

1 Actinide covalency measured by pulsed electron paramagnetic resonance spectroscopy

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10

11 Abstract

12 Our knowledge of actinide chemical bonds lags far behind our understanding of bonding regimes of any
13 other series of elements. This is a major issue given the technological as well as fundamental
14 importance of f-elements. Some key chemical differences between actinides and lanthanides, and
15 between different actinides, can be ascribed to minor differences in covalency, i.e. the degree to which
16 electrons are shared between the f-block element and coordinated ligands. Yet there are almost no direct
17 measures of such covalency for actinides. Herein we report the first pulsed electron paramagnetic
18 resonance (EPR) spectra of actinide compounds. We apply the hyperfine sublevel correlation
19 (HYSCORE) technique to quantify the electron spin density at ligand nuclei (via the weak hyperfine
20 interactions) in molecular thorium(III) and uranium(III) species and therefore the extent of covalency.
21 Such information will be important in developing our understanding of chemical bonding, and therefore
22 reactivity, of actinides.

23

24 Our comprehension of actinide (An) bonding regimes lags behind the rest of the Periodic Table
25 and deepening our understanding is essential for the development of An chemistry, both from a
26 fundamental and technological viewpoint^{1,2}. One important aspect of bonding is the covalency, i.e. the
27 extent to which electrons are shared between the metal ion and coordinated ligands. Covalency in An
28 complexes, and trends in covalency across the An series, are the topics of much research (for some
29 recent examples, see refs. 3-11 and references therein). The covalency in An, which is generally thought
30 to be greater than in the predominantly ionic lanthanide series¹, depends on the hard/soft nature of the

31 ligand set, the formal oxidation state of the An ion, or even “accidental degeneracy” that results from
32 simple energy matching of metal and ligand valence orbitals¹². Such problems have been studied
33 extensively by computational methods¹³⁻¹⁷, but new experimental data is urgently required for validation
34 of these methods and the development of improved models. However, covalency in An bonding is
35 difficult to quantify experimentally^{12,18}, even though measurements by Electron Paramagnetic Resonance
36 (EPR), Mössbauer, photoelectron and ligand K-edge X-ray absorption near-edge (XANES)
37 spectroscopies are well-established for d-block elements¹⁹. XANES has been used to measure An
38 covalency^{12,20}; this synchrotron-based technique involves analysis of transition intensities for excitation of
39 core ligand electrons to vacant metal-ligand anti-bonding orbitals²¹. Nuclear Magnetic Resonance (NMR)
40 spectroscopy can also be used²², but this has only been applied to diamagnetic systems thus far.
41 Complementary data are required for paramagnetic systems because the vast majority of An ions have
42 unpaired electron spin.

43 EPR spectroscopy can measure covalency *via* the “superhyperfine” interaction of primarily metal-
44 based unpaired electrons with ligand nuclei that have a non-zero nuclear spin. However, this is rarely
45 resolved for actinides because of the broad linewidths in continuous wave (CW) EPR that result from fast
46 electron spin relaxation, with examples largely limited to An³⁺-doped CaF₂ (fluorite) and related
47 minerals²³⁻²⁵. CW ENDOR (Electron Nuclear DOuble Resonance) spectroscopy has been applied in a
48 few cases^{26,27}. Modern EPR hyperfine methods are based on *pulsed* rather than CW techniques,
49 allowing detection of much weaker interactions (higher spectral resolution) as well as information on spin
50 dynamics (time resolution). Despite this we are not aware of any reports of pulsed hyperfine methods on
51 An species, and only one brief mention of any pulsed EPR technique (a linear electric field effect study
52 on U³⁺-doped CaF₂)²⁸. This is astonishing, and there is possibly an assumption that electron spin
53 relaxation effects preclude such measurements.

54 We now report comparative pulsed EPR studies on two molecular An organometallic complexes
55 [An(Cp^{tt})₃] [An³⁺ = Th or U; Cp^{tt} = {C₅H₃^tBu₂-1,3}, a derivative of the cyclopentadienyl anion, Cp = C₅H₅].
56 These are ideal first compounds to study as the parent [An(Cp)₃] series (An = Th–Cf) has been a test-
57 bed for computational investigation of An covalency^{13,29-33}. We use the 1- and 2-dimensional electron
58 spin echo modulation methods ESEEM (electron spin echo envelope modulation) and HYSCORE
59 (hyperfine sublevel correlation) to measure the electron spin densities at ¹³C and ¹H nuclei of the ligands.
60 We find greater spin delocalisation in uranium than in the thorium complex and, surprisingly, that the

61 data on the thorium complex are similar to those reported for a late lanthanide analogue³⁴. Such studies
62 on wider ranges of compounds could have important consequences for our understanding of bonding in
63 the f-block.

64

65 **Results and Discussion**

66

67 **Synthesis and Characterisation.** The An³⁺ complexes [An(Cp^{tt})₃] [An = Th (**1**) and U (**2**)] were prepared
68 by modifications of standard procedures (see Supplementary Methods), and characterised by elemental
69 analysis, ¹H NMR, FTIR and electronic absorption spectroscopies. Their solid-state structures were
70 determined by single crystal X-ray diffraction (Figure 1a-c; Supplementary Data: X-ray Crystallography).
71 Three η⁵-Cp^{tt} ligands bind the An³⁺ ion, which lies in the {C2}₃ plane (Figure 1b), giving pseudo-C_{3h}
72 symmetry.

73 CW EPR spectra (Supplementary Data and Discussion: EPR Spectroscopy) of **1** (in toluene
74 solution at 100 K) confirm that the Th³⁺ ion has a 6d¹5f⁰ electronic configuration, giving electronic *g*-
75 values of *g*_z = 1.974, *g*_{x,y} = 1.880 (consistent with a d_{z²}¹ ground state where z is the C₃ axis). CW EPR
76 spectra of **2** are observable below ca. 40 K, and show that the U³⁺ ion has a 5f³ configuration, giving (for
77 a toluene solution at 5 K) effective *g*-values of *g*_x = 3.05, *g*_y = 1.65, *g*_z < 0.5 (the latter is not observed,
78 being beyond our magnetic field range at X-band microwave frequency) which are consistent with a well-
79 isolated lowest energy Kramers doublet arising from the ⁴I_{9/2} ground term (using a Russell-Saunders
80 description). These configurations are supported by magnetic data (Supplementary Data: Magnetic
81 Studies), and also Density Functional Theory (DFT) calculations that give the singly-occupied molecular
82 orbital (SOMO) of **1** as dominated by the Th 6d_{z²} orbital, and the three SOMOs of **2** as dominated by U
83 5f orbitals (Figure 1d,e; see Supplementary Data and Discussion: Computational Studies). Complete
84 Active Space Self-Consistent Field (CASSCF) calculations give *g*_z = 1.989 and *g*_x = *g*_y = 1.886 for **1**, and
85 *g*_x = 2.750, *g*_y = 2.021, *g*_z = 0.30 for the lowest Kramers doublet of **2**, in good agreement with the EPR
86 values. The 6d¹ and 5f³ configurations for **1** and **2** are also consistent with data from other [Th/U(Cp)₃]
87 derivatives³⁵⁻⁴⁰.

88 The state-of-the-art theory for covalency in multi-configurational systems is Quantum Theory of
89 Atoms in Molecules (QTAIM)^{13,33,41}. QTAIM analyses of Restricted Active Space (RAS)SCF-calculated
90 electron densities gives predominantly ionic An-C interactions for **1** and **2**, but the relative covalency is

91 difficult to assign. Calculated electron densities at the An-C bond critical points (ρ_{BCP}) are marginally
92 larger for **2** than for **1**, while the delocalization index (δ , quantifying the degree of electron sharing) is
93 marginally smaller (Supplementary Table 5). Hence, while weak covalency is found, calculations do not
94 distinguish between Th³⁺ and U³⁺, and experimental data is necessary.

95

96 **Pulsed EPR spectroscopy.** In pulsed EPR experiments we detect electron spin echos for **1** and **2**
97 below ca. 100 and 10 K, respectively, with Hahn microwave pulse sequences (Supplementary Data and
98 Discussion: EPR Spectroscopy). Measurements at different static magnetic fields (B_0) give echo-
99 detected field-swept (EDFS) spectra (Figure 2) that are consistent with the CW measurements
100 (Supplementary Figures 7, 8). Compound **2** gives an echo beyond B_0 of 1500 mT, confirming that $g_z <$
101 0.5. As far as we are aware these are the first pulsed EPR spectra reported for actinide compounds. The
102 ability to exploit pulsed EPR is limited by electron spin relaxation. Given the absence of data on
103 actinides, we have measured T_1 (spin-lattice) and T_M (phase memory) relaxation time constants
104 (Supplementary Figures 9-12, Supplementary Tables 6-8). For **1** T_1 is very long, reaching 21 ms
105 measured at 5 K and at $g_{x,y}$ ($B_0 = 366.3$ mT, the EDFS maximum). T_M is temperature independent below
106 ca. 20 K, reaching 3.0 μ s, but is still as long as 0.3 μ s at 100 K. The relatively slow relaxation arises
107 because the 6d¹ configuration means that Th³⁺ is behaving like a spin-only (orbital singlet) d-block ion.
108 The 5f³ configuration of **2** gives rise to much faster relaxation, with T_1 and T_M of ca. 0.9 ms and 0.8 μ s,
109 respectively, measured at 2.7 K and $B_0 = 463.6$ mT (near g_y , the EDFS maximum). However, even these
110 shorter times are ample to implement the multi-pulse sequences necessary for hyperfine methods. In
111 fact, for both **1** and **2** we already observe deep ESEEM (Electron Spin Echo Envelope Modulation) due
112 to ¹H nuclei (Supplementary Figures 9-12). In order to quantify these we have used HYSORE
113 (HYperfine Sub-level CORrelation), a 2D ESEEM technique that correlates nuclear frequencies in the α
114 and β electron spin manifolds resulting in, for weak hyperfine couplings ($2|u_n| > |A|$), cross-peaks about
115 the nuclear Larmor frequencies (u_n)⁴². For **1** and **2**, ¹H and ¹³C signals are observed (Figures 3, 4 and
116 Supplementary Figures 13-15).

117 For **1**, we focus on the ¹³C region because this gives a more direct report of the spin density in
118 the π -type frontier orbitals²⁹⁻³³ of the Cp^{tt} ligands (π -type with respect to the Cp rings; the orbitals which
119 will be involved in any covalent metal-ligand interaction). At $B_0 = 366.3$ mT ($g_{x,y}$) there are two distinct
120 sets of ridges (Figure 3a): one lying on the anti-diagonal (with a spread of $u_n \pm 1$ MHz) and a wider,

121 arched ridge ($u_n \pm 2.4$ MHz). Hence we are observing at least two distinct ^{13}C positions. The hyperfine
122 matrix (\mathbf{A}) at each carbon atom n includes contributions from the C $2p_\pi$ -spin density at n (\mathbf{A}^{Cn} ; we refer to
123 this as the covalent contribution) and from point dipole interactions (\mathbf{A}^{dip}) with spin density at other atoms
124 (Supplementary Equation 4). We have calculated \mathbf{A}^{dip} for each carbon in a Cp^{t} ring, using the crystal
125 structure and assuming unit spin population at Th: calculated spectra⁴³ with this model do not match the
126 experiment (Figure 3a), not coming close to the width of the experimental data. Hence, we added
127 covalent contributions to the hyperfine (summing with the calculated dipolar component): each \mathbf{A}^{Cn}
128 matrix is assumed to be axial with its unique axis in the molecular xy plane because spin density is in the
129 C $2p_\pi$ -orbitals. This gives two variables per site (A_{\parallel}^{Cn} and A_{\perp}^{Cn} , where the labels refer to the local axes of
130 \mathbf{A}^{Cn}). Computational results (Supplementary Figure 16) give the dominant $2p_\pi$ spin density of each Cp^{t}
131 at C2, with smaller contributions at C1,3, and negligible density at C4,5 [the Th ion lies in the $\{\text{C2}\}_3$
132 plane, Figure 1b]. Hence, we assume the larger and smaller ^{13}C couplings arise from C2 and C1,3,
133 respectively. We get excellent simulations with $A_{\parallel,\perp}^{C2} = +3.7, +0.4$ MHz, and $A_{\parallel,\perp}^{C1,3} = +1.1, +0.4$ MHz (Figure
134 3b, Supplementary Figure 13). A simple interpretation (Supplementary Equations 5) gives $2p_\pi$ spin
135 populations of ca. 1.3 and 0.5% for C2 and C1,3, respectively.

136 Because of the larger magnetic moment of ^1H (*cf.* that of ^{13}C), the ^1H HSCORE are more
137 dominated by point dipolar contributions. Nevertheless, the data are not reproduced by a dipole-only
138 model [we have included H2,4,5 and the closest $^1\text{H}(\text{tBu})$ atom], failing to reproduce the width of the
139 experimental data measured at g_z (Figure 3c). Hyperfine coupling to α -protons in π -radicals arises from
140 spin-polarisation of the C-H bonding electrons by the C $2p_\pi$ spin density⁴⁴. The relationship between the
141 ^1H hyperfine and the $2p_\pi$ spin population is well understood and, in general, gives a hyperfine matrix of
142 the form $[a_{\text{H}}/2, a_{\text{H}}, 3a_{\text{H}}/2]$ (where a_{H} is the isotropic component) with the small, middle and large
143 components oriented parallel to the C-H vector, to the $2p_\pi$ direction, and to their cross-product,
144 respectively. Addition of a spin-polarisation contribution of this form for H2 (there are no α -H at C1,3, and
145 there is very little spin density at C4,5) gives an excellent match to the experiment with $a_{\text{H2}} = -1.2$ MHz
146 (Figure 3d, Supplementary Figure 13). This corresponds to a C2 $2p_\pi$ spin population of 1.4%, in
147 excellent agreement with the ^{13}C derived value. The results give a total of ca. 6% spin population on the
148 three Cp^{t} rings.

149 For **2**, in the ^{13}C region, we only detect very weak signals: the signal-to-noise is presumably
150 limited by the much faster relaxation and the low (1.1%) natural abundance of ^{13}C . However, the 100%

151 abundance of ^1H gives good HYSCORE spectra in the $g_{x,y}$ regions (the spectral intensity becomes very
152 weak at higher fields because of the very low g_z). Significantly wider ^1H ridges are found than for **1**
153 ($u_n \pm 2.7$ MHz at g_x for **2** cf. $u_n \pm 2.0$ MHz at $g_{x,y}$ for **1**; Figure 4a). A significant part of this is due to the
154 increased orbital contribution to the hyperfine (which is proportional to $g-g_e$, where g_e is the free-electron
155 g -value): this is incorporated in Supplementary Equation (4) via the electronic \mathbf{g} -tensor (we have used an
156 assumed $g_z = 0.4$ for **2**, and have tested the sensitivity of the results to this parameter; see
157 Supplementary Discussion: EPR Spectroscopy). Calculated spectra based on U-H dipolar interactions
158 only (including H2,4,5 at each ligand) gives two distinct ^1H ridges at g_x , as is observed experimentally
159 (Figure 4a), but these extend beyond the experimental data (Figure 4b; note it is necessary to include all
160 three Cp^{II} ligands in the model because of the significantly rhombic ($g_x \neq g_y$) nature of the \mathbf{g} -tensor, see
161 Supplementary Discussion). However, the leading component of the dipolar interaction has opposite sign
162 to the contribution from C $2p_\pi$ population. Inclusion of a single ^1H (H2) with the same value of a_{H2} as
163 found for **1** does not reproduce the spectrum (Figure 4c). Computational results give a much more even
164 $2p_\pi$ spin distribution about the Cp^{II} rings in **2** than in **1**, with significant population at C4,5 (Supplementary
165 Figure 16). Adding H4,5 to our model, and fixing $a_{\text{H4,5}} = a_{\text{H2}}$, we find excellent agreement with $a_{\text{H2,4,5}} = -$
166 1.6 MHz (Figure 4d), corresponding to ca. 1.9% C $2p_\pi$ spin population at these positions (via
167 Supplementary Equations 5). These parameters give a minimum of ca. 17% spin population in total over
168 the three Cp^{II} ligands in **2** (however, note that we are blind to C1,3).

169 Hence, our experimental EPR data show that there is significantly greater total spin density on
170 the ligands for uranium than for thorium in $[\text{An}(\text{Cp}^{\text{II}})_3]$. This result, which gives a significantly greater
171 difference than that implied by the QTAIM parameters ρ_{BCP} and δ (Supplementary Table 5), initially
172 seems surprising given the greater radial extent of the 6d vs. 5f wavefunctions and the $6d^1$ and $5f^3$
173 ground states for **1** and **2**, respectively. This implies that the angular parts of the wavefunctions are more
174 important here, with only the annular lobe of the $6d_{z^2}$ orbital of **1** having the correct orientation to overlap
175 with ligand frontier orbitals, whilst the singly occupied 5f functions of **2** have greater in-plane character.
176 There is also an interesting comparison to be made between **1** and the ytterbium(III), $4f^{13}$ complex
177 $[\text{Yb}(\text{Cp})_3]$, the only lanthanide $[\text{Ln}(\text{Cp})_3]$ system for which equivalent data have been reported³⁴. ^{13}C
178 HYSCORE data for $[\text{Yb}(\text{Cp})_3]$ are very similar to those for **1** ($u_n \pm 2.0$ MHz at $g_{x,y}$; ^1H data were not
179 reported), suggesting surprisingly similar covalency in these two complexes despite the 4f vs. 5f/6d
180 valence orbitals. While caution should be taken with extrapolating the results from a limited number of

181 compounds, such results highlight the need for new experimental data on systematic families of well-
182 defined complexes. We have shown that such data for actinides can be provided by pulsed EPR
183 techniques.

184

185 **Methods**

186 **General.** All complexes were variously characterised by NMR, EPR, FTIR and NIR/Vis/UV
187 spectroscopies, Evans method solution magnetic moments, SQUID magnetometry (Quantum Design
188 MPMS magnetometer), single crystal X-ray diffraction (Rigaku Oxford Diffraction SuperNova CCD area
189 detector diffractometer), elemental microanalysis, and DFT and CASSCF calculations (see
190 Supplementary Methods). All manipulations were performed using standard Schlenk techniques or in an
191 Inert Purelab HE 2GB glovebox. Solvents were dried by refluxing over potassium and degassed before
192 use.

193 **Synthesis.** [Th(Cp^{tt})₃] (**1**) was prepared by reduction of [Th(Cp^{tt})₃(Cl)]⁴⁵ with excess KC₈ in 1,2-
194 dimethoxyethane (DME), following procedures used for the synthesis of [Th{C₅H₃(SiMe₃)₂-1,3}₃]^{35,36,38}.
195 [U(Cp^{tt})₃] (**2**) was prepared by reaction of [U(I)₃(THF)₄] with three equivalents of [K(Cp^{tt})] in
196 tetrahydrofuran (THF) at –80 °C, and isolated by removal of volatiles *in vacuo* followed by extraction with
197 hexane.

198 **EPR Measurements.** CW X-band EPR measurements were made on a Bruker EMX300 spectrometer;
199 pulsed X-band EPR measurements (on 2 – 10 mM toluene solutions) were made on a Bruker ElexSys
200 E580 spectrometer. Two-pulse electron spin echo measurements used a primary Hahn-echo sequence
201 ($\pi/2 - \tau - \pi - \tau - \text{echo}$), where τ is the inter-pulse delay time, with initial $\pi/2$ and π pulse lengths of 16
202 and 32 ns, respectively. EDFS spectra measure the echo intensity for fixed τ as a function of static
203 magnetic field B_0 . ESEEM measurements (also used to determine T_M) monitor the echo intensity as a
204 function of τ (the ¹H modulations can be suppressed by longer pulse durations). T_1 was measured by the
205 inversion recovery sequence ($\pi - t - \pi/2 - \tau - \pi - \tau - \text{echo}$) with 16 and 32 ns $\pi/2$ and π pulse lengths,
206 respectively, fixed $\tau = 320$ ns and with varying time t . HYSCORE measurements used the four-pulse
207 sequence ($\pi/2 - \tau - \pi/2 - t_1 - \pi - t_2 - \pi/2 - \text{echo}$) with 16 and 32 ns $\pi/2$ and π pulses, respectively, with
208 starting times $t_{1,2} = 0.1$ μs , and for τ between 130 and 200 ns. CW and pulsed EPR spectral simulations
209 used Stoll's EasySpin software⁴³. In the simulations for **2**, we treat the species as an effective spin $1/2$

210 with the effective g -values given in the text above: this treatment is justified as only the lowest energy
211 Kramers doublet of the $^4I_{9/2}$ ground term is populated at the temperatures of the EPR experiments. A full
212 account of the EPR analysis and modelling is given in the Supplementary Data and Discussion.

213
214 **Data availability.** The crystallographic data have been deposited at the Cambridge Crystallographic
215 Data Centre (CCDC) as CCDC 1454075 (**1**), 1454076 (**2**) and 1454105 ([U(Cp^{tt})₃(Cl)]) and can be
216 obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures.

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319

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326

327 **Author contributions**

328 A.F. synthesised and characterised the compounds. F. O. carried out the single crystal X-ray diffraction
329 analysis. A.-M.A., F.T. and E.J.L.M. collected and interpreted EPR spectroscopy and magnetic data.
330 R.B. and A.K. performed and interpreted calculations. D.P.M. provided the initial concept and supervised
331 A.F. D.P.M. and E.J.L.M. wrote the manuscript, with contributions from all co-authors.

332

333 **Additional information**

334 Supplementary information is available in the [online version](#) of the paper. Reprints and permissions
335 information is available online at www.nature.com/reprints. Correspondence and requests for materials
336 should be directed to F.T., D.P.M. and E.J.L.M.

337

338 **Competing financial interests**

339 The authors declare no competing financial interests.

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341

342 **Figure Captions:**

343

344 **Figure 1. Molecular structures, and calculated singly-occupied molecular orbitals (SOMOs), of**
345 **complexes 1 and 2.** (a) Schematic of structure of $[\text{An}(\text{Cp}^{\text{tt}})_3]$, An = Th (**1**) and U (**2**); (b) numbering
346 scheme used for Cp^{tt} ligands, and molecular axis system; (c) molecular structure of **1** from single crystal
347 X-ray diffraction (displacement ellipsoids at 30% probability level; hydrogen atoms omitted for clarity); (d)
348 density functional theory (DFT; PBE0/def(2)-TZVP level) calculated contour plots of the SOMO of **1**
349 ($6d^15f^0$ ground state electronic configuration), and (e) of the three SOMOs of **2** ($5f^3$ ground state
350 configuration).

351

352 **Figure 2. Echo-detected magnetic field-swept (EDFS) EPR spectra of complexes 1 and 2 at X-**
353 **band frequency (9.67 GHz).** (a) EDFS spectrum of **1** (in 2 mM toluene solution at 11 K); (b) EDFS
354 spectrum of **2** (in 5 mM toluene solution at 5 K; the modulations at low field are due to ^1H ESEEM
355 effects). The data were measured with 16 and 32 ns $\pi/2$ and π microwave pulses, respectively. The
356 arrows mark the static magnetic field (B_0) positions used for HYSORE studies.

357

358 **Figure 3. X-band HYSCORE (hyperfine sub-level correlation) spectra for complex 1, measured**
359 **under the conditions in Figure 2.** (a) ^{13}C region at static magnetic field $B_0 = 366.3$ mT (at $g_{x,y}$; ^{13}C
360 Larmor frequency $\nu_n = 3.92$ MHz), with calculation (red) based on a C-Th point dipole model including
361 C1-5. (b) As for (a), but with simulation (red) including point dipole and covalent contribution to ^{13}C
362 hyperfines (see text). (c) ^1H region for **1** at $B_0 = 351.6$ mT (at g_z ; ^1H Larmor frequency $\nu_n = 14.97$ MHz),
363 with calculation (red) based on a H-Th point dipole model including H2,4,5 and the nearest H(^tBu) atom.
364 (d) As for (c), but with calculation including spin polarisation contribution to hyperfine at H2 due to $2p_\pi$ -
365 spin density at C2. The dashed-red anti-diagonal lines mark the ^{13}C or ^1H Larmor frequency at each B_0 .

366

367 **Figure 4. X-band HYSCORE (hyperfine sub-level correlation) data for complex 2, measured under**
368 **the conditions in Figure 2.** (a) ^1H region measured at static magnetic field $B_0 = 244.3$ mT (near g_x ; ^1H
369 Larmor frequency $\nu_n = 10.40$ MHz); the arrows highlight the two unique hyperfine ridges. (b) As for (a),
370 but with calculation (red) based on a H-U point dipole model including H2,4,5. (c) As for (a), but with
371 calculation (red) including point dipole and spin polarisation contribution to hyperfine at H2 only (see
372 text). (d) As for (c), but with calculation (red) including point dipole and spin polarisation hyperfine
373 contributions at H2,4,5 (see text). The dashed-red anti-diagonal lines mark the ^1H Larmor frequency.

374

375 **Summary for Table of Contents:**

376 Covalency in actinide-ligand bonding is poorly understood compared to that in other parts of the Periodic
377 Table due to the lack of experimental data. Here, pulsed electron paramagnetic resonance (EPR)
378 methods are used to directly measure the electron spin densities at coordinated ligands in molecular
379 thorium and uranium complexes.