OUAu}^{+} > \mathrm{OUPt}^{+} > \mathrm{OUIr}^{+}$ (OUOs^{+} was not observed). The OUIr^{+} ion has been predicted as a species comprising a strong formally triple U≡Ir bond, which renders it isoelectronic with dipositive uranyl, $\mathrm{O{=}U{=}O}^{2+}$,[6] and $\mathrm{N{\equiv}U{=}O}^{+}$.[8]

Some bimetallic ions were subjected to collision-induced dissociation (CID). Whereas UAu^{+} fragmented into U^{+} and Au, there was no evidence for dissociation of UPt^{+} or UIr^{+}. Although these results suggest a relatively weak U^{+}–Au bond, consistent with single- rather than multiple-bond character, such CID studies are only qualitative. Electronic structure calculations should be performed to assess the validity of these somewhat speculative interpretations of the CID results regarding the relative bond energies. The CID of OUAu^{+} and OUPt^{+} resulted exclusively in fragmentation to OU^{+} and Au or Pt, suggesting that the U–M_{5d} bonds are weaker than the U–O bonds (there was insufficient OUIr^{+} for a CID study). These latter CID results support the proposed O–U–M_{5d} connectivity – for both the U–M_{5d}–O and U–O–M_{5d} connectivities, some $\mathrm{M}_{5d}\mathrm{O}$ loss would be expected.

To further probe the nature of these UM_{5d}^{+}, they and the constituent atomic metal ions were treated with $\mathrm{N_2O}$, $\mathrm{C_2H_4O}$ (ethylene oxide) and $\mathrm{C_2H_6}$. The results of the primary ion–molecule reactions are summarized in Table 1. In some cases, secondary and higher order reactions were observed, but these are not discussed here.

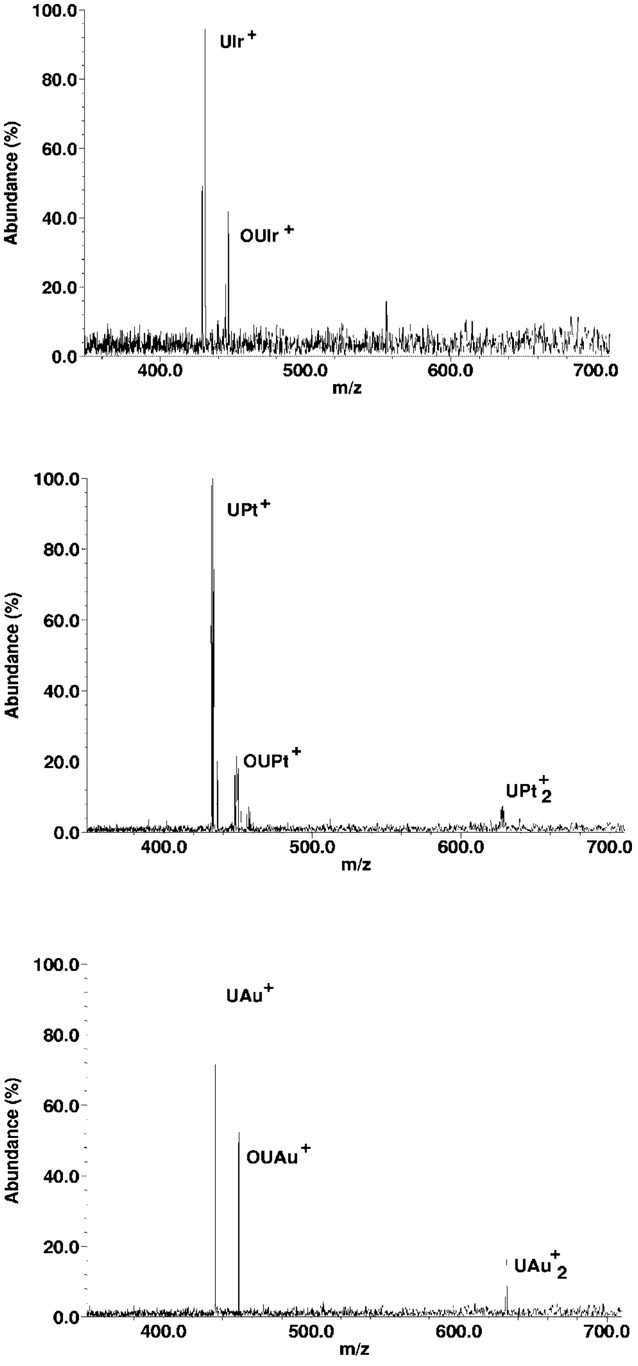

Figure 1. Direct LDI mass spectra for U/Ir (top), U/Pt (middle), and U/Au (bottom) alloys. The two isotopes of Ir and several isotopes of Pt are evident. The minor peaks in the middle spectrum at m/z = 456–460 correspond to the composition $\mathrm{UPtC_2}^{+}$.

For a reaction of thermalized ions to occur, the overall process must be exothermic regardless of kinetic considerations. If a reaction does not proceed it may be due to a kinetic barrier rather than endothermicity. Here we only consider thermodynamic limits based on the requirement for exothermicity; no assumptions are made regarding kinetics. In accord with previous results, both Ir^{+}[13a] and Pt^{+}[13] were oxidized to the monoxides by $\mathrm{N_2O}$, consistent with the requirement that $D[\mathrm{Ir^{+}{-}O}]$ ca. 250 kJ mol^{-1}[14] and $D[\mathrm{Pt^{+}{-}O}]$ ca. 322 kJ mol^{-1}[15] exceed $D[\mathrm{N_2{-}O}]$ = 167 kJ mol^{-1}.[14] That Au^{+} is unreactive with $\mathrm{N_2O}$[13a] may reflect a kinetic or thermodynamic barrier. As reported previously,[8,10a] U^{+} reacts with $\mathrm{N_2O}$ to give UO^{+} and UN^{+}. The three UM_{5d}^{+} ions react with $\mathrm{N_2O}$ to give OUAu^{+}, OUPt^{+} and OUIr^{+}, along with UO^{+} (and $\mathrm{AuN_2}$, $\mathrm{PtN_2}$ and $\mathrm{IrN_2}$ as presumed neutral products). Given the inert charac-

Table 1. Products, rate constants, and efficiencies for primary reactions of atomic and bimetallic ions.[a]

Reactant Ion	N_2O Product(s)	k	k/k_{COL}	C_2H_4O Product(s)	k	k/k_{COL}	C_2H_6 Product(s)	k	k/k_{COL}
U^+[b]	UO^+(60) UN^+(40)	3.26	0.47	UO^+	5.89	0.34	–	<0.01	<0.001
Ir^+	IrO^+	1.38	0.19	$IrCH_2^+$	3.59	0.21	$IrC_2H_4^+$(50) $IrC_2H_2^+$(50)	2.21	0.23
Pt^+	PtO^+	0.17	0.024	$PtCH_2^+$	2.82	0.16	$PtC_2H_4^+$(60) $PtC_2H_2^+$(40)	2.29	0.24
Au^+	–	<0.01	<0.001	$AuCH_2^+$	1.98	0.11	$AuC_2H_4^+$	1.86	0.19
UIr^+	$OUIr^+$(70) UO^+(30)	0.65	0.098	$OUIr^+$	4.01	0.24	–	<0.01	<0.001
UPt^+	$OUPt^+$(80) UO^+(20)	0.64	0.095	$OUPt^+$	3.50	0.21	–	<0.01	<0.001
UAu^+	$OUAu^+$(40) UO^+(40) UN^+(20)	1.93	0.29	$OUAu^+$(60) UO^+(40)	4.60	0.28	–	<0.01	<0.001

[a] Where more than one product was formed, the relative abundances (%) are indicated in parentheses. Rate constants (k) are in units of 10^{-10} cm^3 molecule^{-1} s^{-1}; k/k_{COL} are the reaction efficiencies.[10c] Absolute rate constants are uncertain by ±50%; relative uncertainties are ±20%. [b] Results for the U^+/N_2O and U^+/C_2H_4O reactions are from ref.[10a].

ter of bare Au^+ toward N_2O, the formation of $OUAu^+$ supports the proposed atomic connectivity. The $OUIr^+$ connectivity had been predicted from theory.[6] The UAu^+/N_2O reaction produced $NUAu^+$, for which the thermodynamic requirement is $D[N–UAu^+] \geq \{D[N–NO] = 482\ \text{kJ mol}^{-1}\}$.[14] That both UO^+[8,10a] and UPt^+ are oxidized by N_2O is in agreement with the isolobal analogy between UPt^+ and UO^+.[6,7] The observation that UN^+ is unreactive with N_2O, while formally isoelectronic UIr^+ is oxidized to $OUIr^+$ by N_2O, illustrates that the "autogenic isolobality" concept does not imply absolute correspondence, but rather chemical analogy.[6,7]

Whereas U^+ is oxidized to UO^+ by C_2H_4O,[10a] the three $M_{5d}{}^+$ react to give carbenes, $M_{5d}CH_2{}^+$ (Table 1). Thus, if the neutral product of the $M_{5d}{}^+/C_2H_4O$ reactions is formaldehyde (CH_2O), the thermodynamic requirement is $D[M_{5d}{}^+–CH_2] \geq 334\ \text{kJ mol}^{-1}$; if instead the neutral products are $CO + H_2$, the thermodynamic requirement is $D[M_{5d}{}^+–CH_2] \geq 332\ \text{kJ mol}^{-1}$.[14] Previous experimental studies have established $D[Ir^+–CH_2] = 474 \pm 3\ \text{kJ mol}^{-1}$,[16] $D[Pt^+–CH_2] \geq 464\ \text{kJ mol}^{-1}$,[17] and $D[Au^+–CH_2] \geq 397\ \text{kJ mol}^{-1}$.[18] The formation of the triatomic oxides, rather than carbenes, from the $UM_{5d}{}^+/C_2H_4O$ reactions is reminiscent of the U^+/C_2H_4O reaction. This suggests that the reactivities of the $UM_{5d}{}^+$ are dominated by the oxophilicity of the uranium metal center, and that the product oxides can be represented as $OUM_{5d}{}^+$. In analogy with the ethane results discussed below, the U^+-like, rather than $M_{5d}{}^+$-like, reactivity of the $UM_{5d}{}^+$ with C_2H_4O suggests that the transition-metal center has been rendered inert. The thermodynamic requirement for the C_2H_4O oxidation reactions is $D[O–UM_{5d}{}^+] \geq 354\ \text{kJ mol}^{-1}$[14] ($M_{5d}$ = Ir, Pt, Au). The oxidation of the three $UM_{5d}{}^+$ in a similar manner to bare U^+ provides a further indication of the O–U–M_{5d} connectivities proposed above. Additional calculations are required to establish the energy differences between the different isomers, as well as whether the species are linear (like $UO_2{}^{2+}$) or bent (like ThO_2). The calculations by Gagliardi and Pyykkö[6] indicate that some triatomic uranium-transition metal species adopt a linear structure but the bond angle for $OUIr^+$ (or other $OUM_{5d}{}^+$) was not reported.[6]

The appearance of UO^+ (+ AuC_2H_4) from the UAu^+/C_2H_4O reaction is consistent with a weaker U^+-Au bond as compared with the U^+–Ir and U^+–Pt bonds. Neither the UIr^+/C_2H_4O nor UPt^+/C_2H_4O reactions result in UO^+ (+ $M_{5d}C_2H_4$). This distinctive behavior of UAu^+ supports the interpretation of the CID results discussed above in terms of the relative U–M_{5d} bond strengths.

The results in Table 1 for reactions with ethane are in agreement with earlier reports for U^+/C_2H_6,[19] Ir^+/C_2H_6,[17] and Au^+/C_2H_6;[18] in an ion beam study of the Pt^+/C_2H_6 reaction,[20] only $PtC_2H_4{}^+$ (+ H_2) was reported, not $PtC_2H_2{}^+$ (+ $2H_2$). In contrast to the bare $M_{5d}{}^+$, but like bare U^+, the three $UM_{5d}{}^+$ were unreactive towards C_2H_6: the reactivity of the transition metal center is evidently "shut off" in the $UM_{5d}{}^+$, in distinct contrast to $Pt_2{}^+$, which is as effective at dehydrogenating C_2H_6 as is atomic Pt^+.[20] The reduced reactivity of $UM_{5d}{}^+$ also contrasts with ions such as $PtCu^+$, $PtAg^+$ and $PtAu^+$, which dehydrogenate methane with an efficiency comparable to that of $Pt_2{}^+$.[21] According to the concept of "autogenic isolobality",[6,7] it can be considered that there are no non-bonding valence electrons at the transition metal centers in Au–U^+, Pt =U^+ and Ir≡U^+. With the lack of available valence electrons at the M_{5d} center, reactivity would disappear, as is observed.

In conclusion, we have synthesized several new $AnPt^+$ (An = Th through Cm), and examined the chemistries of UIr^+, UPt^+, and UAu^+ in the general context of "autogenic isolobality", and the prediction of strong actinide–transition metal bonds.[6,7] Our experimental results are consistent with the predicted bonding for these species – specifically, the reactivities of the transition-metal centers are apparently "shut off" in the $UM_{5d}{}^+$ bimetallics. With each of the three reagents, N_2O, C_2H_4O and C_2H_6, the reactivities of the $UM_{5d}{}^+$ ions were evidently dominated by the U metal center, in agreement with the concept of "autogenic isolobality".[6] To further probe Ir as a pseudopnictogen, Pt as a pseudochalcogen, and Au as a pseudohalogen or pseudohydrogen,[22,23] our future efforts will compare directly reactivities of the $UM_{5d}{}^+$ (M_{5d} = Ir, Pt, Au) and isoelectronic UX^+, where X is a pnictogen, chalcogen, or halogen (or H). One noteworthy result of the present work was the synthesis of $IrUO^+$, which was predicted to exist as a stable species isoelectronic with uranyl, OUO^{2+}.[6]

Experimental Section

The experimental procedures, described in detail elsewhere,[5,9,10] are briefly summarized here. The atomic and bimetallic ions were produced by direct LDI of arc-melted actinide–transition metal alloys,[10] An/Pt (An = natural Th-232, Pa-231, depleted U, Np-237, Pu-242, Am-243, Cm-248) and U/M_{5d} (M_{5d} = Os, Ir, Pt, Au). The LDI ions directly entered the source cell of a dual cell Finnigan FT/MS 2001-DT FTICR mass spectrometer equipped with a 3-T magnet and controlled by an Odyssey data system; all experiments were performed in the source cell. The N_2O and C_2H_6 were commercial gases (>99%); the C_2H_4O was a commercial liquid (>99%) degassed prior to use. The reagents were introduced into the spectrometer through a leak valve to pressures of $3 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ Torr. Isolation of ions was achieved using single-frequency, frequency-sweep, or SWIFT excitation. The reactant ions were thermalized by collisions with argon, introduced through a leak valve to a constant pressure in the range of $(1–5) \times 10^{-6}$ Torr, concurrent with the reagent gas. Thermalization of the reactant ions was confirmed by standard procedures.[5,9,10] The CID experiments were carried out by ion excitation and collision with argon.[5] The pseudo-first-order rate constants, k, were determined from the reactant ion decay as a function of time; the collisional rate constants, k_{COL}, were calculated as described previously.[10c]

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