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Actinide-Transition Metal Bonding in Heterobimetallic Uranium- and Thorium-Molybdenum Paddlewheel Complexes

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We report the preparation of four heterobimetallic uranium- and thorium-molybdenum paddlewheel complexes. The characterisation data calculations suggest the presence of Mo→An σ -interactions in all cases. These complexes represent unprecedented actinide-group 6 metal-metal bonds, where before heterobimetallic uranium-metal bonds were restricted to group 7-11 metals.

Metal-metal bond chemistry is a vast, active field of endeavour with implications for developing and understanding bonding models, catalysis, metal surface reactions, electronic and magnetic devices, and bio-inorganic chemistry.¹ Although metal-metal bonding in the d-, p-, and now even s-blocks is developed and burgeoning,^{1,2} that of the f-block and especially actinides (An) is more limited.³ Although there have been recent insights into An-An bonding in theoretical models,⁴ matrix isolation experiments,⁵ or f-block endofullerene compounds,⁶ the range of accessible An-metal linkages obtainable under ambient conditions remains relatively small, being limited to the late transition metals (group 7-11),⁷ or main group metals.⁸ In these cases electron rich metals are able to donate electron density to the hard electropositive An-centres, and despite the bonding being predominately ionic, covalent σ - and π -interactions have been observed in these linkages giving new insight into the nature of actinide bonding.^{8c} It follows, therefore, that there are no discrete uranium-group 3-6 linkages reported to date. This is presumably due to the paucity of feasible synthetic precursors and routes, and the likely fundamentally weak nature of such linkages.

Although we have previously prepared unsupported U-Re, -Ru, -Co, -Rh, and -Ga bonds,^{7a,j-n,8c} group 3-6 metal-uranium linkages have remained elusive following the same synthetic methodologies. As a result, we concluded that supporting ligands are essential to the isolation of An-early transition metal linkages due to the inherent

instability of such a bond. We initially targeted the preparation of An-group 6 linkages as we anticipated that the preparation of these linkages would be more likely than increasingly electron-poor group 3-5 congeners. As phosphinoamide ligands have been utilised in the isolation of complexes containing both U- and Zr- metal linkages,^{7g,9} we surmised that they would be attractive candidates in attempts to isolate An-group 6 complexes.

Scheme 1. Synthesis of complexes **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo**. Reagents and conditions: (i) [Mo(CO)₃(NCMe)₃], toluene, reflux 16 h, −3 MeCN.

Refluxing [XM(MesNPPH₂)₃] (Mes = 2,4,6-trimethylphenyl; X = Cl, M = U, **UCI**; X = I, M = U, **UI**; X = Cl, M = Th, **ThCl**; X = I, M = Th, **ThI**)¹⁰ with [Mo(CO)₃(NCMe)₃]¹¹ in toluene afforded, after work-up and recrystallisation, the heterobimetallic orange U- and yellow Th-Mo complexes [(X)M(MesNPPH₂)₃Mo(CO)₃] (X = Cl, M = U, **UCIMo**; X = I, M = U, **UIMo**; X = Cl, M = Th, **ThCIMo**; X = I, M = Th, **ThIMo**) in crystalline yields of 88, 62, 36, and 41%, respectively, Scheme 1.¹⁰ Despite exhaustive attempts, the Cr and W congeners were not accessible under equivalent reaction conditions; we found that, despite applying forcing conditions, [M'(CO)₃(NCMe)₃] (M' = Cr, W) did not react with **UCI/UI** or **ThCl/ThI**. Utilising alternative precursors such as [M(CO)₆] afforded complex mixtures, from which [(Cl)U(MesNPPH₂)₂]{μ-(MesNPh₂P)₂}Cr(CO)₄ (**UCr**) and [(Cl)U(MesNPPH₂)₂]{μ-(MesNPh₂P)₂}W(CO)₄ (**UW**) were isolated in low yields.¹⁰ The fourth carbonyl of **UCr** and **UW** proved impervious to removal, even under photolytic conditions, and no metal-metal linkages were formed in any case. We note that Mo being the successful 'outlier' compared to Cr and W has been reported previously.¹²

To confirm the formulations of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** we determined their solid-state structures by single crystal

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X-ray diffraction, Figure 1.¹⁰ The four **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** complexes adopt overall similar structures in the solid state, and exhibit three-fold symmetric paddlewheel structures containing distorted trigonal bipyramidal An-ions. The X-An-Mo angles deviate from linearity by *ca.* 10°, at 171.79(4), 169.71(8), 172.18(8), and 170.81(6)°, and the An-Mo distances were found to be 3.1682(4), 3.159(2), 3.2986(11), and 3.310(2) Å, respectively, which compare well to the sum of the covalent radii of U/Th and Mo of 3.08 and 3.12 Å, respectively.¹³ The Th-Mo bonds are ~0.16 Å longer than the U-Mo bonds when the halide is kept constant, which is more than the difference in the sum of the covalent radii of U (1.70 Å) and the larger Th (1.75 Å).¹³

Figure 1. Molecular structures of: (a) **UCIMo**, (b) **UIMo**, (c) **ThCIMo**, (d) **ThIMo** with displacement ellipsoids set at 40% and hydrogen atoms omitted for clarity.

The An-X distances [U1-Cl1 = 2.5535(15); U1-I1 = 2.972(3); Th1-Cl1 = 2.640(3); Th1-I1 = 3.030(2) Å] vary as anticipated on the basis of the different radii of the halides and metals. The An-N_{amide} distances are characteristic of U^{IV}- and Th^{IV}-amide distances.¹⁴ The three phosphine and three carbonyl ligands define an octahedral geometry at Mo that is face-capped by the An in each complex. Interestingly, the C-Mo-P angles for all complexes reported here are compressed 2–8° from the octahedral ideal of 90°, perhaps reflecting the presence of weak An-Mo interactions. The Mo-P distances (~2.62 Å) in **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** can be considered long; for example, in the closely related complex [Mo{(Ph₂PCH₂)₃N}(CO)₃]¹⁵ the Mo-P distances are significantly shorter (av. 2.53 Å). The Mo-C distances in all four complexes span a narrow range of 1.941(13)–2.06(3) Å, which overall suggests slightly longer and by inference weaker Mo-C interactions than found in *fac*-[Mo(CO)₃(NCMe)₃] [av. 1.923 Å].¹¹

The Formal Shortness Ratio (FSR_{MM'} = MM' distance/sum of MM' covalent radii) allows normalised comparison of metal-metal

distances.¹ Using Pyykkö's values,¹³ the FSR for **UCIMo** (1.03) and **UIMo** (1.03) are shorter than for **ThCIMo** (1.05) and **ThIMo** (1.06) but each are consistent with other reported An-M bonds where Th-M linkages typically exhibit greater FSR values (mean values: U-Co: 1.06; U-Re: 1.00; U-Ru: 1.03; U-Ag: 1.06; U-Rh: 0.92; U-Fe: 1.08; U-Ni: 0.91; U-Pd: 0.93; Th-Co: 1.08; Th-Ni: 1.12; Th-Pt: 1.00; Th-Ru: 1.01; Th-Cu: 1.10).^{7a-o,q-s}

The ¹H NMR spectra of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** suggest retention of the symmetric C₃ paddlewheels in solution. Though we were not able to observe ³¹P{¹H} NMR resonances for **UCIMo** and **UIMo**, the single resonances observed in the ³¹P{¹H} NMR spectra of **ThCIMo** (46.18 ppm) and **ThIMo** (45.07 ppm) are consistent with the solid-state structures being retained in solution.¹⁰ The ³¹P{¹H} NMR resonances are shifted to higher frequencies with respect to the starting materials **ThCl** (20.72 ppm) and **ThI** (17.65 ppm),¹⁰ and are more comparable to [Mo(CO)₅(PPh₃)] (37.91 ppm)¹⁶ and consistent with the known trend of higher frequency ³¹P shifts upon complexation to Mo.¹⁷

Table 1. FTIR data for the C≡O stretches of **UCIMo**, **UIMo**, **ThCIMo**, **ThIMo**, *fac*-[Mo(CO)₃(NCMe)₃],¹⁸ and [Mo(CO)₃(PPh₃)₃].¹⁹

Entry	$\tilde{\nu}_1(\text{C}\equiv\text{O})^{\text{[a]}}$	$\tilde{\nu}_2(\text{C}\equiv\text{O})$
UCIMo	1969	1891
UIMo	1969	1904
ThCIMo	1967	1896
ThIMo	1967	1898
<i>fac</i> -[Mo(CO) ₃ (NCMe) ₃]	1915 ^[b]	1783 ^[b]
	1905 ^[c]	1790 ^[c]
	1921 ^[d]	1793 ^[d]
[Mo(CO) ₃ (PPh ₃) ₃]	1949 ^[b]	1835 ^[b]

[a] $\tilde{\nu}$ in (cm⁻¹), [b] nujol mull, [c] KBr disk, [d] CH₃CN solution

The FTIR spectra of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo**, Table 1, show that the C≡O stretches are shifted to higher wavenumbers by ~50/20 cm⁻¹ ($\tilde{\nu}_1$) and ~100/60 cm⁻¹ ($\tilde{\nu}_2$) relative to *fac*-[Mo(CO)₃(NCMe)₃]¹⁸/[Mo(CO)₃(PPh₃)₃]¹⁹, respectively. This suggests weaker Mo-CO back-bonding in **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo**, perhaps reflecting coordination to the An-ion suggesting the Mo-CO stretch may be a Mo→An donation reporter. We attempted to probe this further with cyclic voltammetry, but the **AnX** and **AnXM** complexes reported here do not show any electrochemical response in the solvent accessible window (THF).

The solution magnetic moments of compounds **UCIMo** and **UIMo** at 298 K are $\mu_{\text{eff}} = 2.25$ and 2.39 μ_{B} , respectively. These data are in excellent agreement with SQUID data of 2.26 and 2.30 μ_{B} , respectively, at 298 K. Upon cooling the magnetic moments of the powdered samples fall monotonically, reaching values of 0.26 and 0.28 μ_{B} at 2 K and tending to zero. These data are consistent with the magnetic behaviour of ³H₄ uranium(IV) ions.²⁰

To probe the bonding in **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** we examined the full structures of these complexes with DFT. The geometry optimised structures compare well to the experimental solid state structures, with bond lengths and angles computed to within 0.05 Å and 2° of experiment. We thus conclude that the calculations represent a qualitative electronic structure picture. The computed An MDC-*q* charges for **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** of 2.20, 2.17, 2.18, and 2.14 and the calculated U MDC-*m* spin densities of -2.24 and -2.27 for **UCIMo** and **UIMo**,

respectively, are consistent with the presence of An^{IV} ions and suggest overall donation of electron density from the ligands to actinide metals. The calculated Mo MDC-q charges for **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** span a narrow range (0.62–0.65), consistent with the notion of formally Mo^0 engaged in back-donation to carbonyls and weak donation to the An-ions. Inspection of the Mayer bond orders reveals U-Mo and Th-Mo bond orders of 0.56, 0.56, 0.38, and 0.40 for **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo**, respectively. This is indicative of polarised An-Mo bonds, and it is notable that the U-Mo bond orders are ~ 0.15 higher than the analogous Th-Mo bonds. This is also suggested by the Kohn Sham molecular orbitals that represent the principal An-Mo interactions in **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo**, Figure 2.

Figure 2. Kohn Sham molecular orbitals representing: (a) HOMO–7 of **UCIMo** (344a, -5.347 eV), (b) HOMO–7 of **UIMo** (362a, -5.334 eV), (c) HOMO–2 of **ThCIMo** (347, -5.029 eV), (d) HOMO–2 of **ThIMo** (365, -5.057 eV). Colour key: gray = carbon; green = metal; magenta = phosphorus; maroon = halide; red = oxygen. Hydrogen atoms are omitted for clarity.

Inspection of the Kohn Sham molecular orbital manifolds of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** reveals a common electronic structure pattern. In gross terms they can be classified into three frontier zones comprising a high-lying 5f orbital band, followed by a Mo-CO back-bonding manifold, then U/Th-Mo dative bonds. For **UCIMo**, in the α -spin manifold five vacant 5f-orbitals constitute a LUMO band spanning -2.821 to -3.169 eV. Just below that, two quasi-degenerate singly occupied 5f-orbitals reside at -3.421 – -3.439 eV (HOMO/HOMO–1). HOMO–2 to HOMO–6 represent Mo-CO

back-bonding combinations spanning -4.957 to -5.192 eV. Underneath that relatively dense block (0.25 eV spread) resides HOMO–7 that represents the principal U-Mo dative bond (-5.347 eV). A similar picture emerges for **UIMo**, where in the α -spin manifold the vacant five 5f-orbitals are -2.907 to -3.261 , the quasi-degenerate HOMO/HOMO–1 are singly occupied 5f-orbitals (-3.517 and -3.529 eV), HOMO–2 to HOMO–6 are Mo-CO back-bonding interactions (-4.945 to -5.188 eV), and the U-Mo dative bond is represented by HOMO–7 (-5.334 eV). It is germane to note that replacing Cl with I, the sole difference between **UCIMo** and **UIMo**, results in the uranium 5f-orbitals (vacant LUMOs or occupied HOMO/HOMO–1) being stabilised by ~ 0.1 eV, but this has essentially no impact on the Mo-CO or U-Mo molecular orbital energies, suggesting that those units are reasonably well isolated from the halide. When the HOMO–7 of **UCIMo** and **UIMo** are visualised and inspected it can be seen that they are not just pure σ -donor orbitals but also have orbital coefficient overlap with lobes that form part of the π^* orbitals of the CO ligands. Thus, the notion suggested above that the CO stretching frequency acts as a reporter as to the extent of $Mo \rightarrow U$ donation appears to be valid.^{7m}

The molecular orbital manifolds of **ThCIMo** and **ThIMo** are simpler than for **UCIMo** and **UIMo** due to the restricted, closed shell natures of the former pair. For the former pair the seven vacant 5f-orbitals reside at and above -2.032 and -2.090 eV, respectively, lying *ca.* 0.7 eV higher than the analogous LUMOs of the latter pair, which is consistent with the expected trend that the 5f-orbitals lie generally higher for Th than U. For **ThCIMo** and **ThIMo** the Mo-CO bonding interactions are found principally in the quasi-degenerate HOMO/HOMO–1 orbitals in each case, at -4.874 – -4.896 and -4.930 – -4.941 eV, respectively. Directly below the Mo-CO molecular orbital combinations are Mo-Th dative bond orbitals at -5.029 and -5.057 eV for **ThCIMo** and **ThIMo**, respectively. These Th-Mo bonds lie ~ 0.3 eV higher than the analogous U-Mo bonds, which may reflect more polar bonding in the former than latter.

NBO analysis of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** returns essentially electrostatic Mo-M interactions, and so we probed the U-Mo and Th-Mo bonds further through analysis of the topology of the electron density.¹⁰ In all cases, 3,–1 bond critical points (BCPs) were found between the An- and Mo-ions of **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** indicating that U-Mo and Th-Mo bonds are present in these complexes. The BCP $\rho(r)$ values for **UCIMo**, **UIMo**, **ThCIMo**, and **ThIMo** are low and span the narrow range 0.03–0.04, the $\nabla^2\rho$ values are positive (0.03–0.05), and the $H(r)$ energy terms are small and negative (-0.005 to -0.008), which confirms the presence of a weak single σ -bonding interaction and are consistent with other reported U-M linkages.^{7e,21} The DFT analysis reveals polar metal-metal σ -bonds, reflected by the calculated ellipticity $[\epsilon(r)]$ of the An-Mo bonds which span the range 0.09–0.13; a single σ -bond or triple σ - π - π -bond present symmetrical electron density distributions around the internuclear axes with $\epsilon(r)$ values close to 0, whereas σ - π -double bonds are asymmetric with $\epsilon(r) > 0$. For comparison, calculated $\epsilon(r)_{CC}$ values for the C-C bonds in ethane (H_3C-CH_3), benzene (C_6H_6), ethene ($H_2C=CH_2$), and acetylene ($HC\equiv CH$) are 0.0, 0.23, 0.45, and 0.0, respectively.²² On the basis of these data, the An-Mo bonds reported here are clearly of a σ -nature.

To conclude, we have described the first An-group 6 bonds, where before only a few An-group 7–11 bonds had been reported. These An-Mo bonds exhibit σ -bonding character and extend the

range of partner metals to U and Th further to the left of the periodic table.

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ToC Entry

Heterobimetallic An-Mo (An = U, Th) paddlewheel complexes featuring dative Mo→An bonds are reported.