Fingerprinting the oxidation state of U(IV) by emission spectroscopy

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ABSTRACT. The solid-state structure of the known complex $[Et_4N][U(NCS)_5(bipy)_2]$ has been re-determined and a detailed spectroscopic and magnetic study has been performed in order to confirm the oxidation states of both metal and bipy ligand. Electronic absorption and infrared

spectroscopy suggest that the uranium is in its +4 oxidation state and this has been corroborated by emission spectroscopy and variable temperature magnetic measurements, as well as theoretical calculations. Therefore the bipy ligands are neutral, innocent ligands and not, as would be inferred from just a solid state structure, radical anions.

Emission spectroscopy has been widely utilized in lanthanide chemistry, but for the actinides this technique has not been applied to such an extent.[1] For instance, the sensitivity of this technique has advantages in studying the highly radioactive curium and, to a lesser extent, americium ions in solution. Whilst the uranyl emission is the most widely studied and understood, studies of other oxidation states of uranium have only recently come to the fore. We have recently reported emission from simple halide complexes of U(IV) in non-aqueous solutions[2] and we wish to expand on our attempts to fingerprint this oxidation state using emission spectroscopy. The presence of redox active ligands in the coordination sphere can sometimes cause ambiguity in the metal oxidation state of d-and p-block complexes,[3] but actinide complexes featuring non-innocent ligands are scarce. One of the ligands that is known to display non-innocence is the 2,2′-bipyridine (bipy) ligand, as this can accept one or two electrons into the low lying LUMO and therefore exist as (bipy$^\bullet$)$^-$ and (bipy)$^{2-}$. The oxidation state of this ligand can be determined by the C1-C1′ bond length from the solid state structures, as well as spectroscopic measurements.[4] The uranium compounds [Tp*$_2$U(bipy)],[5] (Tp*=hydrotris(3,5-dimethylpyrazolyl)borate), [Cp*(η^8-C$_8$H$_8$)U(R$_2$bipy)], (R$_2$bipy = bipy, 4,4′-Me$_2$bipy)[6], [(η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$)$_2$An(bipy)], (An = U,[7,8] Th[9]) [(η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$)$_2$Th(bipy)][10] and [Et$_4$N][U(NCS)$_5$(bipy)$_2$], **1**,[11] have all been assigned as containing a bipy radical anion on the basis of structural data, namely the C1-C1′ bond length. The latter compound is intriguing in that it was reported as a U(IV) species, implying a neutral bipy ligand formulation but has varying

C1-C1′ bond lengths that could suggest a bipy radical anion; if this were the case the oxidation state of the uranium center would be +5. The synthesis of **1** involved simply the reaction of bipy with [Et$_4$N]$_4$[U(NCS)$_8$], without additional reagents. All other compounds listed above, with the exception of [Cp*(η^8-C$_8$H$_8$)U(R$_2$bipy)], are formed in the presence of a reducing agent – single electron transfer reactivity of bipy is known for transition metals such as Cr(II),[12] but without the presence of a reducing agent neutral bipy species are commonly formed. In the [Cp*(η^8-C$_8$H$_8$)U(R$_2$bipy)] example it has been postulated that one of the COT dianions acts as the reducing agent.[6] It is worth noting that diimine ligands such as dipp-BIAN (dipp-BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthylene) can facilitate single electron transfer to U(III),[13] whereas the α-diimine [(mes)N=C(Me)C(Me)=N(mes)] requires the use of external reducing agents to do this type of electron transfer chemistry.[14] In this contribution we use emission spectroscopy to elucidate the oxidation state of the uranium center in **1**, which has been supported by a re-determination of the X-ray structure, magnetic measurements and DFT calculations.

[Et$_4$N][U(NCS)$_5$(bipy)$_2$], **1**, was prepared in an analogous manner to that reported in the literature[11] to give green crystals upon recrystallisation from acetonitrile. We have reported upon the use of emission spectroscopy for fingerprinting the U(IV) oxidation state in compounds where ligand based charge transfer bands do not encroach into the visible region of the spectrum,[2] as this affords a fast quenching mechanism and emissions ending on f-orbitals are not observed. As the charge transfer bands in **1** are confined to the UV region we would predict that an emission profile would be observed that is similar to our previously reported examples, if **1** contains a U(IV) centre. The excitation and emission spectra are shown in Figure 1, and this

corroborates the assignment of the metal oxidation state. The lifetime of 3 ns can be compared to 8-12 ns in the uranium halide complexes [Li(THF)$_4$][UX$_5$(THF)] (X = Cl, Br), [Et$_4$N]$_2$[UCl$_6$] or [UCl$_4$(THF)$_3$] and [U(DO3A)]Br (DO3A = [4,7,10-tris-carboxymethyl-,1,4,7,10-tetraaza-cyclododec-1-yl]-acetic acid).[15] The emissions are weak and comparable to the Raman bands of the solvent, thus precluding determination of an accurate quantum yield. However, in this example we have shown the utility of emission spectroscopy to confirm the oxidation state of a U(IV) species.
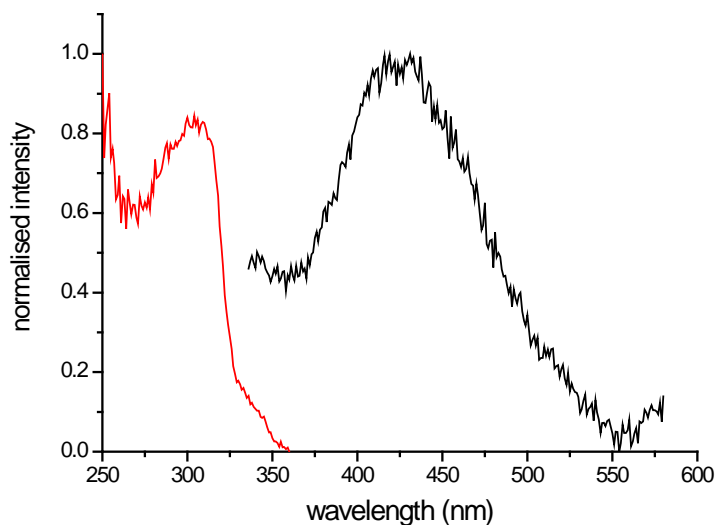

Figure 1. Excitation (red) and emission (black) of **1** in MeCN at room temperature (λ_{ex} = 420 nm; λ_{em} = 325 nm).

The infrared and Raman spectra for **1** show bands attributable to the NCS ligand with ν(N=C) = 2016 (IR), 2030 (R) cm^{-1} and ν(C=S) = 763 (IR) and 768 (R) cm^{-1}. There are no strong absorptions between 900 and 1000 cm^{-1} in the infrared spectrum, which would be typical of bipy radical ion, but bands at ca. 1600 cm^{-1} infer a neutral bipy. Finally, the bands associated with

bipy in the Raman spectrum do not change significantly compared to uncoordinated bipy (Figure S1, Supporting Information). The electronic absorption spectrum can be used to characterize the oxidation state of the bipy ligand. The uncoordinated bipy radical anion displays intense ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}) bands at ~820, 530, and 385 nm, whilst two intense bands at ~610 and 373 nm are seen for $(bipy)^{2-}$.[16] Well characterised Cr[17] and group 5 metal[18] complexes featuring bipy radical anions display bands at ca. 1100 nm and ca. 520 nm. The UV-vis-nir spectrum of **1** is shown in Figure 2 and bands at 236 and 305 nm can be assigned to the n-π* transition of the NCS ligand and the π-π* transition of the neutral bipy ligand respectively. There are no strong bands in the NIR region, which reinforces the spectroscopic assignment of a neutral bipy ligand. The bands that do appear in the visible and NIR region can be assigned to f-f transitions as the extinction coefficients are small. Therefore the electronic absorption spectrum suggests that the oxidation state of the uranium in **1** remains +4.
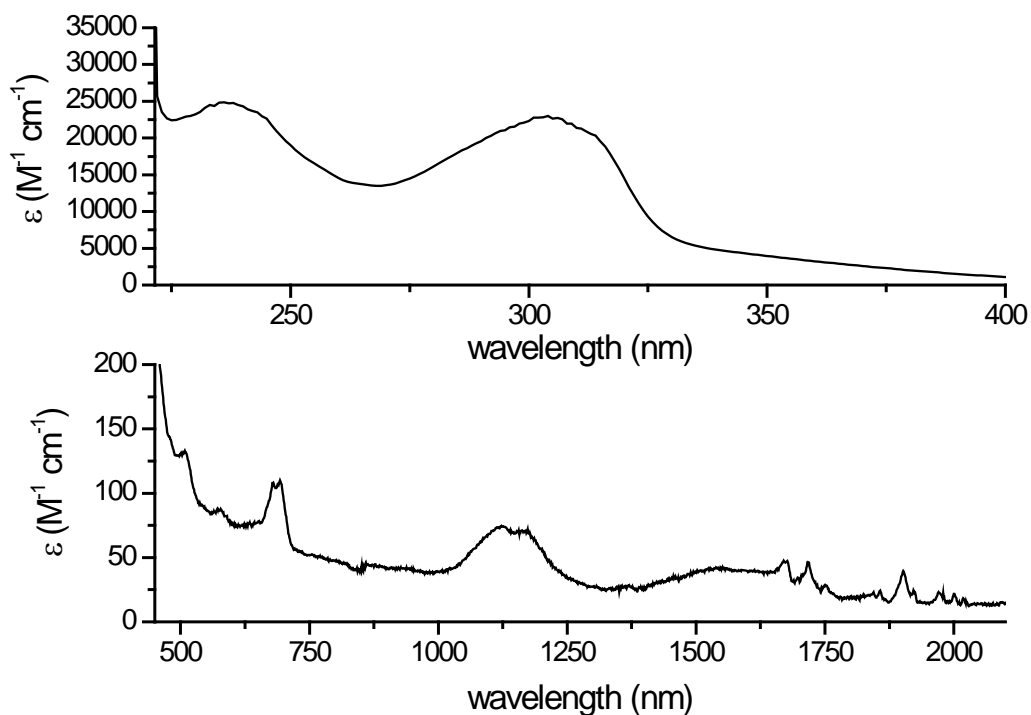
Figure 2. UV-vis/NIR spectrum of **1** in MeCN.

In order to unequivocally confirm the oxidation state of both the metal and the ligand, the variable temperature magnetic profile was examined using SQUID measurements (Figure 3). The magnetic moment at 300 K is 2.90 μ_B, significantly lower than expected for a $^3H_4$ ground state ion (3.58 μ_B); reduced magnetic moments are common in uranium(IV) compounds and sometimes ascribed to enhanced covalency which quenches the spin-orbit coupling, or the presence of strong field ligands.[19] Upon decreasing the temperature there is a precipitous drop to 0.35 μ_B at 2 K. This magnetic profile is typical for the +4 oxidation state of uranium (U(V) species typically have a room temperature magnetic moment of 1.9 to 2.5 μ_B at room temperature

and ca 1 μ_B at low temperatures).[20] The influence of the magnetization upon varying field (Figure S2, Supporting Information) and lack of frequency dependence of the AC susceptibility (Figure S3, Supporting Information) corroborates the assignment of a U(IV) ion.[21]
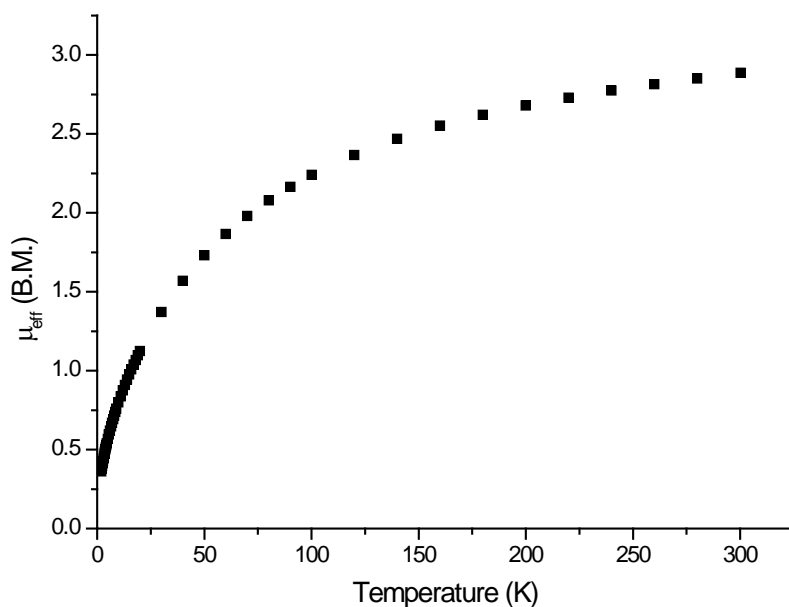

Figure 3. Temperature dependent magnetic susceptibility at 0.1 T for **1** from 2 to 300 K.

Single crystals of **1** were grown from acetonitrile solutions and the solid state structure is shown in Figure 4. It is worth noting that the cell parameters are identical to the original report, but the better refinement allows more precise metric parameters to be recorded. Thus, whilst the U-N, N=C and C=S bond lengths are similar to the earlier report, the C1-C1′ bond in the bipy are now 1.486(8) and 1.471(8) Å thus corroborating the spectroscopic assignment of the bipy as a neutral, innocent ligand. We have investigated the reactivity of [Et4N]4[U(NCS)8] with the other redox active ligands TCNE and the α-diimine [(dipp)N=C(Me)C(Me)=N(dipp)] (dipp = 2,6-

7

diisopropylphenyl), but under all conditions the starting material was reclaimed, probably highlighting the hard nature of the U(IV) ion which is incompatible with the softer nitrogen ligands.
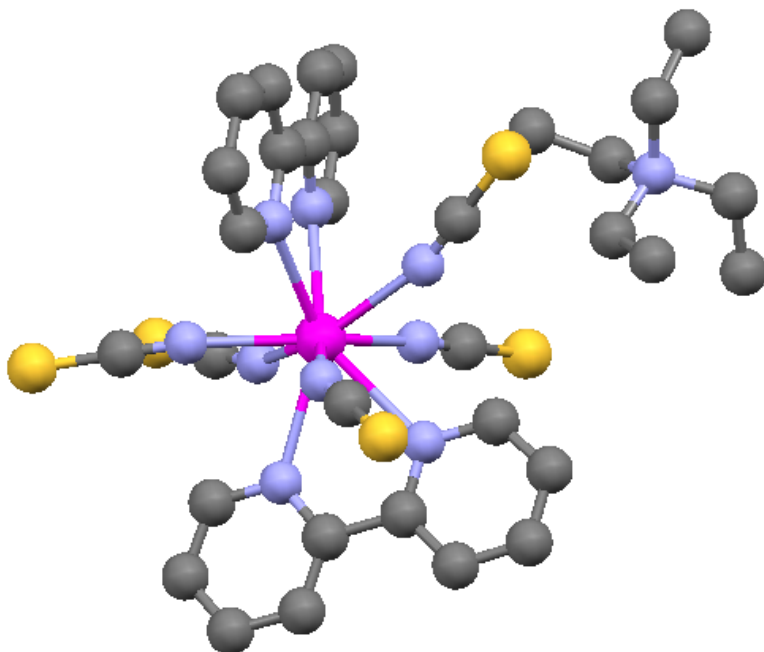

Figure 4. Solid-state structure of **1**. Selected bond lengths (Å) and angles (°).

Given that lower than expected room-temperature magnetic susceptibility values could be ascribed to enhanced covalency, and the fact that N-heterocyclic donor ligands show promise in Ln/An separation by overlap of the heterocyclic π* orbitals with uranium 6d- or 5f-orbitals[22] we have turned to DFT and related methods to probe the bonding in **1**. DFT geometry optimisation at the BP86/SV(P) level results in C1-C1′ bond length of 1.482 Å in both ligands, in excellent agreement with solid state values (the equivalent value in free bipy is 1.499 Å). Calculation of harmonic vibrational frequencies at the same level identifies vibrations with substantial C1-C1′ character at 1593, 1468, 1464, 1302, and 1301 cm^{-1} (in free bipy such vibrations are found at 1594 and 1294 cm^{-1}). Thus, DFT adds further support for the assignment of a neutral bipy ligand

that is only very slightly perturbed by coordination to U. For comparison, N≡C stretches are found between 2037 and 2047 cm^{-1} and C=S stretches between 864 and 880 cm^{-1}. These values are somewhat higher than the experimental observations, but in the range expected for DFT calculations with medium-sized basis sets.

DFT data shows that the HOMO is mainly based on the bipy whilst the LUMO is of thiocyanate character (Figure 5). The lowest energy orbital that has bipy π* character is the LUMO+4, which is 1.69 eV higher in energy than the HOMO (α-spin). Natural bond orbital (NBO) analysis indicates a charge on U of +1.618, with an electron configuration of [core]$7s^{0.24}5f^{2.65}6d^{1.07}7p^{0.46}$. NBO analysis finds no evidence for bonding orbitals shared between U and bipy N. Instead, 2nd order orbital effects are present corresponding to donation from lone pairs on bipy N into formally empty orbitals, with mainly d and f character, on U are located, which amount to 65 to 70 kcal/mol of stabilisation in total. No evidence for significant back donation from U into formally empty bipy orbitals is found in NBO data.

HOMO   LUMO   LUMO+4

Figure 5. Selected molecular orbitals of **1** at the BP86/SV(P) level of theory.

In summary, we have shown that emission spectroscopy can be used to fingerprint the +4 oxidation state of uranium in an ambiguous complex. A re-determination of the solid state structure gives more precise bond lengths and spectroscopic and magnetic studies confirm that the bipy ligands are indeed neutral and the oxidation state of the uranium is +4. A computational study supports the assignment of oxidation state, and suggests that the bonding between the bipy and uranium centre is better described as donation from N lone pairs into empty orbitals on U, as opposed to covalency.

ASSOCIATED CONTENT

Supporting Information. CIF files, tables and text giving crystallographic data for **1**, complete experimental details, and vibrational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS. Freed upon appeal: the previously reported complex [Et$_4$N][U(NCS)$_5$(bipy)$_2$] has been reinvestigated and found to contain innocent bipy ligands and uranium in its +4 oxidation state.
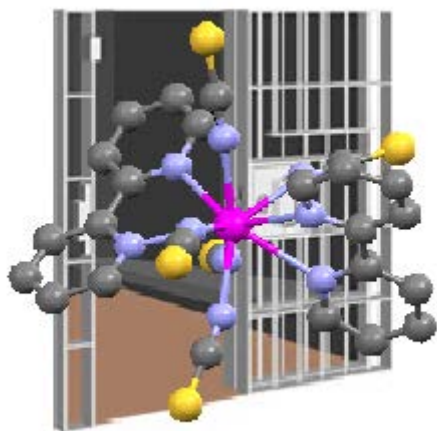
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