

Perplexing EPR Signals from $5f^36d^1$ U(II) Complexes

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Abstract

Metal complexes with unpaired electrons in orbitals of different angular momentum quantum numbers (e.g., f and d orbitals) are unusual and opportunities to study the interactions among these electrons are rare. X-band EPR data were collected at <10 K and 77 K on ten U(II) complexes with $5f^36d^1$ electron configurations and on Ce(II), Pr(II), and Nd(II) complexes with $4f^n5d^1$ electron configurations. The U(II) compounds unexpectedly display similar two-line axial signals with $g_{\parallel} = 2.04$ and $g_{\perp} = 2.00$ at 77 K and U(III)-like spectra at 5 K. In contrast, U(II) complexes with a $5f^4$ configuration are EPR silent. Unlike U(II), the congener Nd(II) complex is EPR-silent although it possesses an analogous $4f^35d^1$ configuration. The Ce(II) complex with a $4f^15d^1$ configuration is also EPR silent, but a signal is observed for the Pr(II) complex, which has a $4f^25d^1$ configuration. Whether or not an EPR signal is expected for these complexes depends on the coupling between f and d electrons. If the coupling is sufficiently strong, no signal is expected for ions with an even number of electrons, which is the observation for the lanthanide species. If the coupling is very weak, separate EPR signals for the f and d systems might be observed even in

systems with an even number of electrons. The Coulomb interaction between 5f and 6d electrons is strong in trivalent uranium systems, which results in strong coupling between the 5f and 6d electrons. This coupling will be weaker in divalent uranium systems, but it is still expected to be sufficiently strong to preclude an EPR signal from compounds with a $5f^36d^1$ configuration. Some potential sources of the EPR signal from the U(II) complexes are discussed.

Introduction

Understanding the chemistry and electronic structure of the actinide elements is a topic of great interest for both the fundamental and practical reasons.¹⁻⁵ The heaviest elements provide the opportunity to explore how the various factors (Coulomb repulsion, spin-orbit coupling, ligand field) determine their electronic structures. On the practical side, the chemistry of the actinide elements contains the information needed to develop efficient separation processes and more effective nuclear waste remediation.⁶⁻¹¹ The electronic structures of these metals can play a pivotal role in the physical properties and reactivity of actinide complexes and have been extensively investigated.^{12,13,22,14-21} A notable example of physical properties arising from coupling among electrons with different orbital angular momentum quantum numbers is the ultra-hard magnetism of divalent lanthanide complexes in which the magnetic properties are due to the strong coupling between 4f and 5d electrons.²³

New electronic configurations for actinide complexes have recently been reported for molecular complexes in the +2 oxidation state. Although the presence of molecular species containing U(II) was suggested as early as the 1980s,²⁴⁻²⁹ it was not until 2013 when the first, unambiguous molecular example of U(II) was isolated in $[\text{K}(\text{crypt})][\text{Cp}'_3\text{U}]$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$).³⁰ Surprisingly, the uranium ion was assigned a $5f^36d^1$ electron configuration based on structural,

UV-visible, and theoretical analysis.³⁰ This mixed principal quantum number electron configuration was unexpected since reduction of a $5f^3$ U(III) ion would be expected to yield a $5f^4$ configuration. However, gas phase studies of U(II) ions show that the $5f^36d^1$ configuration was only 210 cm^{-1} higher in energy than the $5f^4$ configuration.^{31–34} Isomorphous lanthanide Ln(II) complexes, $[\text{K}(\text{crypt})][\text{Cp}'_3\text{Ln}]$, of Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu also have mixed principal quantum number $4f^n5d^1$ electron configurations.^{35–39}

Other U(II) complexes have been synthesized including $[\text{M}(\text{chelate})][\text{Cp}''_3\text{U}]$ (M = Li, Na, K, Cs; chelate = crypt, 18-crown-6, 12-crown-4, (THF)_x; Cp'' = $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$), $[\text{K}(\text{crypt})][\text{U}(\text{NR}_2)_3]$ (R = SiMe₃), $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_4\text{H})_3\text{U}]$, $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)\text{U}(\text{NR}_2)_2]$, $(\text{C}_5^i\text{Pr}_5)_2\text{U}$, and $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{A})]$ (A = NR₂, OC₆H₂¹Bu_{2-2,6-Me-4}, OC₆H₂Ad_{2-2,6-¹Bu-4}, CH(SiMe₃)₂, C₅H₅, C₅Me₄H).^{40–45} These complexes have electronic structures consistent with a $5f^36d^1$ electron configuration. However, in other ligand environments, the electronic structure of U(II) is consistent with a $5f^4$ electron configuration. Complexes of this type include $[\text{K}(\text{crypt})][(\text{}^{\text{Ad,Me}}\text{ArO})_3\text{U}]$,⁴⁶ $(\text{NHAr}^{i\text{Pr}6})_2\text{U}$,⁴⁷ and $[\text{K}(\text{crypt})][\text{U}(\text{TDA})_2]$ ⁴⁸ [$\text{NHAr}^{i\text{Pr}6}$ = 2,6-(2,4,6-¹Pr₃C₆H₂)₂C₆H₃); TDA = OC(¹Bu)N(C₆H₃¹Pr_{2-2,6})]. This apparent dichotomy in electron configurations may be due to the ligand geometry around the U(II) center.⁴⁹ More recently, $[\text{K}(\text{crypt})][(\text{C}_5^i\text{Pr}_5)_2\text{U}]$ was synthesized which was assigned as a U(I) complex with a $5f^36d^2$ electron configuration.⁵⁰

The current study was initiated to determine if EPR spectroscopy could be used to differentiate the two different types of U(II) electron configurations and if it could be used to identify highly reactive U(II) species that had low thermal stability. EPR spectroscopy has been used extensively to identify U(V) and U(III) species,^{12,15,59–68,51,69,52–58} but few EPR studies on U(II) compounds have been reported. $[\text{K}(\text{crypt})][\{(\text{}^{\text{Ad,Me}}\text{ArO})_3\text{mes}\}\text{U}]$ and $\text{U}(\text{NHAr}^{i\text{Pr}6})_2$ were

found to be EPR silent in both perpendicular and parallel modes.^{46,47} [K(crypt)][U(TDA)₂] has a signal at $g = 2.00$ due the presence of a mono-reduced arene component of a ligand.⁴⁸ The uranium center in all three of these compounds has been assigned a $5f^4$ electron configuration. While this work was in progress, the $5f^36d^1$ U(II) compound (C₅ⁱPr₅)₂U was found to be EPR silent in perpendicular mode.⁵⁰

We report here EPR studies on $5f^36d^1$ U(II) compounds carried out to determine if they display a characteristic type of EPR spectrum as is observed for $6d^1$ Th(III) compounds since the EPR signature for Th(III) has been very valuable in identifying this ion.^{12,15,77,22,70–76} To address this issue, we report EPR studies of ten $5f^36d^1$ U(II) compounds, along with data on some related U(III) species as well as some $4f^n$ Ln(III) and $4f^n5d^1$ Ln(II) lanthanide compounds for comparison. Lanthanide(II) complexes with an even number of unpaired electrons are EPR silent; however, the ten uranium(II) samples described here display similar two-line axial signals with $g_{\parallel} = 2.04$ and $g_{\perp} = 2.00$ at 77 K and U(III)-like spectra at 5 K.

Results

Sample Preparation. The homoleptic U(II) compounds [K(crown)(THF)₂][Cp''₃U], [K(crypt)][Cp'₃U], [K(crypt)][Cp^{tet}₃U], and [K(crypt)][U(NR₂)₃] (R = SiMe₃) were synthesized via literature routes and isolated as crystalline materials.^{30,40,42} For measurements on solid samples, crystalline materials were ground in a mortar and pestle in an inert atmosphere glovebox and placed in an EPR tube for data collection. For solution measurements, the crystalline solids were dissolved in THF, quickly transferred to an EPR tube, and immediately frozen at 77 K in liquid nitrogen. The heteroleptic U(II) compounds [K(crypt)][(C₅Me₅)₂U(NR₂)], [K(crypt)][(C₅Me₅)U(NR₂)₂], [K(crypt)][(C₅Me₅)₂U(Cp^{tet})], and [K(crypt)][(C₅Me₅)₂U(C₅H₅)],

were generated via reduction of the corresponding U(III) species with KC_8 and cryptand at low temperature in THF^{43,45} and immediately placed in the EPR sample tube for data collection since the compounds decompose readily at room temperature. $\text{U}(\text{OAr})_3$ ($\text{OAr} = \text{OC}_6\text{H}_3^t\text{Bu}_{2-2,6}$)⁷⁸ and $(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)(\text{THF})$ ⁷⁹ were reduced similarly with KC_8 in the presence of crypt in THF to generate the species “[K(crypt)][U(OAr)₃]” and “[K(crypt)][(C₅Me₅)₂U(NPh₂)]” and immediately frozen. All manipulations involving the synthesis of U(II) species were performed rapidly inside the glovebox with glassware precooled to $-35\text{ }^\circ\text{C}$ due to the thermal instability of the compounds.

[K(crypt)][Cp^{tet}₃U] and Cp^{tet}₃U (Cp^{tet} = C₅Me₄H). The 5 K EPR spectra of a powdered sample of the crystallographically confirmed U(II) compound, [K(crypt)][Cp^{tet}₃U], and its precursor, Cp^{tet}₃U, are shown in Figure 1. The spectrum of [K(crypt)][Cp^{tet}₃U] was modeled using $g = 3.005, 2.10,$ and 1.660 and that of Cp^{tet}₃U was modeled using $g = 2.380, 2.195,$ and 1.985 . Both spectra strongly resemble the g_{\perp} signal of Cp³U for which $g = 2.44$ and 2.06 (the remaining g value is < 0.7).⁵⁴

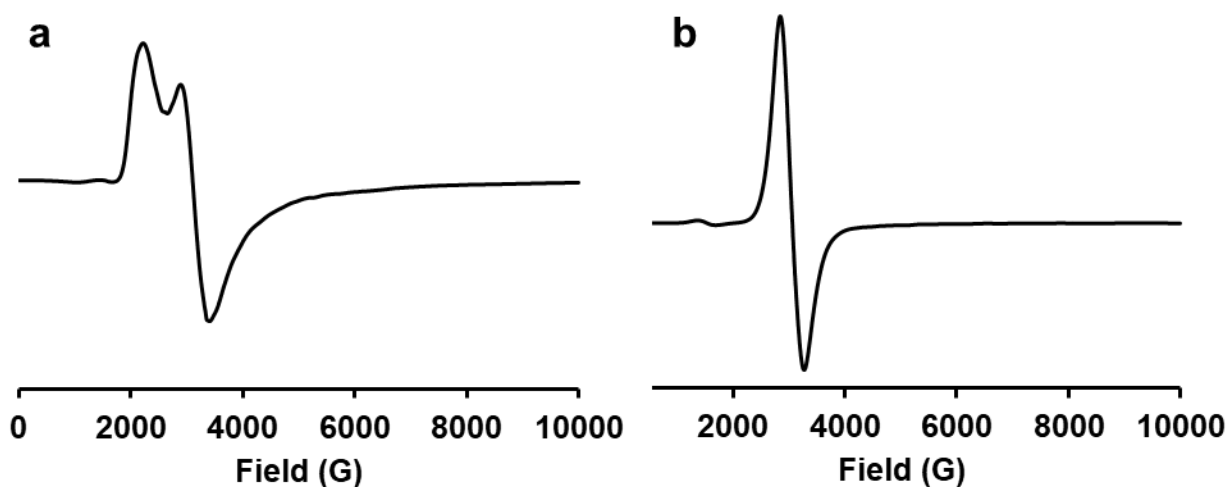


Figure 1: X-band, perpendicular mode EPR spectrum of [K(crypt)][Cp^{tet}₃U] (a) and Cp^{tet}₃U (b) taken as powdered samples at 5 K.

Figure 2 compares the EPR spectrum of powdered $[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$ at 5 K with those at 10 K and 77 K in frozen THF, shown in Figures 2b and 2c, respectively. In frozen THF at 10 K, a signal is observed with $g_{\parallel} = 2.04$ and $g_{\perp} = 2.00$, and the “U(III)-like” signal is greatly broadened, presumably due to rapid spin-lattice relaxation. At 77 K in frozen THF, the “U(III)-like” signal has disappeared, and only the signal near $g = 2$ remains. No signal was detected in parallel mode.

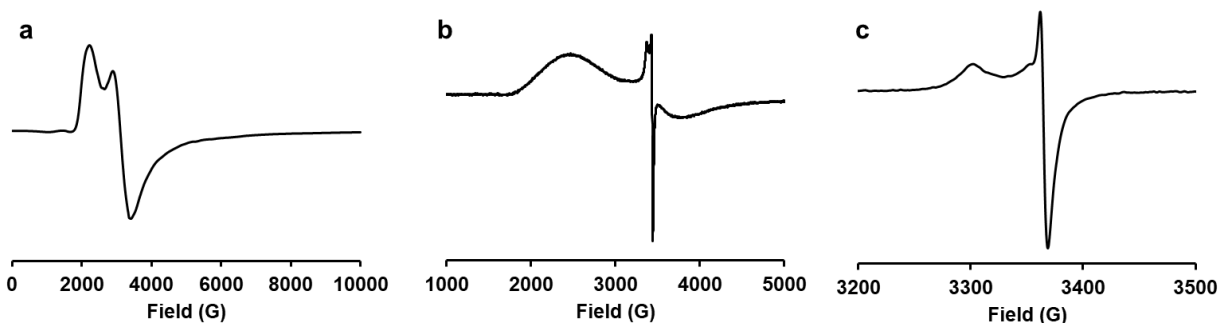


Figure 2: X-band, perpendicular mode EPR spectra of $[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$: (a) a powdered sample at 5 K, (b) a frozen THF solution at 10 K, and (c) a frozen THF solution at 77 K.

Since EPR spectroscopy is so sensitive, it seemed possible that the spectra in Figure 2 were due to a uranium-containing impurity. However, identical spectra were observed across multiple different sample batches. The most likely decomposition product would be the $\text{Cp}^{\text{tet}}_3\text{U}$ starting material. The signal at 77 K near $g = 2$ is not consistent with the spectrum of $\text{Cp}^{\text{tet}}_3\text{U}$. On the other hand, the signal observed in powdered $[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$ at 5 K is consistent with U(III) although it is different than the signal of $\text{Cp}^{\text{tet}}_3\text{U}$.

To further investigate the possibility that the spectrum arose from a decomposition product, the sample temperature was raised to allow decomposition and presumably formation of more of

the decomposition product. However, raising the sample temperature to 298 K led to an immediate disappearance of the two-line signal shown in Figure 1 and the appearance of a single sharp feature at $g = 2.00$ after one minute, Figure S2–5. Subsequent cooling did not regenerate the original spectrum.

Nine Other $5f^36d^1$ U(II) Complexes. Figure 3 shows X-band EPR spectra in frozen solution at 77 K of nine other U(II) compounds assigned the $5f^36d^1$ electron configuration. The g values of these spectra are given in Table 1. The spectrum shown in Figure 3g has a much larger signal at $g = 2$, which is attributed to electrone formation. All compounds display axial spectra with g values of approximately 2.04 and 2.00, which are very similar to those observed at 77 K for [K(crypt)][Cp^{tet}₃U] in Figure 2. An overlay of the spectra is shown in Figure S1. EPR spectra of solutions of the reduction products collected at 10 K are similar, Figures S6–S14. None of the samples displayed a signal in parallel mode. These signals also differ from the EPR spectra of the corresponding U(III) precursor, Figures S15–21.

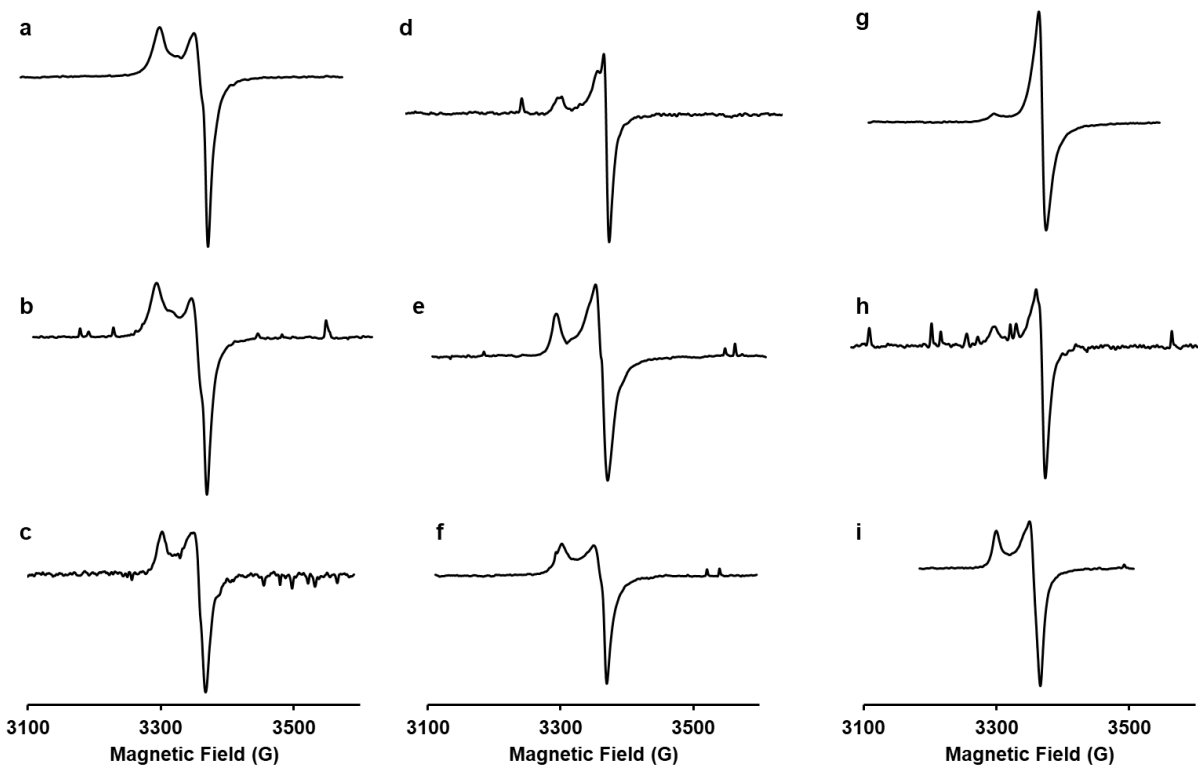


Figure 3: X-band perpendicular mode EPR spectra taken as a frozen THF solution at 77 K of (a) $[\text{K}(\text{crown})(\text{THF})_2][\text{Cp}''_3\text{U}]$, (b) $[\text{K}(\text{crypt})][\text{Cp}'_3\text{U}]$, (c) $[\text{K}(\text{crypt})][\text{U}(\text{NR}_2)_3]$, (d) $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{NR}_2)]$, (e) $[\text{K}(\text{crypt})][\text{U}(\text{OAr})_3]$, (f) $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_5\text{Me}_4\text{H})]$, (g) $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_5\text{H}_5)]$, (h) $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)]$, and (i) $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)\text{U}(\text{NR}_2)_2]$. No features were observed outside the window shown. The small, narrow features are due bubbling N_2 moving the EPR tubes.

Table 1: The g values of the EPR signal observed for U(II) compounds. Data were collected at X-band frequency in perpendicular mode at 77 K (crypt = 2.2.2-cryptand, crown = 18-crown-6, $\text{Cp}^{\text{tet}} = \text{C}_5\text{Me}_4\text{H}$, $\text{Cp}' = \text{C}_5\text{H}_4\text{R}$, $\text{Cp}'' = \text{C}_5\text{H}_3\text{R}_2$, $\text{R} = \text{SiMe}_3$, $\text{OAr} = \text{OC}_6\text{H}_3^t\text{Bu}_{2-2,6}$).

Compound	g_{\parallel}	g_{\perp}
$[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$	2.04	2.01
$[\text{K}(\text{crown})(\text{THF})_2][\text{Cp}''_3\text{U}]$	2.04	2.01
$[\text{K}(\text{crypt})][\text{Cp}'_3\text{U}]$	2.04	2.01
$[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_5)_2\text{U}(\text{Cp}^{\text{tet}})]$	2.04	2.00

[K(crypt)][(C ₅ Me ₅) ₂ U(NR ₂)]	2.04	2.00
[K(crypt)][U(OAr) ₃]	2.04	2.00
[K(crypt)][U(NR ₂) ₃]	2.04	2.00
[K(crypt)][(C ₅ Me ₅) ₂ U(C ₅ H ₅)]	2.04	2.00
[K(crypt)][(C ₅ Me ₅) ₂ U(NPh ₂)]	2.04	2.00
[K(crypt)][(C ₅ Me ₅)U(NR ₂) ₂]	2.04	2.00

It is conceivable that the signals observed for the U(II) compounds generated *in situ* with KC₈, Figures 1-3, arise from impurities in the graphite. Both natural and synthetic graphite contain iron and the KC₈ reductant could provide a source of iron or nickel.⁸⁰ However, these putative graphite signals are not observed in the spectra of any of the [K(crypt)][Cp^{tet}₃Ln] complexes described in the next section or any of the 5f⁴ complexes made with potassium graphite. Although graphite contamination is possible in *in situ* generated samples, it seems less likely in isolated crystalline samples and crystals of [K(crypt)][Cp^{tet}₃U], [K(crown)(THF)₂][Cp^{tr}₃U], [K(crypt)][Cp^{tr}₃U], and [K(crypt)][U(NR₂)₃] show the similar two-line patterns to the U(II) compounds generated *in situ*.

To test further the possibility that the signals arise from graphite impurity, reduction of Cp^{tr}₃U with a Li smear and a Cs smear were examined by EPR. Both graphite-free reactions generated EPR spectra like the previous ten presented (Figures S22–24). In addition, EPR spectra of KC₈ in THF alone and with crypt or 18-crown-6 failed to generate the signals observed for the U(II) samples.

Ln(III) and Ln(II) Spectra. For further comparison with the uranium spectra, the EPR spectra of 4fⁿ Cp^{tet}₃Ln and 4fⁿ5d¹ [K(crypt)][Cp^{tet}₃Ln] complexes^{81,82} of Ln = Ce, Pr, Nd generated with KC₈ are shown in Figure 5 and summarized in Table 3. This provided EPR data on 4f¹, 4f², and 4f³ systems with Ce(III), Pr(III), and Nd(III), respectively, and on 4f¹5d¹, 4f²5d¹, and 4f³5d¹ compounds with Ce(II), Pr(II), and Nd(II), respectively. The spectrum shown in Figure 5b

(Cp^{tet}₃Pr) has the same g-value as Cp^{tet}₃Ce and is likely due to a Ce impurity in the Pr starting material. Among the lanthanide complexes, those with an even number of unpaired electrons have no EPR signal while those with an odd number of electrons do display a signal.

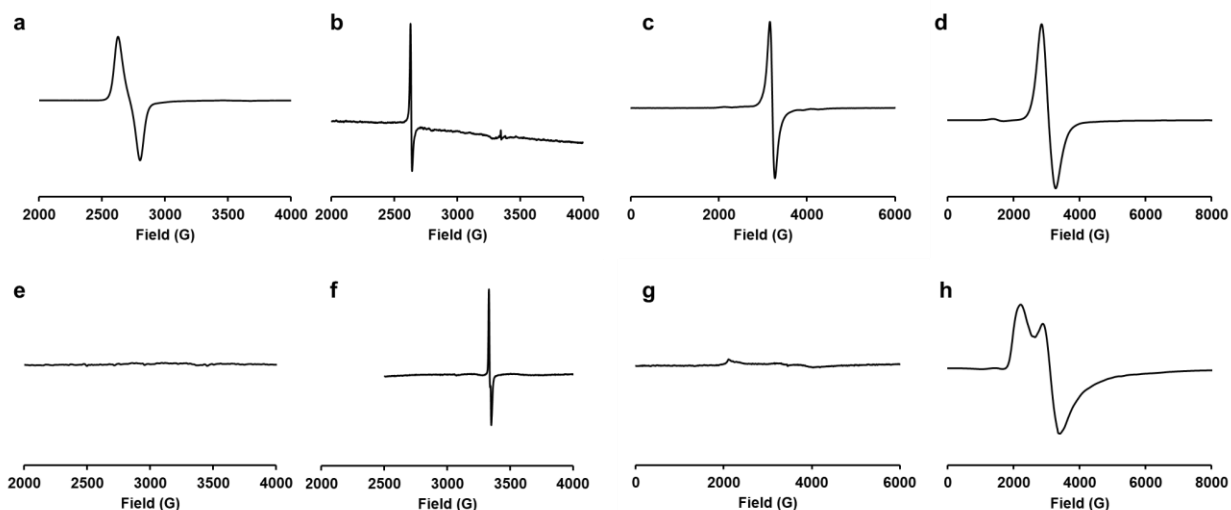


Figure 5: X-band, perpendicular mode spectrum of Cp^{tet}₃Ce (a), Cp^{tet}₃Pr (b), Cp^{tet}₃Nd (c), Cp^{tet}₃U (d), [K(crypt)][Cp^{tet}₃Ce] (e), [K(crypt)][Cp^{tet}₃Pr] (f), [K(crypt)][Cp^{tet}₃Nd] (g), and [K(crypt)][Cp^{tet}₃U] (h) taken as a powdered sample at 5 K.

Table 3: Cp^{tet}₃M and [K(crypt)][Cp^{tet}₃M] g values from EPR

	Electron configuration	g values
Cp ^{tet} ₃ Ce	4f ¹	2.54
[K(crypt)][Cp ^{tet} ₃ Ce]	4f ¹ 5d ¹	silent
Cp ^{tet} ₃ Pr	4f ²	Silent 2.54 ^a
[K(crypt)][Cp ^{tet} ₃ Pr]	4f ² 5d ¹	2.00
Cp ^{tet} ₃ Nd	4f ³	2.15
[K(crypt)][Cp ^{tet} ₃ Nd]	4f ³ 5d ¹	silent
Cp ^{tet} ₃ U	5f ³	2.380, 2.195, 1.985
[K(crypt)][Cp ^{tet} ₃ U]	5f ³ 6d ¹	3.005, 2.10, 1.660

a) Signal is attributed to Cp^{tet}₃Ce resulting from Ce impurities in the starting material.

Discussion

The observation of EPR signals from U(II) samples is intriguing and perplexing. In frozen THF, all U(II) compounds with $5f^36d^1$ electron configurations show similar EPR spectra with g values of 2.04 and 2.00. These spectral features were observed across ten compounds at both 10 K and 77 K and appear characteristic of these samples. These signals are due to a highly thermally unstable species as evidenced by their disappearance after one minute at room temperature. Since the EPR signals are observed in the presence of the U(II) compounds, which are also highly thermally unstable, it is natural to assume that the signal at 77 K is due to the U(II) ion. However, this assignment is problematic.

For discussing the EPR spectra of the complexes studied here, it is useful to describe the electronic structure using total angular momentum quantum number, J , and the magnetic quantum number, m_J , which can have values ranging from $+J$ to $-J$. The value of J is determined by coupling between the spin and orbital angular momenta of the electrons to give a ground state term whose degeneracy is $2J+1$. The interaction between the metal and ligand orbitals removes this degeneracy and creates states that can be described as mixtures of components with different values of m_J : $\psi = \sum c_i |m_J\rangle$, where $|m_J\rangle$ represents a state with a given value of m_J and c_i is the coefficient for its contribution to the wavefunction. For ions with half integral values of J , an axially symmetric ligand field (like the complexes discussed here) will create a set of pairs of states (Kramers doublets) where the absolute values of c_i are the same for the pairs, but m_J have opposite signs in the members of pair. For ions with integral values of J , an axially symmetric ligand field will create both singlets and doublets. The selection rule for observing an EPR signal in perpendicular mode is that the ground state doublet (or higher multiplet) must contain states with m_J that differ by 1. For complexes with a half-integral value of J (odd number of unpaired electrons), this is true

if the two states in the Kramers doublet contain the state $|m_J = \pm 1/2\rangle$. Other states in the Kramers doublet also fulfill the selection rule, e.g. $\psi = c_1|\mp 5/2\rangle + c_2|\pm 3/2\rangle$. For complexes with integral values of J (even number of unpaired electrons), the ground state could be a singlet, which is not EPR active, and the doublets rarely contain states with m_J that differ by 1. As a result, complexes with integral J values are typically not EPR active in perpendicular mode.

In the case of complexes with $f^n d^1$ configurations, whether or not an EPR spectrum may be observed depends on the coupling between the f and d electrons. If the coupling is sufficiently strong, the d electron will be coupled with the f^n electrons to give a total angular momentum J , and complexes with an odd number of unpaired electrons may be EPR active and those with an even number are unlikely to be EPR active. The spectra of the lanthanide complexes in Table 3 are consistent with this description. On the other hand, if the f^n electrons and the d^1 electron are only weakly coupled, it may be possible to observe separate EPR spectra from the coupled f^n electrons and from the d^1 electron. Qualitatively, this appears to be consistent with the EPR signals of U(II).

While the configuration $f^n d^1$ is rare for ground states, it is common for excited states. The electronic structure of the excited state of U(III) in LaCl_3 and CeCl_3 was studied using crystal field theory to determine the values of the interaction parameters.⁸³ The metal site in LaCl_3 and CeCl_3 has the same symmetry, D_{3h} , as $[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$ and $\text{Cp}^{\text{tet}}_3\text{U}$. The Coulomb repulsion parameters (Slater F parameter) for the $5f$ and $6d$ electrons are $\sim 20,000 \text{ cm}^{-1}$.⁸³ Consequently, $5f$ and $6d$ electrons in the excited $5f^2 6d^1$ excited state U(III) in LaCl_3 are strongly coupled. While Coulomb repulsion will be weaker in divalent uranium complexes, it should still be sufficiently strong to couple the $5f^3$ and $6d^1$ electrons, so no EPR spectrum would be expected for $[\text{K}(\text{crypt})][\text{Cp}^{\text{tet}}_3\text{U}]$ in perpendicular mode, which does not match the observed results in Figures 1 and 2.

If [K(crypt)][Cp^{tet}₃U] is not the source of the EPR signal at 77 K, some other thermally unstable species must be responsible. The EPR signal shows no hyperfine coupling, which eliminates organic radicals and any metal having a non-zero nuclear spin, including potassium. Organic radicals are also not consistent with the $g = 2.04$ peak observed for the unknown species. The g -values of the unknown species are most similar to those of first-row transition metal with a low-spin $3d^7$ configuration, especially Fe(I). While few Fe(I) species have been reported, their EPR spectra typically display one peak with $g \approx 2.0$ and one with $g = 2.2 \pm 0.2$, which is consistent with the species observed in the frozen THF at 77 K.⁸⁴ Another option is Ni(I) complexes, which typically have g values between 2.08–2.00,^{85–87} although the signal rhombicity is more dependent on the metal geometry than the Fe(I) examples. Although graphite contains transition metal impurities which might explain the signals,⁸⁰ the fact that the characteristic signals could be generated from reduction of Cp^{tr}₃U with graphite free Li and Cs (Figures S22–24) indicates that graphite is not the source.

Another possible source of the signal is a U(I) species, where the expected configuration for U(I) would be $5f^36d^2$ with two electrons in the $6d_z^2$ orbital based on the configuration observed for Th(II).^{88,89} While the recently isolated compound [K(crypt)][(C₅ⁱPr₅)₂U] was assigned as a U(I) complex with a $5f^36d^2$ configuration, the two $6d$ electrons were described as occupying the $6d_z^2$ and $6xy/6x^2-y^2$ orbitals instead of pairing in the $6d_z^2$ orbital which resulted in a complicated EPR spectrum.⁵⁰ The EPR spectrum of a tris-cyclopentadienyl U(I) complex with a $5f^36d^2$ configuration should resemble that of the analogous tris-cyclopentadienyl U(III) complex. The EPR signal from [K(crypt)][Cp^{tet}₃U] at 5 K is consistent with U(I) as well as U(III).

Conclusion

X-band EPR spectra of ten $5f^36d^1$ U(II) compounds have been collected and show a similar two-line pattern in frozen THF at both 10 K and 77 K. This is unexpected based on theoretical analysis. The possibility that the spectra arise from impurities or decomposition to U(I) cannot be ruled out, but no experimental data were obtainable to support either of these ideas. At this point, the results have to be viewed as an unexplained phenomena. However, they do show that $5f^36d^1$ U(II) samples can be differentiated from $5f^4$ U(II) complexes by EPR spectroscopy.

ASSOCIATED CONTENT

Supporting Information is available free of charge at <http://pubs.acs.org/xyz> and includes: Experimental details and EPR spectra (PDF).

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Notes

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References

- 1 M. B. Jones and A. J. Gaunt, *Chem. Rev.*, 2013, **113**, 1137–1198.
- 2 S. T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 8604–8641.
- 3 M. A. Boreen and J. Arnold, *Dalton Trans.*, 2020, **49**, 15124–15138.
- 4 D. H. Woen and W. J. Evans, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. J.-C. Bünzli and V. K. Pecharsky, Elsevier B.V., 1st edn., 2016, pp. 1–57.
- 5 F. Ortu, A. Formanuk, J. R. Innes and D. P. Mills, *Dalton Trans.*, 2016, **45**, 7537–7549.
- 6 J. Su, T. Cheisson, A. McSkimming, C. A. P. Goodwin, I. M. DiMucci, T. E. Albrecht-Schönzart, B. L. Scott, E. R. Batista, A. J. Gaunt, S. A. Kozimor, P. Yang and E. J. Schelter, *Chem. Sci.*, 2021, **12**, 13343–13359.
- 7 W. H. Runde and B. J. Mincher, *Chem. Rev.*, 2011, **111**, 5723–5741.
- 8 C. J. Dares, A. M. Lapidés, B. J. Mincher and T. J. Meyer, *Science*, 2015, **350**, 652–655.

- 9 J. D. Burns and B. A. Moyer, *Inorg. Chem.*, 2016, **55**, 8913–8919.
- 10 J. Zhang, *J. Nucl. Mater.*, 2014, **447**, 271–284.
- 11 X. Sun, H. Luo and S. Dai, *Chem. Rev.*, 2012, **112**, 2100–2128.
- 12 A. Formanuk, A.-M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes and D. P. Mills, *Nat. Chem.*, 2017, **9**, 578–583.
- 13 S. G. Minasian, J. L. Krinsky and J. Arnold, *Chem. Eur. J.*, 2011, **17**, 12234–12245.
- 14 J. Du, J. A. Seed, V. E. J. Berryman, N. Kaltsoyannis, R. W. Adams, D. Lee and S. T. Liddle, *Nat. Commun.*, 2021, **12**, 5649.
- 15 A. B. Altman, A. C. Brown, G. Rao, T. D. Lohrey, R. D. Britt, L. Maron, S. G. Minasian, D. K. Shuh and J. Arnold, *Chem. Sci.*, 2018, **9**, 4317–4324.
- 16 S. G. Minasian, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. A. Kozimor, R. L. Martin, D. K. Shuh and T. Tylliszczak, *Chem. Sci.*, 2014, **5**, 351–359.
- 17 S. G. Minasian, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. D. Conradson, S. A. Kozimor, R. L. Martin, D. E. Schwarz, D. K. Shuh, G. L. Wagner, M. P. Wilkerson, L. E. Wolfsberg and P. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 5586–5597.
- 18 S. L. Staun, D. C. Sergentu, G. Wu, J. Autschbach and T. W. Hayton, *Chem. Sci.*, 2019, **10**, 6431–6436.
- 19 J. Su, E. R. Batista, K. S. Boland, S. E. Bone, J. A. Bradley, S. K. Cary, D. L. Clark, S. D. Conradson, A. S. Ditter, N. Kaltsoyannis, J. M. Keith, A. Kerridge, S. A. Kozimor, M. W. Löble, R. L. Martin, S. G. Minasian, V. Mocko, H. S. La Pierre, G. T. Seidler, D. K. Shuh, M. P. Wilkerson, L. E. Wolfsberg and P. Yang, *J. Am. Chem. Soc.*, 2018, **140**, 17977–17984.
- 20 S. A. Kozimor, P. Yang, E. R. Batista, K. S. Boland, C. J. Burns, D. L. Clark, S. D.

- Conradson, R. L. Martin, M. P. Wilkerson and L. E. Wolfsberg, *J. Am. Chem. Soc.*, 2009, **131**, 12125–12136.
- 21 J. N. Cross, J. Su, E. R. Batista, S. K. Cary, W. J. Evans, S. A. Kozimor, V. Mocko, B. L. Scott, B. W. Stein, C. J. Windorff and P. Yang, *J. Am. Chem. Soc.*, 2017, **139**, 8667–8677.
- 22 J. R. Walensky, R. L. Martin, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2010, **49**, 10007–10012.
- 23 C. A. Gould, K. R. McClain, D. Reta, J. G. C. Kragoskow, D. A. Marchiori, E. Lachman, E. Choi, J. G. Analytis, R. D. Britt, N. F. Chilton, B. G. Harvey and J. R. Long, *Science*, 2022, **375**, 198–202.
- 24 A. B. McLaren, B. Kanellakopulos and E. Dornberger, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 223–225.
- 25 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Chem. Commun.*, 2005, 4681.
- 26 E. D. Eastman, L. Brewer, R. A. LeBromley, P. W. Gilles and N. L. Lofgren, *J. Am. Chem. Soc.*, 1951, **73**, 3896–3898.
- 27 L. Andrews, M. Zhou, B. Liang, J. Li and B. E. Bursten, *J. Am. Chem. Soc.*, 2000, **122**, 11440–11449.
- 28 B. Liang, L. Andrews, N. Ismail and C. J. Marsden, *Inorg. Chem.*, 2002, **41**, 2811–2813.
- 29 P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, V. W. Day, S. H. Vollmer and V. W. Day, *Organometallics*, 1982, **1**, 170–180.
- 30 M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 13310–13313.
- 31 J. Blaise and J. F. Wyart, in *International Tables of Selected Constants*, Centre National de la Recherche Scientifique, Paris, France, 1992, Volume 20.

- 32 X. Cao and M. Dolg, *Mol. Phys.*, 2003, **101**, 961–969.
- 33 L. Brewer, *J. Opt. Soc. Am.*, 1971, **61**, 1666.
- 34 B. A. Palmer and R. Engleman, Jr., *J. Opt. Soc. Am. B*, 1984, **1**, 609.
- 35 M. R. MacDonald, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 15914–15917.
- 36 M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857–9868.
- 37 M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2015, **137**, 369–382.
- 38 J. C. Wedal and W. J. Evans, *J. Am. Chem. Soc.*, 2021, **143**, 18354–18367.
- 39 M. R. MacDonald, J. E. Bates, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2012, **134**, 8420–8423.
- 40 C. J. Windorff, M. R. MacDonald, K. R. Meihaus, J. W. Ziller, J. R. Long and W. J. Evans, *Chem. Eur. J.*, 2016, **22**, 772–782.
- 41 D. N. Huh, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2018, **57**, 11809–11814.
- 42 A. J. Ryan, M. A. Angadol, J. W. Ziller and W. J. Evans, *Chem. Commun.*, 2019, **55**, 2325–2327.
- 43 J. C. Wedal, S. Bekoe, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2020, **39**, 3425–3432.
- 44 F. S. Guo, N. Tsoureas, G. Z. Huang, M. L. Tong, A. Mansikkamäki and R. A. Layfield, *Angew. Chem. Int. Ed.*, 2020, **59**, 2299–2303.
- 45 J. C. Wedal, J. W. Ziller, F. Furche and W. J. Evans, *Inorg. Chem.*, 2022, **61**, 7365–7376.
- 46 H. S. La Pierre, A. Scheurer, F. W. Heinemann, W. Hieringer and K. Meyer, *Angew.*

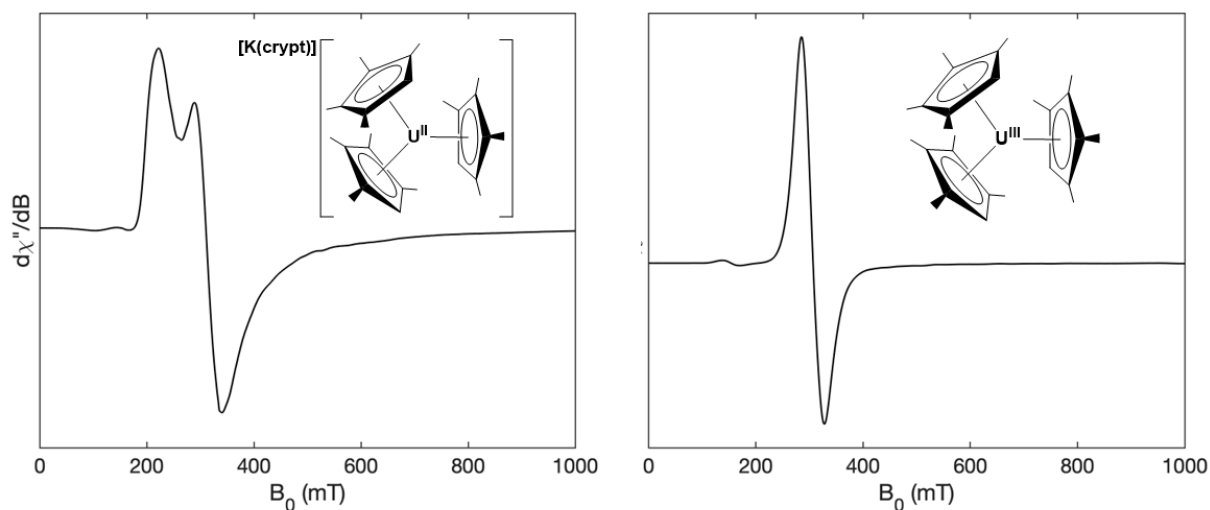
- Chem. Int. Ed.*, 2014, **53**, 7158–7162.
- 47 B. S. Billow, B. N. Livesay, C. C. Mokhtarzadeh, J. Mccracken, M. P. Shores, J. M. Boncella and A. L. Odom, *J. Am. Chem. Soc.*, 2018, **140**, 17369–17373.
- 48 M. D. Straub, E. T. Ouellette, M. A. Boreen, R. D. Britt, K. Chakarawet, I. Douair, C. A. Gould, L. Maron, I. Del Rosal, D. Villarreal, S. G. Minasian and J. Arnold, *J. Am. Chem. Soc.*, 2021, **143**, 19748–19760.
- 49 J. C. Wedal, F. Furche and W. J. Evans, *Inorg. Chem.*, 2021, **60**, 16316–16325.
- 50 L. Barluzzi, S. R. Giblin, A. Mansikkamäki and R. A. Layfield, *J. Am. Chem. Soc.*, 2022, **144**, 18229–18233.
- 51 J. Selbin, J. D. Ortego and G. Gritzner, *Inorg. Chem.*, 1968, **7**, 976–982.
- 52 A. J. Lewis, E. Nakamaru-Ogiso, J. M. Kikkawa, P. J. Carroll and E. J. Schelter, *Chem. Commun.*, 2012, **48**, 4977–4979.
- 53 D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes and S. T. Liddle, *Nat. Commun.*, 2016, **7**, 1–14.
- 54 W. W. Lukens, M. Speldrich, P. Yang, T. J. Duignan, J. Autschbach and P. Kögerler, *Dalton Trans.*, 2016, **45**, 11508–11521.
- 55 E. J. Soulié and P. C. Lesieur, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 4053.
- 56 H. Nakai, X. Hu, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Inorg. Chem.*, 2004, **43**, 855–857.
- 57 C. A. P. Goodwin, F. Tuna, E. J. L. McInnes, S. T. Liddle, J. McMaster, I. J. Vitorica-Yrezabal and D. P. Mills, *Chem. Eur. J.*, 2014, **20**, 14579–14583.
- 58 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717–720.

- 59 I. Castro-Rodríguez and K. Meyer, *Chem. Commun.*, 2006, 1353.
- 60 E. J. Soulié, G. Folcher and H. Marquet-Ellis, *Can. J. Chem.*, 1982, **60**, 1751–1753.
- 61 C. A. Hutchison, P. M. Llewellyn, E. Wong and P. Dorain, *Phys. Rev.*, 1956, **102**, 292–292.
- 62 S. H. Carpenter, N. J. Wolford, B. S. Billow, T. V Fetrow, N. Cajiao, A. Radović, M. T. Janicke, M. L. Neidig and A. M. Tondreau, *Inorg. Chem.*, 2022, **61**, 12508–12517.
- 63 J. T. Coutinho, M. Perfetti, J. J. Baldoví, M. A. Antunes, P. P. Hallmen, H. Bamberger, I. Crassee, M. Orlita, M. Almeida, J. van Slageren and L. C. J. Pereira, *Chem. Eur. J.*, 2019, **25**, 1758–1766.
- 64 J. Riedhammer, J. R. Aguilar-Calderón, M. Miehl, D. P. Halter, D. Munz, F. W. Heinemann, S. Fortier, K. Meyer and D. J. Mindiola, *Inorg. Chem.*, 2020, **59**, 2443–2449.
- 65 J. A. Seed, M. Gregson, F. Tuna, N. F. Chilton, A. J. Wooles, E. J. L. McInnes and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2017, **56**, 11534–11538.
- 66 N. J. Wolford, X. Yu, S. C. Bart, J. Autschbach and M. L. Neidig, *Dalton Trans.*, 2020, **49**, 14401–14410.
- 67 M. A. Boreen, T. D. Lohrey, G. Rao, R. D. Britt, L. Maron and J. Arnold, *J. Am. Chem. Soc.*, 2019, **141**, 5144–5148.
- 68 J. Jung, S. T. Löffler, J. Langmann, F. W. Heinemann, E. Bill, G. Bistoni, W. Scherer, M. Atanasov, K. Meyer and F. Neese, *J. Am. Chem. Soc.*, 2020, **142**, 1864–1870.
- 69 K. R. Meihaus, S. G. Minasian, W. W. Lukens, S. A. Kozimor, D. K. Shuh, T. Tyliczszak and J. R. Long, *J. Am. Chem. Soc.*, 2014, **136**, 6056–6058.
- 70 J. C. Wedal, S. Bekoe, J. W. Ziller, F. Furche and W. J. Evans, *Dalton Trans.*, 2019, **48**, 16633–16640.

- 71 D. N. Huh, S. Roy, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2019, **141**, 12458–12463.
- 72 W. K. Kot, G. V. Shalimoff, N. M. Edelstein, M. A. Edelman and M. F. Lappert, *J. Am. Chem. Soc.*, 1988, **110**, 986–987.
- 73 P. C. Blake, N. M. Edelstein, P. B. Hitchcock, W. K. Kot, M. F. Lappert, G. V. Shalimoff and S. Tian, *J. Organomet. Chem.*, 2001, **636**, 124–129.
- 74 J. S. Parry, F. G. N. Cloke, S. J. Coles and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1999, **121**, 6867–6871.
- 75 N. A. Siladke, C. L. Webster, J. R. Walensky, M. K. Takase, J. W. Ziller, D. J. Grant, L. Gagliardi and W. J. Evans, *Organometallics*, 2013, **32**, 6522–6531.
- 76 R. R. Langeslay, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2016, **138**, 4036–4045.
- 77 R. R. Langeslay, G. P. Chen, C. J. Windorff, A. K. Chan, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2017, **139**, 3387–3398.
- 78 W. G. Van der Sluys, C. J. Burns, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1988, **110**, 5924–5925.
- 79 C. R. Graves, B. L. Scott, D. E. Morris and J. L. Kiplinger, *Organometallics*, 2008, **27**, 3335–3337.
- 80 A. Ambrosi, C. K. Chua, B. Khezri, Z. Sofer, R. D. Webster and M. Pumera, *Proc. Natl. Acad. Sci.*, 2012, **109**, 12899–12904.
- 81 T. F. Jenkins, D. H. Woen, L. N. Mohanam, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2018, **37**, 3863–3873.
- 82 H. Schumann, M. Glanz, H. Hemling and F. Ekkehard Hahn, *Z. Anorg. Allg. Chem.*, 1995,

- 621**, 341–345.
- 83 W. Wang, G. K. Liu, M. G. Brik, L. Seijo and D. Shi, *Phys. Rev. B*, 2009, **80**, 155120.
- 84 A. V. Polezhaev, C. J. Liss, J. Telser, C. Chen and K. G. Caulton, *Chem. Eur. J.*, 2018, **24**, 1330–1341.
- 85 D. D. Dawson, V. F. Oswald, A. S. Borovik and E. R. Jarvo, *Chem. Eur. J.*, 2020, **26**, 3044–3048.
- 86 M. Mohadjer Beromi, G. Banerjee, G. W. Brudvig, N. Hazari and B. Q. Mercado, *ACS Catal.*, 2018, **8**, 2526–2533.
- 87 R. J. Somerville, C. Odena, M. F. Obst, N. Hazari, K. H. Hopmann and R. Martin, *J. Am. Chem. Soc.*, 2020, **142**, 10936–10941.
- 88 R. R. Langeslay, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *Chem. Sci.*, 2015, **6**, 517–521.
- 89 J. C. Wedal, J. M. Barlow, J. W. Ziller, J. Y. Yang and W. J. Evans, *Chem. Sci.*, 2021, **12**, 8501–8511.

Table of Contents Entry



Ten $5f^3 6^1 U(II)$ compounds have identical EPR spectra, unique from $5f^3 U(III)$ and $5f^4 U(II)$ compounds