Actinide covalency measured by pulsed electron paramagnetic resonance spectroscopy

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Abstract

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

Our comprehension of actinide (An) bonding regimes lags behind the rest of the Periodic Table and deepening our understanding is essential for the development of An chemistry, both from a fundamental and technological viewpoint. One important aspect of bonding is the covalency, i.e. the extent to which electrons are shared between the metal ion and coordinated ligands. Covalency in An complexes, and trends in covalency across the An series, are the topics of much research (for some recent examples, see refs. 3-11 and references therein). The covalency in An complexes, which is generally thought to be greater than in the predominantly ionic lanthanide series, depends on the
hard/soft nature of the ligand set, the formal oxidation state of the An ion, or even “accidental degeneracy” that results from simple energy matching of metal and ligand valence orbitals. Such problems have been studied extensively by computational methods, but new experimental data is urgently required for validation of these methods and the development of improved models. However, covalency in An bonding is difficult to quantify experimentally, even though measurements by Electron Paramagnetic Resonance (EPR), Mössbauer, photoelectron and ligand K-edge X-ray absorption near-edge (XANES) spectroscopies are well-established for d-block elements. XANES has been used to measure An covalency, this synchrotron-based technique involves analysis of transition intensities for excitation of core ligand electrons to vacant metal-ligand anti-bonding orbitals. Nuclear Magnetic Resonance (NMR) spectroscopy can also be used, but this has only been applied to diamagnetic systems thus far. Complementary data are required for paramagnetic systems because the vast majority of An ions have unpaired electron spin.

EPR spectroscopy can measure covalency via the “superhyperfine” interaction of primarily metal-based unpaired electrons with ligand nuclei that have a non-zero nuclear spin. However, this is rarely resolved for actinides because of the broad spectral linewidths in continuous wave (CW) EPR that result from fast electron spin relaxation, with examples largely limited to An$^{3+}$-doped CaF$_2$ (fluorite) and related minerals. CW ENDOR (Electron Nuclear DOuble Resonance) spectroscopy has been applied in a few cases. Modern EPR hyperfine methods are based on pulsed rather than CW techniques, allowing detection of much weaker interactions (higher spectral resolution) as well as information on spin dynamics (time resolution). Despite this we are not aware of any reports of pulsed hyperfine methods on An species, and only one brief mention of any pulsed EPR technique (a linear electric field effect study on U$^{3+}$-doped CaF$_2$). This is astonishing, and there is possibly an assumption that electron spin relaxation effects preclude such measurements.

We now report comparative pulsed EPR studies on two molecular An organometallic complexes [An(Cp$^n$)$_3$] [An$^{3+}$ = Th or U; Cp$^n$ = \{C$_5$H$_5$Bu$_2$-1,3\}$_3$], a derivative of the cyclopentadienyl anion, Cp = C$_5$H$_5$]. These are ideal first compounds to study because the parent [An(Cp)$_3$] series (An = Th-Cf) has been a test-bed for computational investigation of An covalency. We use the 1- and 2-dimensional electron spin echo modulation methods ESEEM (electron spin echo envelope modulation) and HYSCORE (hyperfine sublevel correlation) to measure the electron spin densities at $^{13}$C and $^1$H nuclei of the ligands. We find greater spin delocalisation in uranium than in the thorium complex and, surprisingly, that the
data on the thorium complex are similar to those reported for a late lanthanide analogue\textsuperscript{34}. Such studies on wider ranges of compounds could have important consequences for our understanding of bonding in the f-block.

Results and Discussion

**Synthesis and Characterisation.** The An\textsuperscript{3+} complexes [An(Cp\textsuperscript{tt})\textsubscript{3}] [An = Th (1) and U (2)] were prepared by modifications of standard procedures (see Methods and Supplementary Methods), and characterised by elemental analysis, \textsuperscript{1}H NMR, FTIR and electronic absorption spectroscopies. Their solid-state structures were determined by single crystal X-ray diffraction (Figure 1a-c; Supplementary Data: X-ray Crystallography). Three \( \eta^5 \)-Cp\textsuperscript{tt} ligands bind the An\textsuperscript{3+} ion, which lies in the \{C2\}_3 plane (Figure 1b), giving pseudo-\( C_3h \) symmetry.

CW EPR spectra (Supplementary Data and Discussion: EPR Spectroscopy) of 1 (in toluene solution at 100 K) confirm that the Th\textsuperscript{3+} ion has a 6d\textsuperscript{1}5f\textsuperscript{0} electronic configuration, giving electronic g-values of \( g_z = 1.974 \) and \( g_{xy} = 1.880 \) (consistent with a d\textsuperscript{z2} \textsuperscript{1} ground state where z is the C\textsubscript{3} axis). CW EPR spectra of 2 are observable below ca. 40 K, and show that the U\textsuperscript{3+} ion has a 5f\textsuperscript{3} configuration, giving (for 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, being beyond our magnetic field range at X-band microwave frequency) which are consistent with a well-isolated lowest energy Kramers doublet arising from the \( ^4I_{9/2} \) ground term (using a Russell-Saunders description). These configurations are supported by magnetic data (Supplementary Data: Magnetic Studies), and also Density Functional Theory (DFT) calculations that give the singly-occupied molecular orbital (SOMO) of 1 as dominated by the Th 6d\textsubscript{z2} orbital, and the three SOMOs of 2 as dominated by U 5f orbitals (Figure 1d,e; see Supplementary Data and Discussion: Computational Studies). Complete Active Space Self-Consistent Field (CASSCF) calculations give \( g_z = 1.989 \) and \( g_x = g_y = 1.886 \) for 1, and \( g_x = 2.750 \), \( g_y = 2.021 \), \( g_z = 0.30 \) for the lowest Kramers doublet of 2, in good agreement with the EPR values. The 6d\textsuperscript{1} and 5f\textsuperscript{3} electronic configurations for 1 and 2 are also consistent with studies on other [Th/U(Cp)\textsubscript{3}] derivatives\textsuperscript{35-40}.

The state-of-the-art theory for covalency in multi-configurational systems is Quantum Theory of Atoms in Molecules (QTAIM)\textsuperscript{13,33,41}. QTAIM analyses of Restricted Active Space (RAS)SCF-calculated electron densities gives predominantly ionic An-C interactions for 1 and 2, but the relative covalency is
difficult to assign. Calculated electron densities at the An-C bond critical points ($\rho_{\text{BCP}}$) are marginally larger for 2 than for 1, while the delocalization index ($\delta$, quantifying the degree of electron sharing) is marginally smaller (Supplementary Table 5). Hence, while weak covalency is found, calculations do not distinguish between Th$^{3+}$ and U$^{3+}$, and experimental data is necessary.

**Pulsed EPR spectroscopy.** In pulsed EPR experiments we detect electron spin echos for both complexes 1 and 2 (in toluene solution) below ca. 100 and 10 K, respectively, with Hahn microwave pulse sequences (Supplementary Data and Discussion: EPR Spectroscopy). Measurements at different static magnetic fields ($B_0$) give echo-detected field-swept (EDFS) spectra (Figure 2) that are consistent with the CW measurements (Supplementary Figures 7,8). Complex 2 gives an echo beyond $B_0$ of 1500 mT, confirming that $g_x < 0.5$. As far as we are aware these are the first pulsed EPR spectra reported for actinide compounds. The ability to exploit pulsed EPR is limited by electron spin relaxation. Given the absence of data on actinides, we have measured $T_1$ (spin-lattice) and $T_M$ (phase memory) relaxation time constants (Supplementary Figures 9-12, Supplementary Tables 6-8). For 1 $T_1$ is very long, reaching 21 ms measured at 5 K and at $g_{x,y}$ ($B_0 = 366.3$ mT, the EDFS maximum). $T_M$ is temperature independent below ca. 20 K, reaching 3.0 µs, but is still as long as 0.3 µs at 100 K. The relatively slow relaxation arises because the 6d$^1$ configuration means that Th$^{3+}$ is behaving like a spin-only (orbital singlet) d-block ion. The 5f$^3$ configuration of 2 gives rise to much faster relaxation, with $T_1$ and $T_M$ of ca. 0.9 ms and 0.8 µs, respectively, measured at 2.7 K and $B_0 = 463.6$ mT (near $g_y$, the EDFS maximum). However, even these shorter times are ample to implement the multi-pulse sequences necessary for hyperfine methods.

In fact, for both 1 and 2 we already observe deep ESEEM (Electron Spin Echo Envelope Modulation) modulations due to interaction with $^1$H nuclei on the ligands (Supplementary Figures 9-12). In order to quantify these interactions we have used HYSCORE (HYperfine Sub-level CORrelation), a 2D ESEEM technique that correlates nuclear frequencies in the $\alpha$ and $\beta$ electron spin manifolds resulting in, for weak hyperfine couplings ($2|u_n| > |A|$), cross-peaks about the nuclear Larmor frequencies ($u_n$)$^{42}$. For 1 and 2, $^1$H and $^{13}$C signals are observed (Figures 3, 4 and Supplementary Figures 13-15).

For complex 1, we focus on the $^{13}$C region because this gives a more direct report of the spin density in the $\pi$-type frontier orbitals$^{29-33}$ of the Cp$^{ll}$ ligands ($\pi$-type with respect to the Cp rings; the orbitals which will be involved in any covalent metal-ligand interaction). At $B_0 = 366.3$ mT ($g_{x,y}$) there are two distinct sets of ridges (Figure 3a): one lying on the anti-diagonal (with a spread of $u_n\pm1$ MHz) and a
wider, arched ridge \( (u_n \pm 2.4 \text{ MHz}) \). Hence we are observing at least two distinct \(^{13}\text{C} \) positions. The hyperfine matrix \( (\mathbf{A}) \) at each carbon atom \( n \) includes contributions from the \( \text{C} \) 2\( p_n \)-spin density at \( n \) \( (\mathbf{A}^{\text{Cn}}; \) we refer to this as the covalent contribution) and from point dipole interactions \( (\mathbf{A}^{\text{dp}}) \) with spin density at other atoms (Supplementary Equation 4). We have calculated \( \mathbf{A}^{\text{dp}} \) for each carbon in a \( \text{Cp}^n \) ring, using the crystal structure and assuming unit spin population at \( \text{Th} \): calculated spectra\(^{43} \) with this model do not match the experiment (Figure 3a), not coming close to the width of the experimental data. Hence, we added covalent contributions to the hyperfine (summing with the calculated dipolar component): each \( \mathbf{A}^{\text{Cn}} \) matrix is assumed to be axial with its unique axis in the molecular \( xy \) plane because spin density is in the \( \text{C} \) 2\( p_n \)-orbitals. This gives two variables per site \( (A_{||}^{\text{Cn}} \) and \( A_{\bot}^{\text{Cn}} \), where the labels refer to the local axes of \( \mathbf{A}^{\text{Cn}} \). Computational results (Supplementary Figure 16) give the dominant 2\( p_n \) spin density of each \( \text{Cp}^n \) at \( \text{C2} \), with smaller contributions at \( \text{C1,3} \), and negligible density at \( \text{C4,5} \) [the \( \text{Th} \) ion lies in the \{\( \text{C2} \)\}_3 \) plane, Figure 1b]. Hence, we assume the larger and smaller \(^{13}\text{C} \) couplings to arise from \( \text{C2} \) and \( \text{C1,3} \), respectively. We get excellent simulations with \( A_{||}^{\text{C2}} = +3.7, +0.4 \text{ MHz} \), and \( A_{||}^{\text{C1,3}} = +1.1, +0.4 \text{ MHz} \) (Figure 3b, Supplementary Figure 13). A simple interpretation (Supplementary Equations 5) gives 2\( p_n \) spin populations of ca. 1.3 and 0.5\% for \( \text{C2} \) and \( \text{C1,3} \), respectively.

Because of the larger magnetic moment of \(^1\text{H} \) (\textit{cf.} that of \(^{13}\text{C} \)), the \(^1\text{H} \) HYSCORE are more dominated by point dipolar contributions. Nevertheless, the data are not reproduced by a dipole-only model [we have included H2,4,5 and the closest \(^1\text{H}(\text{tBu}) \) atom], failing to reproduce the width of the experimental data measured at \( g_z \) (Figure 3c). Hyperfine coupling to \( \alpha \)-protons in \( \pi \)-radicals arises from spin-polarisation of the C-H bonding electrons by the \( \text{C} \) 2\( p_n \) spin density\(^{44} \). The relationship between the \(^1\text{H} \) hyperfine and the 2\( p_n \) spin population is well understood and, in general, gives a hyperfine matrix of the form \[ a_{||} / 2, a_{\bot}, 3a_{||} / 2 \] (where \( a_{\bot} \) is the isotropic component) with the small, middle and large components oriented parallel to the C-H vector, to the 2\( p_n \) direction, and to their cross-product, respectively. Addition of a spin-polarisation contribution of this form for H2 (there are no \( \alpha \)-H at \( \text{C1,3} \), and there is very little spin density at \( \text{C4,5} \)) gives an excellent match to the experiment with \( a_{\text{H2}} = -1.2 \text{ MHz} \) (Figure 3d, Supplementary Figure 13). This corresponds to a \( \text{C2} \) 2\( p_n \) spin population of 1.4\%, in excellent agreement with the \(^{13}\text{C} \) derived value. The results give a total of ca. 6\% spin population on the three \( \text{Cp}^n \) rings.

For complex 2, in the \(^{13}\text{C} \) region, we only detect very weak signals: the signal-to-noise is presumably limited by the much faster relaxation and the low (1.1\%) natural abundance of \(^{13}\text{C} \). However,
the 100% abundance of $^1$H gives good HYSCORE spectra in the $g_{x,y}$ regions (the spectral intensity becomes very weak at higher fields because of the very low $g_z$). Significantly wider $^1$H ridges are found than for 1 ($u_n \pm 2.7$ 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 increased orbital contribution to the hyperfine (which is proportional to $g-g_e$, where $g_e$ is the free-electron g-value); this is incorporated in Supplementary Equation (4) via the electronic g-tensor (we have used an assumed $g_z = 0.4$ for 2, and have tested the sensitivity of the results to this parameter; see Supplementary Discussion: EPR Spectroscopy). Calculated spectra based on the assumption of U-H dipolar interactions only (including H2,4,5 at each ligand) give two distinct $^1$H ridges at $g_x$, as is observed experimentally (Figure 4a), but these extend beyond the experimental data [Figure 4b; note it is necessary to include all three Cp$^{\text{III}}$ ligands in the model because of the significantly rhombic ($g_x \neq g_y$) nature of the g-tensor, see Supplementary Discussion: EPR Spectroscopy]. However, the leading component of the dipolar interaction has opposite sign to the contribution from the C 2p$_n$ population. Inclusion of a single $^1$H (H2) with the same value of $a_{n2}$ as found for 1 does not reproduce the spectrum (Figure 4c). Computational results give a much more even 2p$_{n}$ spin distribution about the Cp$^{\text{III}}$ rings in 2 than in 1, with significant population at C4,5 (Supplementary Figure 16). Adding H4,5 to our model, and fixing $a_{H4,5} = a_{H2}$, we find excellent agreement with $a_{H2,4,5} = -1.6$ MHz (Figure 4d), corresponding to ca. 1.9% C 2p$_{n}$ spin population at these positions (via Supplementary Equations 5). These parameters give a minimum of ca. 17% spin population in total over the three Cp$^{\text{III}}$ ligands in 2 (however, note that we are blind to C1,3).

Hence, our experimental EPR data show that there is significantly greater total spin density on the ligands for uranium than for thorium in [An(Cp$^{\text{III}}$)$_3$]. This result, which gives a significantly greater difference than that implied by the QTAIM parameters $\rho_{BCP}$ and $\delta$ (Supplementary Table 5), initially seems surprising given the greater radial extent of the 6d vs. 5f wavefunctions and the 6d$^1$ and 5f$^3$ ground state electronic configurations for 1 and 2, respectively. This implies that the angular parts of the wavefunctions are more important here, with only the annular lobe of the 6d$_{z^2}$ orbital of 1 having the correct orientation to overlap with ligand frontier orbitals, whilst the singly occupied 5f functions of 2 have greater in-plane character. There is also an interesting comparison to be made between 1 and the ytterbium(III), 4f$^{13}$ complex [Yb(Cp)$_3$], the only lanthanide [Ln(Cp)$_3$] system for which equivalent data have been reported$^{34}$. $^{13}$C HYSCORE data for [Yb(Cp)$_3$] are very similar to those for 1 ($u_n \pm 2.0$ MHz measured at $g_{x,y}$; $^1$H data were not reported), suggesting surprisingly similar covalency in these two
complexes despite the 4f vs. 5f/6d valence orbitals. While caution should be taken with extrapolating the results from a limited number of compounds, such results highlight the need for new experimental data on systematic families of well-defined complexes. We have shown that such data for actinides can be provided by pulsed EPR techniques.

Methods

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

Synthesis. \([\text{Th}(\text{Cp}^\text{tt})_3] \) (1) was prepared by reduction of \([\text{Th}(\text{Cp}^\text{tt})_3(\text{Cl})]^{45}\) with excess KC\(_8\) in 1,2-dimethoxyethane (DME), following procedures used for the synthesis of \([\text{Th}(\text{C}_8\text{H}_8(\text{SiMe}_3)_2-1,3)]_{3}^{35,36,38}\). \([\text{U}(\text{Cp}^\text{tt})_3] \) (2) was prepared by reaction of \([\text{U}(\text{I})_3(\text{THF})_4] \) with three equivalents of \([\text{K}(\text{Cp}^\text{tt})] \) in tetrahydrofuran (THF) at \(-80^\circ\text{C}\), and isolated by removal of volatiles \textit{in vacuo} followed by extraction with hexane.

EPR Measurements. CW X-band EPR measurements were made on a Bruker EMX300 spectrometer; pulsed X-band EPR measurements (on 2 – 10 mM toluene solutions) were made on a Bruker ElexSys E580 spectrometer. Two–pulse electron spin echo measurements used a primary Hahn–echo sequence \((\pi/2 – \tau – \pi – \tau – \text{echo})\), where \(\tau\) is the inter–pulse delay time, with initial \(\pi/2\) and \(\pi\) pulse lengths of 16 and 32 ns, respectively. EDFS spectra measure the echo intensity for fixed \(\tau\) as a function of static magnetic field \(B_0\). ESEEM measurements (also used to determine \(T_M\)) monitor the echo intensity as a function of \(\tau\) (the \(^1\text{H} \) modulations can be suppressed by longer pulse durations). \(T_1\) was measured by the inversion recovery sequence \((\pi – t – \pi/2 – \tau – \pi – \tau – \text{echo})\) with 16 and 32 ns \(\pi/2\) and \(\pi\) pulse lengths, respectively, fixed \(\tau = 320\) ns, and with varying time \(t\). HYSCORE measurements used the four–pulse sequence \((\pi/2 – \tau – \pi/2 – t_1 – \pi – t_2 – \pi/2 – \text{echo})\) with 16 and 32 ns \(\pi/2\) and \(\pi\) pulses, respectively, with starting times \(t_{1,2} = 0.1\) \(\mu\)s, and for \(\tau\) between 130 and 200 ns. CW and pulsed EPR spectral simulations...
used Stoll’s EasySpin software\textsuperscript{43}. In the simulations for 2, we treat the species as an effective spin $\frac{1}{2}$
with the effective $g$-values given in the text above: this treatment is justified as only the lowest energy
Kramers doublet of the $^{4}\!\!_{1}/_{2}$ ground term is populated at the temperatures of the EPR experiments. A full
account of the EPR analysis and modelling is given in the Supplementary Data and Discussion.

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

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

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

Competing financial interests
The authors declare no competing financial interests.

Figure Captions:

Figure 1. Molecular structures, and calculated singly-occupied molecular orbitals (SOMOs), of complexes 1 and 2. (a) Schematic of structure of [An(Cp°)₃], An = Th (1) and U (2); (b) numbering scheme used for Cp° ligands, and molecular axis system; (c) molecular structure of 1 from single crystal X-ray diffraction (displacement ellipsoids at 30% probability level; hydrogen atoms omitted for clarity); (d) density functional theory (DFT; PBE0/def(2)-TZVP level) calculated contour plots of the SOMO of 1 (6d¹⁵f⁰ ground state electronic configuration), and (e) of the three SOMOs of 2 (5f³ ground state configuration).

Figure 2. Echo-detected magnetic field-swept (EDFS) EPR spectra of complexes 1 and 2 at X-band frequency (9.67 GHz). (a) EDFS spectrum of 1 (in 2 mM toluene solution at 11 K); (b) EDFS spectrum of 2 (in 5 mM toluene solution at 5 K; the modulations at low field are due to ¹H ESEEM effects). The data were measured with 16 and 32 ns π/2 and π microwave pulses, respectively. The arrows mark the static magnetic field (B₀) positions used for HYSCORE studies.
Figure 3. X-band HYSCORE (hyperfine sub-level correlation) spectra for complex 1, measured 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 Larmor frequency $\nu_n = 3.92$ MHz), with calculation (red) based on a C-Th point dipole model including C1-5. (b) As for (a), but with simulation (red) including point dipole and covalent contribution to $^{13}$C hyperfines (see text). (c) $^1$H region for 1 at $B_0 = 351.6$ mT (at $g_z$; $^1$H Larmor frequency $\nu_n = 14.97$ MHz), with calculation (red) based on a H-Th point dipole model including H2,4,5 and the nearest H(tBu) atom. (d) As for (c), but with calculation including spin polarisation contribution to hyperfine at H2 due to $2p_\pi$ spin density at C2. The dashed-red anti-diagonal lines mark the $^{13}$C or $^1$H Larmor frequency at each $B_0$.

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

Summary for Table of Contents:

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