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Density Functional Theory (DFT) Calculations of VI/V Reduction Potentials of Uranyl Coordination Complexes in Non-aqueous Solutions

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Abstract

Of particular interests within the +6 uranium complexes is the linear uranyl(VI) cation and it forms numerous coordination complexes in solution and exhibits incongruent redox behavior depending on coordinating ligands. In this study, to determine the reduction potentials of uranyl complexes in non-aqueous solution, a hybrid density functional theory (DFT) approach was used in which two different DFT functionals such as B3LYP and M06 were applied. The bulk solvent effects were invoked through the conductor-like polarizable continuum model. The solute cavities were described with the united-atom Kohn-Sham (UAKS) cavity definition. Inside the cavity the dielectric constant matches the value of vacuum and outside the cavity the dielectric constant value is the same as that of the solvent of interest, for example, dimethylsulfoxide(DMSO), dimethylformamide(DMF), dichloromethane(DCM), acetonitrile and pyridine. With the help of the Nernst equation the calculated reduction potentials with respect to the Ferrocene (Fc) reference electrode are converted into reduction free energies (RFEs). Uranyl complexes of organic ligands which range from mono- to hexa-dentate coordination modes were investigated in non-aqueous solutions of DMSO, DMF, DCM, acetonitrile and pyridine solution. The effect of spin-orbit correction and reference electrode on the RFEs and various methods such as direct method and isodesmic reaction model were explored. Overall, our computational determination of RFEs of uranyl complexes in various non-aqueous solutions demonstrates that the RFEs can be obtained within ~0.2 eV of experimental values.

Keywords:

Reduction potential; density functional theory (DFT); reduction free energies (RFEs); non-aqueous solutions; Isodesmic method; Conductor-like Polarizable Continuum Model (CPCM); solvation effect; explicit solvation; electronic effect; uranyl cation; nuclear waste management.

1. Introduction

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Actinides are radioactive hazardous materials among which uranium and plutonium oxides are used in nuclear reactors as mixed oxide fuels for electricity generation. Though nuclear reactors used for power generation, the radioactive wastes produced are very problematic and challenging to be disposed of, since the half-life periods of those wastes are huge; thus, these materials will stay for thousands of years and may have long term effects to the environment. Proper understanding of actinide solution chemistry at a molecular level detail would provide effective strategies for remediation planning. One of the most important actinide species are the actinyl ions which are experimentally characterized as linear cations and have been found to form a range of coordination complexes with inorganic and organic ligands in aqueous and non-aqueous solutions.^{1–4} Depending on the number of coordination sites of the ligands, these actinyl ions can able to form coordination numbers up to six at their equatorial plane. As far as the stability of these linear actinyl cations is concerned $[O=An=O]^{2+}$, where $An=U$ and Pu are more stable. In contrast, the Np analogue shows significantly low stability in its +6 oxidation state; yet, several complexes have been reported to be stable. The reduced actinyl cations are unstable and rapidly undergo disproportionation reaction in aqueous solution, except the reduced neptunyl cation.

Handling actinides in experimental laboratory requires more sophisticated instruments and dedicated facilities which are quite expensive and demanding. The advantage of studying actinides using computational techniques is safe and provides more precise understanding before tackling tedious experimental tasks and even can able to guide experimentalists. In recent years, computational approaches have been employed as important tools to predict several essential properties of actinides relevant to nuclear waste management and safe disposal such as electronic structure and bonding⁵, hydration^{6–8}, speciation^{9–12}, redox chemistry^{13–20}, spectral properties^{21–24}, reaction mechanisms^{25–33} and electron transfer reactions.^{34–41}

Penta-valent uranyl(V) ions are unstable and readily disproportionate to form U(IV) and uranyl(VI) complexes in aqueous solution. Disproportionation reaction of actinyl(V) ions in aqueous solution was computationally studied by Steele *et al.*²⁷ Neptunyl(V) ion is stable in contrast to its neighbouring penta-valent equivalents, such as uranyl(V) on the left and plutonyl(V) on the right, in aqueous solution. However, in highly concentrated alkaline carbonate solution (pH ~11.95) the uranyl(V) tris-carbonate ion could be stabilised and the structural parameters were determined using Extended X-ray Absorption Fine Structure (EXAFS) methods.⁴² Also very recently, a penta-valent $[UO_2Cl_4]^{3-}$ ion has been reported to be stabilised in a room temperature ionic liquid solution (a mixture of 1-ethyl-3-methylimidazolium tetrafluoroborate and its chloride ($EMI^+BF_4^-/Cl^+$)).⁴³

When the stabilisation of uranyl(V) ion is taken into account, there are certain particular experimental conditions⁴⁴ that have to be considered; one of the most important conditions is the exclusion of protons from the solution, *i.e.* non-aqueous solution must be employed. The reason is that the presence of protons typically leads to disproportionation reaction. The next important condition is to provide specific protection for the uranyl(V) in its equatorial plane with sterically bulky organic multi-dentate ligands. By providing steric bulkiness around the uranyl ion, the formation of cation-cation interaction is prevented. Such interactions and successive protonations have been found by Steele *et al.*²⁷ to be responsible for an inner-sphere electron transfer followed by disproportionation in the proposed mechanism and

computational studies by Sundararajan *et al.*^{28,29} further confirm the importance of cation-cation interaction. View Article Online
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In non-aqueous solutions, uranyl(V) ions have been successfully stabilised and X-ray crystal structures have also been reported. The uranyl(V) complex, $[\text{UO}_2(\text{OPPh}_3)_4](\text{OTf})$ (OPPh_3 =triphenyl phosphine oxide; OTf =triflate or trifluoromethanesulfonate) has been one of the first crystallographically characterised complexes.⁴⁵ In addition, the uranyl(V) complexes such as $[\text{UO}_2(\text{Ar}_2\text{nacnac})(\text{py})_2]$, $[\text{UO}_2(\text{Ar}_2\text{nacnac})(\text{bipy})]$, $[\text{UO}_2(\text{Ar}_2\text{nacnac})(\text{phen})]$, $[\text{UO}_2(\text{Ar}_2\text{nacnac})(\text{TMEDA})]$ and $[\text{UO}_2(\text{Ar}_2\text{nacnac})(\text{MeIm})_2]$ complexes (where $\text{Ar}_2\text{nacnac} = [(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2]\text{CH}$; py = pyridine; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; TMEDA = tetra methyl ethylene di amine and MeIm = 1-methylimidazole) have been X-ray crystallographically characterised. However, the interesting similarity among these stable uranyl(V) complexes is that these complexes have sterically bulky multi-dentate organic ligands coordinated to the uranyl(V) ion in the equatorial plane which can prevent the formation of the potential cation-cation interaction⁴⁶ between two uranyl(V) cations. Indeed, this cation-cation interaction followed by successive protonations on the 'yl' O-atoms leads to disproportionation reaction and forms stable uranyl(VI) and U(IV) species.^{27–29,31}

In contrast to the reported uranyl(V) complexes stabilised by the presence of multi-dentate bulky organic ligands, in pyridine solution uranyl(V) ion has been reported to be stable under anaerobic conditions and X-ray structure is available.⁴⁷ In addition, the uranyl(VI) to (V) reduction potential has been reported.⁴⁸ Furthermore, penta-valent $[\text{UO}_2\text{X}]$ ($\text{X} = \text{I}^-$ and SO_3CF_3^-) complexes in non-aqueous solutions have been characterised by XRD technique.⁴⁹ The contradictions between steric and non-steric behaviour of ligands towards the stabilization of the uranyl(V) is not well understood at the molecular level.

Although the cation-cation interaction has been found to be responsible for the inner-sphere electron transfer reaction, several uranyl(V) cation-cation complexes have been reported to be stable and their X-ray crystal structures are available.^{50–53} However, with these cation-cation complexes, alkali metal ions, particularly K^+ and Rb^+ ions are found to be complexed to the 'yl' oxygen atoms. The alkali metal cations polarise the uranyl 'yl' oxygens and neutralise the overall negative charge of the cation-cation complexes, which provides stabilisation to these species. It is interesting to note that the smallest alkali metal cation, Li^+ ion has been found to promote the disproportionation reaction.⁵¹

Mizuoka *et al.* have been able to characterise an $[\text{U}^{\text{V}}\text{O}_2(\text{saloph})\text{DMSO}]^-$ complex in DMSO solution with the help of infra-red (IR) spectro-electrochemical technique and this study has provided a direct evidence for the weakening of the uranyl $\text{U}=\text{O}$ bonds in the $[\text{U}^{\text{V}}\text{O}_2(\text{saloph})\text{DMSO}]^-$ complex based on the smaller $\text{U}=\text{O}$ asymmetric stretching vibrational frequency compared to the corresponding uranyl(VI) complex. The asymmetric vibrational stretching frequency of the uranyl $\text{U}=\text{O}$ bonds was reported to decrease by 125 cm^{-1} for the $[\text{U}^{\text{V}}\text{O}_2(\text{saloph})\text{DMSO}]^-$ complex compared to the uranyl(VI) equivalent.⁵⁴ In addition, uranyl(V) complexes such as $[\text{U}^{\text{V}}\text{O}_2(\text{salophen})\text{DMSO}]^-$, $[\text{U}^{\text{V}}\text{O}_2(\text{dbm})_2\text{DMSO}]^-$, and $[\text{U}^{\text{V}}\text{O}_2(\text{saldien})]^-$ in DMSO solution have been characterised using the EXAFS method.⁵⁵

The uranyl(VI/V) reduction potentials of Schiff-base macro cyclic ligands were predicted in dichloromethane (DCM) solution at the COSMO//PBE/AE-TZP level of theory by Shamov *et al.*⁵⁶ Here in this study, we have reinvestigated these complexes and compared our predicted reduction potentials with the results of Shamov *et al.*⁵⁶ More elaborate discussions will be presented later. Berard *et al.*⁵⁷ have studied the reduction potentials of actinyl(VI/V)

complexes of a poly pyrrolic macro cyclic ligand in tetrahydrofuran (THF) solution at the ZORA/PBE/TZP/COSMO level. However, there are no actinyl(VI/V) experimental reduction potentials available for the neptunyl and plutonyl complexes of the poly pyrrolic macro cyclic ligand. The usage of small-core effective core potentials (SC-ECP) for the actinide atoms has been reported to reproduce experimental reduction potentials of actinyl aqua complexes in aqueous solution within ~ 0.40 eV of experimental reduction potentials.^{14,58}

In this study, we predict the reduction free energies (RFEs) of a number of uranyl complexes in different non-aqueous solvents such as DMSO, DMF, DCM, acetonitrile, and pyridine and the results are compared with the experimental RFEs. For this purpose, density functional theory (DFT) approach is employed. The results indicate the RFEs of uranyl complexes in non-aqueous solvents can be predicted within ~ 0.2 eV of experiment.

2. Experimental uranyl(VI/V) RFEs

By applying the Nernst equation ($\Delta G = -nFE$) the experimental reduction potentials reported with respect to reference electrodes are converted into reduction free energies (RFEs). In this study, The RFEs of $[\text{UO}_2(\text{L}_n)]^{m+/(m-1)+}$, where L represents coordinating ligands, this 'n' of L varies, for example, if L is a mono-dentate ligand, then 'n' becomes 5; if L is a bi-dentate ligand, then 'n' becomes 2 and the fifth-vacant coordination site is occupied by a mono-dentate solvent ligand. For instance, if the experiment is conducted in non-aqueous solvents such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetonitrile and pyridine, then one of the molecules of these solvents satisfies the fifth-vacant site. In addition, three bi-dentate ligands can satisfy the the equatorial coordination of uranyl ion and such complexes are well known for nitrate and carbonate type ligands. The experimental reduction potentials for the investigated uranyl complexes in DMSO solution were taken from the references^{44,54,59–66} and for the DMF solution from the references.^{54,62,65–68} The experimental reduction potentials for the uranyl complexes explored in DCM solution were from Hayton *et al.*^{69–72}, Sessler *et al.*⁷³ and from D.S.Royal's PhD thesis.⁶⁵ While the experimental reduction potentials for the uranyl complexes investigated in acetonitrile solution were obtained from the references^{60,74,75,69} and for the uranyl complexes investigated in pyridine solutions from the references.^{51,65}

2.1. Model Uranyl complexes investigated

Structural features of uranyl complexes are discussed in this section. Depending on the denticity of the ligand, various coordination modes are possible which is elaborated subsequently. Ligand structures of the investigated model uranyl complexes are presented in this section. The ligands are presented in an order based on the denticity of the ligands starting with mono- and progressing to penta-dentate and finally hexa-dentate ligands and corresponding abbreviations of the ligands are provided in Supporting Information (SI) Table S2.

The chemical structures of the investigated mono- to hexa-dentate ligands are provided in Figures S1 to S4 (see SI). The mono-dentate ligands such as DMSO, DMF and pyridine can able to bind up to five ligands within the equatorial plane of an uranyl ion similar to the actinyl aqua complexes; however, for the uranyl(VI) aqua complex experiments have shown that there exists an equilibrium between penta- and tetra-aqua uranyl complexes and the penta-aqua complex is the most abundant and stable.^{76–78} For the uranyl(V) aqua complex, computational studies have predicted both tetra-⁷⁹ and penta-isomers.¹⁸ It is worth mentioning here that we have also investigated hexa-isomer similar to the previous study on actinyl (uranyl and plutonyl) aqua complexes.⁷⁸ We were able to identify a stable hexa-isomer for the

solvate complexes in both the oxidised and reduced states. However, the predominant species are penta-solvate complexes and crystal data have been reported; thus, we do not disclose any results for hexa-solvate complexes for further discussion.

In contrast to the β -diketonate ligands, bi-dentate ligands such as L1-L5 do not provide enough room, due to steric hindrance, for the fifth coordination site to be filled by a mono-dentate solvate ligand. The bi-dentate ligands (L1, L2, L3, L4 and L5) of the uranyl complexes investigated in DCM solution are shown in Figure S2. The bi-dentate L1 ligand and the β -diketonate ligands such as 'acac', 'dbm' and 'hfacac' (see Figure S2 for structures) form mixed ligand uranyl complexes designated as 'L1+acac', 'L1+dbm' and 'L1+hfacac'. The presence of the isopropyl groups of L1 prevents the fifth coordination site being occupied. However, to minimise the computational cost, the isopropyl groups were replaced by methyl ($-\text{CH}_3$) groups in our calculations and this is expected not to affect the computed RFE results. Uranyl ion binds with two molecules of L2, L3 and L5 ligands and the steric hindrance of bulky-organic group prevents the interaction of mono-dentate ligand and the fifth coordination site is not fulfilled. For the L3 and L5 ligands, to minimize the computational cost, the t-Bu groups were replaced by methyl ($-\text{CH}_3$) groups in the model complex. The bi-dentate L4 ligand and two of the mono-dentate Ph_2MePO ligands coordinate uranyl ion and this ligand combination is collectively termed as the 'L4+M'. The bi-dentate ligand DPPMO_2 and the ligand L4 (see Figure S2 for structures) coordinate with uranyl ion and this ligand combination is termed as 'L4+DP'. Furthermore, the t-Bu groups in L4 were replaced by methyl ($-\text{CH}_3$) groups.

The 'sap' ligand is the only tri-dentate ligand studied in our investigation; remaining two coordination sites of uranyl ion in uranyl-sap complex is satisfied by two DMSO ligands from bulk solvent. For the uranyl complex of CMPO ligand (for the name, see SI table S2), two bi-dentate nitrate ligands occupy the equatorial plane, totally there are three bi-dentate ligands present in the uranyl-CMPO complex. This structure has been confirmed by X-ray crystallography.⁸⁰ Whereas, for the 'uranyl-sldh' complex, the experiment showed that there was an acetate ligand present in the equatorial plane of the uranyl ion with the 'sldh' ligand and the final fifth site is filled by a solvate DMSO ligand.⁶⁴

Although there are five coordination sites available for the 'ac-o-ac' ligand (see SI, Fig. S3), the ether type O-atom does not coordinate with the uranyl ion in the equatorial plane and the fifth-coordination site is completed by a DMSO ligand.⁵⁹ For the uranyl complex of the 'salacen' ligand (see SI, Fig. S3 for structure), the imino groups do not participate in coordination to the uranyl ion. The uranyl cation in this complex has two mono-dentate carboxyl groups and two hydroxyl groups. The hydrogen atoms present on the hydroxyl groups form hydrogen bonds with the imino nitrogen atoms. In the uranyl complex of the 'appn' ligand (see SI, Fig. S3 for structure), the nitrogens do not participate in coordination with the uranyl ion; however, H-atoms present on these nitrogens form hydrogen bonding interactions with the carbonyl group oxygens. In both of the uranyl 'salacen' and 'appn' complexes, the fifth coordination site is fulfilled by a DMSO ligand. In the uranyl complexes of the tetra-dentate 'saolph1-5' ligands, the vacant fifth coordination site of the uranyl ion is filled by a mono-dentate water molecule. In addition to these uranyl complexes, a uranyl complex of the tetra-dentate ligand 'tsmc' (see SI, Fig.S3 for structure) investigated in acetonitrile solution contains a nonyl alcohol (1-Nonanol) to satisfy the fifth coordination site of the uranyl ion. To minimise the computational cost, the t-Bu groups present in the 'salan' and 'saloph-tbu' ligands were replaced by methyl groups ($-\text{CH}_3$).

The penta-dentate ligands (see SI, Fig. S4 for structures) completely occupy the equatorial plane of the coordination sphere of the uranyl ion, hence there is no vacant coordination site left open for the coordination of mono-dentate solvent ligands. For the uranyl complexes of the penta-dentate ligand 'saldien-(NEt₂)₂', the ethyl groups present on the N-atoms were replaced by H-atoms to minimise the computational cost.

For the hexa-dentate ligands (AP1, AP2 and AP3) of the uranyl complexes investigated in DCM solution see SI, Fig. S5. The [UO₂]^{2+/+} ions fit inside the cavity of the hexa-dentate ligands (AP1-3); hence, there is no possibility for solvent molecules to enter into the coordination sphere of uranyl ions at the equatorial plane and participate in bonding interactions.

3. Results and Discussions

We present our results, firstly the structural isomerism of certain uranyl complexes, secondly determination Fc/Fc⁺ redox couple, followed by MD results of uranyl(VI) ion in DMSO solution for the explicit cluster model. Then, the predicted RFEs of the uranyl model complexes are discussed; starting from the direct method of RFE prediction and followed by the isodesmic model reactions and its advantages over the direct method are given. Finally, the computed RFEs are analyzed and different contributions to the determined RFEs, for instance, electronic and solvation effects are quantified.

3.1. Structural Isomerism in the investigated model uranyl complexes

To understand the effect of structural isomerism on the relative energies of uranyl complexes, in particular, uranyl complexes with unsymmetrical beta-diketonate ligands, different ligand orientations are considered. The lowest energy structure is further used for the RFE determination. The possible isomeric structures are shown in Fig. 1. For example, if R1=R2, then there is no isomerism; if R1 and R2 are different substituents, then there are three different ways to represent the complex. If we consider both the substituents R1 and R2 on different ligands but adjacent to L (L=DMSO or DMF), it is the *trans* isomer. However, if R1 on different ligands are adjacent to L or R2 on different ligands are adjacent to L, then *cis-a* and *cis-b* isomers result, respectively. It is interesting to note that the *trans* isomers are found to be energetically slightly higher than one of the *cis* isomers. The calculated relative energies of the isomers of the bis β-diketonate uranyl(VI) complexes are collated in Table 1. In these unsymmetrical β-diketonate uranyl complexes, the substituent groups with the most electronegative F-atoms favour *cis-b* isomer (see Table 1) as they are able to form strong hydrogen bonding interactions with the mono-dentate ligand, for example, DMSO or DMF. Experimentally, the [UO₂(tffacac)₂(H₂O)] complex has been characterised as a *cis* isomer with the CF₃ groups of the 'tffacac' ligands exist on the same side as the mono-dentate water ligand. However, this picture is somewhat complicated as a crown ether molecule is present in the crystal structure which bridges two [UO₂(tffacac)₂(H₂O)] units.⁸¹ Gagliardi *et al.*⁸² have studied the structural isomerism of a plutonyl(VI) complex of 'tffacac' ligand. However, there was no mono-dentate ligand coordinated to the plutonyl ion in the [PuO₂(tfacac)₂] complex. Although there was no mono-dentate ligand present in the plutonyl complex, *cis* and *trans* isomers are possible. The calculated results show that the *cis*-isomer is more stable than the *trans* isomer⁸² and this result is in agreement with our findings here for one of the *cis* isomers.

3.2. Electrode potentials of Fc/Fc⁺ couple

Although we typically use the calculated Fc/Fc⁺ electrode potential as a reference for determining the reduction potentials of uranyl complexes in non-aqueous solution, there is an empirical way to predict the Fc/Fc⁺ potential from the calculated absolute redox potentials of uranyl complexes, which were estimated at the B3LYP/B2(CPCM)//B3LYP/B1 level of theory.

$$E_{\text{abs}}^0 = -\Delta G_{\text{red(s)}}^{\text{VI/V}} \quad (1)$$

$$E_{\text{abs}}^0 = E_{\text{expt}}^0 + E_{\text{Ref}}^0 \quad (2)$$

The absolute redox potentials are calculated according to the above equation (9) for each of the non-aqueous solutions. Plotting the computationally estimated absolute (E_{abs}^0) potential values with respect to the experimental (E_{expt}^0) values of the uranyl complexes gives a straight line (eqn.2) with an intercept value in the y-axis, which is an approximate estimate of the absolute potential of the reference electrode (E_{Ref}^0) (see Fig. S6).

We now consider the computationally predicted absolute potentials (E_{abs}^0) of the uranyl complexes investigated in DMSO solution, which are plotted against the respective E_{Expt}^0 values (Fig.S6). Similarly, the absolute values of the Fc/Fc⁺ reference electrode potentials in non-aqueous solutions such as DMF, DCM, acetonitrile and pyridine solutions are also determined, and are presented in Table 2 along with the variance with respect to the calculated Fc/Fc⁺ potential.

Our estimated absolute potential value of 5.202 eV, for the Fc/Fc⁺ in DMSO solution is in good agreement with the reported bench-mark value of 5.043 eV.⁸³ For the Fc/Fc⁺ potentials determined in DMSO, DMF and DCM solutions, the empirically estimated Fc/Fc⁺ absolute potential values are ~ 0.79-0.94 eV higher than the calculated Fc/Fc⁺ reference potentials. In contrast, the empirically determined Fc/Fc⁺ potential in acetonitrile solution (5.239 eV) is in good agreement with experimentally determined Fc/Fc⁺ absolute potential of 4.980 eV.^{83,84} Although the estimated Fc/Fc⁺ potential value is in good agreement with the experimental value, there is still a discrepancy of ~0.715 eV between the experimental and calculated potential of uranyl complexes in acetonitrile solution. Also, an outlier complex, [UO₂-ncp] was removed from the straight line fitting since the inclusion was found to decrease the correlation (R^2) value from 0.66 to 0.56 for the uranyl complexes investigated in acetonitrile solution.

Despite the high correlation value ($R^2=0.90$), the estimated Fc/Fc⁺ potential value for the pyridine solution is 1.31 eV higher than the calculated Fc/Fc⁺ potential. This difference is significantly higher than the Fc/Fc⁺ reference potentials in other investigated non-aqueous solutions.

For the species investigated in DCM solution, whilst plotting the E_{abs}^0 vs. E_{Expt}^0 , a few uranyl complexes such as the [UO₂-AP1], [UO₂(L3)₂], [UO₂-salddt], [UO₂-sal-ph-dien] and [UO₂-saldien-N(Et₂)₂] are not included in the plot, since the inclusion of these complexes significantly decreases the correlation value (R^2) from 0.69 to 0.23. The [UO₂-AP1] complex is not included in the plot, because this complex exhibits a ligand-based reduction process. Although the [UO₂(L3)₂], [UO₂-salddt], [UO₂-sal-ph-dien] and [UO₂-saldien-N(Et₂)₂] complexes have exhibited metal-based reduction processes, the reason for them to be so far from the fitted straight line is unclear; however, this may be due to differences in the concentrations of the uranyl complexes used in experimental solutions. The concentrations of

uranyl ions present in the experimental solutions are 1 mM for [UO₂-AP1], 3 mM for [UO₂(L3)₂] and 5 mM for [UO₂-salddt], [UO₂-sal-ph-dien] and [UO₂-saldien-N(Et₂)₂] complexes in DCM solution.⁶⁵ Also, we could argue that using different electrolytes for the redox potential determination may have a significant impact on the determined reduction potentials,⁸⁵ which essentially reflects in the obtained correlation between the experimental and our theoretical results.

Overall, the empirical estimation of Fc/Fc⁺ absolute potentials has resulted in significantly higher values (~0.72-1.31 eV) than the calculated Fc/Fc⁺ absolute potentials. Interestingly, the Fc/Fc⁺ absolute potential in acetonitrile and DMSO (COSMO-RS predicted value) solution are reproduced within a reasonably acceptable accuracy of the experimental⁸⁴ and previously reported bench-mark values⁸³, respectively.

It should be noted that the previously reported computational result obtained by the accurate compound G3 method overestimated the ionization potential (IP) of Ferrocene (Fc) by ~0.20 eV.⁸³ The experimentally recommended Fc/Fc⁺ ionization potential is 6.81 eV⁸⁶ and this is in agreement with another experimental study reported later and the value is 6.82 eV.⁸⁷ When we have checked our computed Fc/Fc⁺ IP (includes ZPE and free energy corrections) at the B3LYP/B2//B3LYP/B1 level (gas-phase) with the aforementioned value, our calculation underestimates the experimental IP value by 0.60 eV and this may be the primary reason for the underestimation of Fc/Fc⁺ redox couple. On the other hand, the B3LYP/B1 level of theory predicted IP of Fc is ~0.82 eV less than the actual experimental value. In our studies, we have decided to mend our calculated RFEs by adding 0.60 eV as the Fc/Fc⁺ reference electrode correction.

3.3. Explicit DMSO cluster model: MD results

To effectively mimic the local effects, for instance, hydrogen bonding interactions, explicit solvent molecules are placed around the solute. This has been shown to predict the reduction potentials of actinyl aqua complexes⁸⁸ accurately. However, to identify the local solvation structure around the solute molecule, a systematic QM approach may be prohibited due to expensive computations. To overcome this, classical molecular dynamics simulations approach has been employed to obtain an average solvent molecular structure around the solute molecule; here the solute is uranyl cation. Classical molecular dynamics simulations of a uranyl ion in DMSO solution has reproduced the experimentally determined equatorial coordination number as five. The simulation study has also produced local solvation environment of uranyl-DMSO complex. The obtained radial distribution curve (RDF) $g(r)$ as a function of the U-O_{DMSO} distances and the integral of $g(r)$ are shown in Fig.2. A sharp peak at 2.45 Å is in good agreement with DFT (2.42 Å) and experimentally determined U-O_{DMSO} distances (2.38 Å).⁸⁹ The peak at 2.45 Å corresponds to the directly coordinated five DMSO molecules in the equatorial plane of the uranyl ion. A uranyl-DMSO cluster model was extracted from a snap shot (see Fig.3) and used for the optimization at the B3LYP/B1 level. There are totally twelve DMSO molecules present in the explicit cluster model among which five of them directly bound with the uranyl ion at its equatorial plane. An image of snap shot of classical molecular dynamics simulation and the B3LYP/B1 optimized explicit uranyl-DMSO cluster model structures are shown in Fig.3. The explicit DMSO molecules are given in tube format and the uranyl ion bound DMSO molecules are shown in ball-stick format. This explicit cluster model is also used for the RFE determination of uranyl-DMSO complex and the results are compared with each other.

3.4. RFEs of uranyl complexes: Direct method (vs calculated Fc/Fc^+)

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The DFT determined uranyl(VI/V) RFEs of the uranyl complexes in various non-aqueous solutions using the direct method, in which the calculated Fc/Fc^+ is used as a reference, are plotted against the relevant experimental RFEs (see Fig. 4). There are certain outlier uranyl complexes within the graphical plot. Among the outliers, two of them belong to the complexes investigated in DMSO solution and the other two belong to the group of complexes investigated in DCM solution. Interestingly, the two different groups of outliers show contrasting behaviours. For instance the predicted RFEs of the two outlying complexes investigated in DMSO solution are found to be underestimated by ~ 0.5 eV of experimental RFEs; whereas, the other two outlying complexes investigated in DCM solution are found to be ~ 0.5 eV overestimated. Figures S7 and S8 show a straight line fits for the experimental versus predicted RFEs of uranyl complexes examined in various non-aqueous solutions and the correlation of the straight line is 0.72 and the removal of the outliers from the straight fit increases the correlation from 0.72 to 0.83 (see Fig. S8).

Now we turn to discuss the outlier complexes and the anticipated reasons for the deviations from the straight line fit. The 'uranyl-tsmc' complex has a mono-dentate 'Nonyl-OH' coordinated to the uranyl ion. During the experimental determination of reduction potential in DMSO solution the complex could possibly undergo ligand exchange reaction with the solvent DMSO molecules present in the bulk experimental solution.⁶⁰ To probe the effect of ligand exchange on the predicted RFE, we investigated the RFE of the 'uranyl-tsmc' complex with a DMSO molecule for the fifth coordination of the uranyl ion. The removal of the mono-dentate alcoholic ligand by the DMSO molecule improves the predicted RFE ~ 0.15 eV closer towards the experimental value.

For the 'uranyl-sldh' complex, the experimental study suggests that during the reduction potential determination, the species present in the solution may comprise of an acetate ion in the equatorial plane of the uranyl ion.⁶⁴ However, our calculations of model structures and the predicted RFE of the model 'uranyl-sldh' complex confirms that the specified species would be more likely to be different than the experimentally proposed one.

The reduction potential of the 'uranyl-saldien- $\text{N}(\text{Et})_2$ ' complex was more likely to be determined either in a completely different condition than the other complexes.⁶⁵ There are other arguments, such as electrolyte solutions, concentration of the uranyl ion present in the experimental solution, ionic strength, counter ions which could be put for the deviation of the 'uranyl-saldien- $\text{N}(\text{Et})_2$ ' from the other uranyl complexes.

For the 'uranyl-AP1' complex, one-electron reduction leads to a singly reduced $[\text{uranyl-AP1}]^-$ complex which has an unpaired electron density smeared over the conjugated double bonds of the periphery of the hexa-dentate ligand rather than on the uranyl ion. In lieu of the metal (uranyl) reduction, the ligand reduction takes place which is the primary reason for this 'uranyl-AP1' complex to deviate from the straight line fit of the predicted RFEs against the experimental RFEs. The lower unoccupied molecular orbital (LUMO) and higher occupied molecular orbital (HOMO) of the singly reduced $[\text{UO}_2\text{-AP1}]^-$ complex are shown in Fig. 12. Energies of these orbitals clearly demonstrate that the delocalized ligand based orbital is energetically a low-lying orbital than the metal-based localized f-orbital. The participation of ligand in redox process is termed as the non-innocence (redox-active) behavior.⁹⁰ Such ligand non-innocence behaviors have been reported for the $[\text{UO}_2\text{-cyclo}[6]\text{pyrrole}]$ and $[\text{UO}_2(\text{gha})\text{DMSO}]$ (gha = glyoxal bis(2-hydroxanil)ate) complexes.^{91,92} The predicted ligand reduction of the $[\text{UO}_2\text{-AP1}]$ complex in our calculation is also in agreement with the previous

computational studies of similar uranyl complexes of highly π -conjugated hexa-dentate ligands.^{56,91} It is clearly seen that the highly conjugated π -system has an orbital (HOMO) of lower energy than the metal f-orbital (LUMO).

The RFEs of the uranyl complexes of the hexa-dentate alaskapyrine ligands, AP1-3 are discussed here in more detail. Shamov *et al.* have already computationally estimated the reduction potentials of the 'uranyl-AP1-3' complexes in DCM solution; here our predicted values of the reduction potentials are compared with the Shamov *et al.*'s predictions.⁵⁶ They have predicted the reduction potentials of the [UO₂-(AP1-3)] complexes at the COSMO//PBE/AE-TZP level of theory in DCM solvent using the Fc/Fc⁺ reference potential calculated at the same level as was used for the uranyl complexes. The predicted reduction potentials were directly compared with the experimental reduction potentials reported by Sessler *et al.*⁷³ However, the reported experimental reduction potentials of these three uranyl [UO₂-(AP1-3)] complexes in DCM solution were recorded with respect to the Ag/Ag⁺ reference electrode. Although the Fc/Fc⁺ redox couple was determined with respect to the Ag/Ag⁺ reference electrode as 0.68 eV whilst reporting the reduction potentials of the uranyl [UO₂-(AP1-3)] complexes with respect to the Fc/Fc⁺ reference electrode, the authors did not include the 0.68 eV so as to determine the reduction potentials against the Ag/Ag⁺ reference electrode. Shamov *et al.* have compared their predicted reduction potentials of the [UO₂-(AP1-3)] complexes with the reduction potentials reported with respect to the Ag/Ag⁺ reference electrode. Herein, to get the uranyl(VI/V) reduction potential with respect to the Fc/Fc⁺ couple, we have added the 0.68 eV to the potential reported with respect to the Ag/Ag⁺ couple. We have also reinvestigated the reduction potentials of these three complexes in DCM solution at the B3LYP/B2(CPCM)//B3LYP/B1 level using the Fc/Fc⁺ reference potential calculated at the same level as used for the uranyl complexes (see Table 3).

The replacement of 'Nonyl alcohol' (=Nonyl-OH) by an acetonitrile ligand in the [UO₂-tsmc-(Nonyl-OH)] complex is found to have a marginal effect (+0.05 eV) on the predicted uranyl (VI/V) RFE in acetonitrile solution. The 'uranylsaloph1-5' complexes have a mono-dentate water ligand present in the equatorial plane. However, we have tested the RFE prediction by replacing the water by an acetonitrile ligand given the experimental reduction potentials were determined in acetonitrile solution.⁷⁵ The predicted RFE of the [UO₂-saloph1-acetonitrile] complex is found to be 0.013 eV less than that of the [UO₂-saloph1-H₂O] complex, this suggests that the replacement of water by acetonitrile has no significant impact on the uranyl(VI/V) RFEs. In addition, it should be noted that in a Car-Parinello Molecular Dynamics (CPMD) study by Bühl *et al.*⁹³ confirmed that water is bound in preference to acetonitrile ligand in acetonitrile solution.

The calculated MUEs of the predicted RFEs of the uranyl model complexes using DFT approach are summarised in Table 4. The effects of spin-orbit coupling and reference electrode correction on the predicted RFEs are also calculated not only to the individual group level but also for all uranyl model complexes. In addition, the calculated MUEs are presented as graphical plots (see Fig.6 and SI Fig.S9).

The uranyl(VI/V) RFEs can be predicted within ~0.527 eV of experimental RFE values in non-aqueous solution and the inclusion of an approximate spin-orbit effect to the predicted RFEs further increases the overall MUE value by ~0.30 eV. As discussed earlier, our computational approach underestimates the gas-phase ionisation potential of Fc by ~0.6 eV and we introduced this value as a correction to the predicted RFE. The reference electrode correction leads to improve the predicted RFEs of uranyl complexes in non-aqueous solutions and the RFEs are obtained within ~0.162 eV of experimental RFEs. An improvement of

~0.37 eV is obtained for the addition of reference electrode correction. Including both the spin-orbit correction and the reference electrode correction does not make significant difference in the overall MUEs; however, which is ~0.10 eV higher than the overall MUE of the RFEs predicted with the inclusion of reference electrode correction.

Whilst examining the M06 predicted RFEs, similar to the B3LYP computed results, addition of spin-orbit interaction effect is found to increase the overall MUE by ~0.30 eV. The reference electrode correction for the M06 functional is 0.285 eV, adding this correction to the predicted RFEs decreases the MUE to give the overall MUE ~0.40 eV of experiment which is ~0.25 eV higher than the MUE obtained for the B3LYP predicted RFE results with the reference electrode correction. When both the spin-orbit and the reference electrode correction are considered together, these two corrections cancel out each other, as a consequence no change in the overall MUE (~0.60 eV) occurs. The highest deviation is predicted for the uranyl complexes investigated in pyridine solution (~1 eV) for the M06 functional; yet, reasons for this unusual increase of the predicted RFEs are unclear.

Overall, the spin-orbit interaction effect is found to have increased the deviation of predicted RFEs from the experimental RFEs. This deviation may be attributed to the fact that the approximate spin-orbit interaction correction was determined for a bare uranyl(V) cation. Furthermore, this may only apply for the uranyl complexes which have loosely bound coordinating ligands. However, in the past this has been applied, for instance, Shamov *et al.*⁵⁶ used this correction and predicted accurate reduction potentials successfully; however, some issues have been found by us with their experimental comparisons. The reference electrode correction for both the DFT functionals are found to predict the reliable RFEs close towards the experimental RFEs within ~0.16 eV for the B3LYP and 0.40 eV for the M06 functionals. Among the two DFT functionals investigated, B3LYP functional performed better than the M06 functional. Although the RFEs using M06 functional were predicted at the B3LYP optimised geometries, we believe that the B3LYP functional has reproduced good geometries for the model uranyl complexes and the optimisation at the M06 level would not likely to change the geometrical parameters significantly.

3.5. RFEs of uranyl complexes: vs empirically estimated Fc/Fc⁺

As discussed earlier in RFE predictions, there is an empirical way to predict the absolute potential value of the Fc/Fc⁺ reference electrode. Using the empirically estimated reference electrode potential in lieu of the calculated values, the RFEs of uranyl complexes can be predicted. Here, the reference electrode correction is not considered since the empirically estimated Fc/Fc⁺ couple free energies are higher than the actual calculated values (see Table 2). Although the reference electrode correction is not considered, to find out the effect of spin-orbit interaction effect on the RFEs, the spin-orbit correction of -0.31 eV is included to the predicted RFEs. It is quite interesting to note here that the inclusion of spin-orbit correction value to the RFEs is found to improve the RFEs towards experimental RFEs and this is evident from the smaller MUE values calculated for the RFEs with the spin-orbit correction (see Table 5). The predicted RFEs of uranyl complexes using empirically estimated Fc/Fc⁺ reference couple are plotted (see Fig.S10) against the experimental RFE values and a straight line fit is obtained and the correlation for the straight line fit is 0.60 which is smaller than the correlation values obtained for the previously discussed direct method (0.72 and 0.83).

Figure 7 shows graphical representations of the calculated MUEs for the RFEs of uranyl complexes. The RFEs of uranyl complexes can be predicted within ~0.40 eV using

empirically estimated Fc/Fc^+ reference couples. A closer look at the individual MUEs of the solvents are quite different among themselves. The highest MUE is obtained for pyridine (0.92 eV) and the next is DCM solvent (0.52 eV); whereas, the remaining MUEs are in the 0.20-0.30 eV range. For the B3LYP functional predicted RFEs, the addition of spin-orbit correction leads to a small decrease in the overall MUE values and is the same with the M06 functional predicted RFEs. However, examining the MUEs for the RFEs predicted using the M06 functional at the individual solvent level reveal that for the DMSO and ACN solvent the MUE errors are found to increase by 0.04 and 0.29 eV, respectively; whereas, for the other solvents the MUEs are found to decrease by ~ 0.30 eV. The reason for this contradicting behavior is quite unclear; however, the empirical nature of the Fc/Fc^+ reference electrode couple may have inaccuracies.

3.6. RFEs of uranyl complexes: Isodesmic reaction model

So far we have discussed the prediction RFEs of uranyl complexes using calculated and empirically estimated Fc/Fc^+ reference couples. In contrast, in this section, the RFEs are predicted using an isodesmic reaction scheme in which the experimentally known RFE of one of the uranyl complexes is used to serve as a reference during the course. The MUEs for the isodesmic reaction scheme predicted RFEs of uranyl complexes are collected in Table 6 and a graphical representation of the MUEs is presented in Fig. 8. The predicted RFEs for the uranyl complexes are plotted against the available experimental RFEs (see Fig. S11) and the obtained correlation for straight line fit (0.67) are close to the correlation value previously obtained for the direct method (0.72 including anomalies).

The isodesmic reference used for the prediction of RFEs of uranyl complexes in DMSO solution is the solvate $[\text{UO}_2-(\text{DMSO})_5]^{2+/+}$ complex. In addition, to understand how the presence of explicit DMSO molecules improves the isodesmic predicted RFEs, the explicit DMSO cluster model $[\text{UO}_2-(\text{DMSO})_5]^{2+/+} \cdot 7\text{DMSO}$ complex was also investigated as the isodesmic reference complex. Using the $[\text{UO}_2-(\text{DMSO})_5]^{2+/+}$ complex as the isodesmic reference complex predicted the RFEs to within ~ 0.28 eV of the experimental RFEs. However, using the explicit cluster model of the DMSO complex ($[\text{UO}_2-(\text{DMSO})_5]^{2+/+} \cdot 7\text{DMSO}$) as the isodesmic reference enabled the accurate prediction of the RFEs to within ~ 0.10 eV of the experimental RFEs. Thus, the addition of explicit DMSO molecules improves the RFEs by ~ 0.20 eV. However, for the M06 functional, the MUE of the predicted RFEs are ~ 0.15 eV higher than the B3LYP results for the complexes investigated in DMSO solution. Similar to this explicit cluster model of the uranyl-DMSO complex, using the $[\text{UO}_2-\text{saldtd}]^{0/1-}$ complex as the isodesmic reference enables accurate prediction of RFEs to within ~ 0.095 eV of the experimental values. There are also few more rigid penta-dentate ligand systems that have been considered as isodesmic reference complexes, the MUE values of the predicted RFEs of the uranyl complexes using these other reference complexes are slightly higher (the calculated RFEs are provided in SI Table S5).

The reference uranyl complex considered for the isodesmic reaction in DMF solution is the $[\text{UO}_2(\text{DMF})_5]^{2+/+}$ complex, which predicts the RFEs of the investigated uranyl complexes in DMF solution to within 0.16, 0.29 eV of the experimental RFEs for both the B3LYP and M06 DFT functional methods, respectively. Hence, no other reference system is considered for the prediction of the RFEs. On the other hand, the remaining complexes investigated in DMF solution have mono-dentate DMF co-ordinated to the uranyl ion in its equatorial plane, and this may lead to ligand exchange reactions. However, this is expected not to affect the RFEs significantly.

Choosing a good reference complex is imperative for the isodesmic reaction scheme. The uranyl complexes of the penta- and hexa-dentate ligands can be considered as good candidates for the isodesmic reference complexes in DCM solution. As discussed earlier, the experimental RFE of hexa-dentate uranyl complexes are corrected to new values so that we have not considered those complexes as isodesmic references. However, here the predicted RFEs of uranyl complexes in DCM solution employing the $[\text{UO}_2\text{-salddt}]^{0/1-}$ complex as the reference complex is presented. The RFEs of the uranyl complexes in DCM solution are predicted to within $\sim 0.15\text{-}0.17$ eV of the experimental RFEs. Overall the isodesmic reaction models can be used as an alternative method for the prediction of RFEs of uranyl complexes in DCM solution.

The reference complex used for the prediction of the RFEs of uranyl complexes in acetonitrile solution through the isodesmic reaction is the $[\text{UO}_2(\text{L4+DP})]$ complex. The reason for the selection of this complex is due to the fact that it is the only complex which does not have a mono-dentate ligand in the equatorial plane of uranyl ion. If it had a mono-dentate ligand in its equatorial plane, then it might undergo ligand exchange with the acetonitrile solvent molecules. The highest deviation (0.33 eV) from the experimental RFE is observed for the uranyl complex, $[\text{UO}_2\text{-(CMPO + 2NO}_3)]^{0/1-}$, in which the CMPO ligand was found to be mono-dentate in the reduced state. However, it should be noted that the RFEs of the remaining complexes investigated in acetonitrile are predicted to within about ~ 0.07 eV of the experimental RFEs. The predicted RFEs using the M06 functional have exhibited a similar MUE value (~ 0.13 eV). Overall using the isodesmic model, the RFEs can be predicted within $\sim 0.10\text{-}0.13$ eV of the experimental RFEs.

The reference complex used for the prediction of the RFEs in pyridine solution is the $[\text{UO}_2(\text{Py})_5]^{2+/+}$ and interestingly the $[\text{UO}_2(\text{Py})_5]^+$ has been experimentally characterised as a stable uranyl(V) complex. The use of $[\text{UO}_2(\text{Py})_5]^{2+/+}$ as an isodesmic reference predicted the RFEs to within ~ 0.43 eV of the experimental RFEs. This deviation may be due to the fact that the complexes investigated in pyridine are neutrals with the exception of the $[\text{UO}_2(\text{Py})_5]^{2+/+}$ and $[\text{UO}_2\text{-saloph-tBu}_2\text{-Py-K}]^{+/0}$ and this could lead to different electronic structures to those of the neutral complexes. Using the $[\text{UO}_2(\text{Py})_5]^{2+/+}$ complex as the isodesmic reference has been found to overestimate the RFEs by ~ 0.30 eV. On the other hand, using the other experimental RFE value (0.46 eV)⁴⁸ as the reference for the $[\text{UO}_2(\text{Py})_5]^{2+/+}$ reduction process leads to predict the RFEs of uranyl complexes to within $\sim 0.12\text{-}0.19$ eV of experimental RFEs.

To conclude this section, the RFEs of uranyl complexes can be predicted to within $\sim 0.1\text{-}0.2$ eV of experiments using the isodesmic reaction model as an alternative method. Due to the fact that the isodesmic reaction models effectively cancel out errors in the RFE prediction gives an added advantage and makes this method as an alternative choice rather than the direct method. The direct method involves the calculations of reference electrode free energies in solution and any error in the reference electrode would potentially lead to the prediction of deviated RFEs. However, care should be taken to choose proper reference complex which should typically have similar electronic structure with other complexes under investigation.

3.7. Analysis of predicted RFEs

Here in this section, the predicted RFEs of the uranyl complexes in DMSO solution are discussed in more detail by splitting the predicted RFEs into the gas-phase and solvation free energy terms. The $\Delta G^{\text{VI/V}}_{\text{red(s)}}$ is composed of the $\Delta G^{\text{VI/V}}_{\text{red(g)}}$ and $\Delta\Delta G_{\text{soln}}$ terms (see eqn. 3).

$$\Delta G_{\text{red(s)}}^{\text{VI/V}} = \Delta G_{\text{red(g)}}^{\text{VI/V}} + \Delta \Delta G_{\text{solv}} \quad (3)$$

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where the $\Delta G_{\text{red(g)}}^{\text{VI/V}}$ term represents the gas-phase RFE and the $\Delta \Delta G_{\text{solv}}$ term corresponds to the solvation free energy difference between the oxidised and reduced species.

Except for the $[\text{UO}_2-(\text{DMSO})_5]^{2+/+}$ complex, the remaining investigated uranyl complexes in DMSO are neutral complexes. The one-electron reduction process makes the neutral complexes to become anionic complexes. The transformation of neutral to negatively charged species makes the solvation free energy term negative, thus makes the overall reduction thermodynamically a favourable process. When the magnitude of the charge increases, the solvation effects are thermodynamically favourable and electronic effects are unfavourable. This is applicable for the anionic complexes. For the cationic complexes the reduction process usually decreases the overall charge and this makes the solvation effects as thermodynamically unfavourable and the electronic effects as favourable. However, there is another category of complexes that should be taken into account and these are the neutral ones. The reduction process produces the anionic complexes (charge, -1) from the neutral complexes; in this case also the solvation effects are thermodynamically favourable. In addition to the solvation effect, the electronic effects favour the one-electron reduction.

When the β -diketonate uranyl complexes are compared for the electronic and solvation effects, the electronic effects clearly show that the electron density around the uranyl ion plays a critical role. The electronic effects are shown in order from lower to higher (see Table 7) values; this order is in agreement with the nature of the substituent present on the ligand. As one descends from the first column of the Table 7, the ligands have greater electron density on them. Higher electron density around the uranyl ion makes the reduction reaction more difficult. The introduction of electron withdrawing groups lower the electron density around the uranyl ion and this lowering favours the reduction process. However, the solvation free energies are not significantly different among these β -diketonate uranyl complexes (see Fig. 9) and this is due to the fact that the solvation effect depends on the size of the cavity created as well as increase of overall charge. Here, the substituents do not significantly affect the cavity size.

The cationic uranyl complexes such as $[\text{UO}_2(\text{DMF})_5]^{2+/+}$, $[\text{UO}_2(\text{DMSO})_5]^{2+/+}$, $[\text{UO}_2(\text{Py})_5]^{2+/+}$, $[\text{UO}_2-(\text{L4}+\text{M})]^{+/0}$, $[\text{UO}_2-(\text{L4}+\text{DP})]^{1+/0}$ and $[\text{UO}_2\text{-saloph-tBu}_2\text{-Py-K}]^{+/0}$ complexes have shown a decrease of overall charge during the one-electron reduction process. As a consequence, an outcome of positive solvation free energies result which confirms that the solvation contribution to the reduction process for these complexes is thermodynamically unfavourable and the electronic effects predominate over the solvation effects (see Fig. 10).

Substitution effects have been identified for the VI/V reduction potentials of uranyl complexes of 'L1+ β -diketonate' ligands in DCM solution. The investigated β -diketonate ligands contain different substituent groups, for instance, electron donating $-\text{CH}_3$ group, electron withdrawing groups such as $-\text{Ph}$ and CF_3 groups. As consequence of electron donating/withdrawing effect of the substituents, the intrinsic uranyl(VI/V) reduction potential is altered. The experimental RFEs are found to differ by up to ~ 0.23 – 0.43 eV depending on the substituent present on the β -diketonate ligand.⁷⁰ For the 'acac' ligand, the presence of the electron donating $-\text{CH}_3$ groups increases electron density around the $[\text{UO}_2]^{2+}$ ion and this increases the RFE and makes the reduction harder. However, when the $-\text{CH}_3$ groups in the 'acac' ligand are replaced by $-\text{Ph}$ groups, which are able to withdraw as well as delocalise the incoming electron, then a decrease in the experimental RFE by 0.23 eV is observed. When the $-\text{CH}_3$ groups are replaced by the electron withdrawing $-\text{CF}_3$ groups then a decrease in the

experimental RFE, by 0.43 eV, from the 'L1+acac' uranyl complex RFE is seen⁷⁰. The electronic effects displayed in the experimental RFEs of these complexes are the same as seen for the calculated gas-phase RFEs; however, here the solvation effects are found to not significantly differ from each other.

The analysis of RFEs reveals that the electronic and solvation effects can be quantified. When the overall charge of the uranyl complex decreases (2+ to 1+, this happens for the solvate complexes such as DMSO and DMF) during the reduction, the electronic effect predominates over the solvation effect. In contrast, when the overall charge increases (neutral to 1-), the solvation effect predominates over the electronic effects. Furthermore, the presences of electron donating groups in the coordinating ligand enhance the electron density around uranyl which in turn makes the reduction harder. However, the presences of electron withdrawing groups decrease the electron density around uranyl and make the reduction favour.

4. Conclusions

In our study the RFEs of a range of uranyl complexes containing organic ligands which range from mono- to hexa-dentate coordination modes have been investigated in non-aqueous solutions such as DMSO, DMF, DCM, acetonitrile and pyridine, using two flavours of hybrid DFT functionals (B3LYP and M06) with the CPCM/UAKS solvation model, in which the solute cavities were described using the UAKS cavity definition.

MD simulations of uranyl ion in DMSO solvent have reproduced the U-O_{DMSO} bond distances similar to the experimental and DFT calculated values. In addition, the simulation study accurately predicted the equatorial U-O_{DMSO} coordination number to be 5, which is in excellent agreement with the experiment and theory. An explicit cluster model of a uranyl DMSO complex has also been investigated and the introduction of explicit DMSO molecules into the equatorial plane of the uranyl-DMSO complex is found to improve the RFE of the [UO₂(DMSO)₅]²⁺ complex by 0.28 eV towards the experimental RFE. Overall, the addition of an explicit sphere of DMSO molecules improves the predicted RFEs similar to what was observed for the actinyl aqua complexes containing explicit hydration sphere.⁸⁸

Our computational approach, denoted as the B3LYP/B2//B3LYP/B1 level of theory, underestimated the gas-phase ionisation potential of Fc by 0.60 eV, which resulted in the underestimation of uranyl(VI/V) RFEs. We corrected our predicted RFEs of the uranyl complexes with the introduction of the 0.60 eV as the reference electrode correction and we were able to predict the RFEs of uranyl complexes in non-aqueous solutions within ~0.16 eV of experimental RFEs. The hybrid B3LYP functional predicted RFEs are more accurate than the M06 functional predicted RFEs. For the direct method of RFE prediction, the addition of spin-orbit correction is found to increase the MUE by ~0.30 eV. The RFEs of the uranyl complexes investigated in pyridine solution are found to show larger MUEs for both the DFT functionals, the reason for the unusual behaviour is quite unclear.

The absolute potentials of the Fc/Fc⁺ reference electrode in non-aqueous solutions have been estimated from the plot of E⁰_{abs} vs. E⁰_{Expt}. The estimated Fc/Fc⁺ absolute potentials from these plots are significantly higher (0.40-1.30 eV) than the calculated Fc/Fc⁺ absolute potentials. However, the empirically estimated Fc/Fc⁺ potential value predicted for the Fc/Fc⁺ electrode in acetonitrile solution is in good agreement with the experimental absolute potential (4.980 eV)⁸⁴ and additionally in DMSO solution the estimated Fc/Fc⁺ absolute potential is slightly off (~ 0.20 eV) compared to the high level *ab initio* predicted Fc/Fc⁺ absolute value (5.043

eV). The empirically estimated absolute Fc/Fc^+ reference electrode free energy values can be used to predict the RFEs of uranyl complexes in non-aqueous solutions within $\sim 0.20\text{--}0.30$ eV of experimental RFE values. It should be noted that the RFEs predicted using the estimated Fc/Fc^+ couple do not include any reference electrode correction values but it requires the approximate spin-orbit correction to be added. For the M06 functional predicted RFEs, the addition of spin-orbit correction was found to slightly increase the MUEs in particular for the DMSO and acetonitrile solvents; however, the overall MUE (including the remaining complexes investigated in DMF, DCM and pyridine) was found to decrease for the addition of approximate spin-orbit correction to the predicted RFEs.

Using the isodesmic reaction method, we have reproduced the RFEs of the uranyl complexes in non-aqueous solution to within ~ 0.12 eV of the experimental RFEs. The determination of the absolute values of the reference Fc/Fc^+ electrode in non-aqueous solution gives errors due to the underestimation of ionic potential of Fc^+ . The isodesmic reaction models do not require the absolute value of the reference electrode for the RFE prediction, which is an added advantage over the direct method. The direct method requires not only the reference electrode correction, the spin-orbit correction as well for the penta-valent uranyl(V) complexes; whereas, in the isodesmic model, the spin-orbit effect cancels out. Another interesting aspect is the cancellation of errors which leads to the prediction of RFEs within ~ 0.10 eV experimental RFEs. Despite the proven accuracy of the isodesmic reaction model, choosing a suitable reference complex for the RFE prediction is crucial. In general, the smaller MUEs obtained for the isodesmic reaction predicted RFEs than the direct method confirms that the isodesmic reaction method is likely to serve as an alternative method for the prediction of actinide redox potentials in solution.

The deviations of the predicted RFEs from the experimental RFEs can be attributed to several factors. The experimental electrolyte solution may contain different species in solution which could be completely different from the gas-phase model; counter ions present in the experimental solution may also have an impact, though in solution the counter ions are dispersed, solvated and perhaps be relevant to neutralize the overall charge in the case where the complexes are not neutral.

In DCM solution, for the $[\text{UO}_2\text{-AP1}]$ complex, ligand reduction has been observed. Here, the presence of π -conjugation in AP1 ligand gives rise to an orbital of lower energy than the f -orbital on the U-atom, which leads to favour ligand reduction. In contrast, for the uranyl complexes of the AP2 and AP3 hexa-dentate ligands, metal (U) reduction have been confirmed and this is due to the disruption of π -conjugation of the ligands by the presence of aliphatic moieties which prevent extensive conjugation in the AP2 and AP3 coordinating ligands. A partial metal reduction for the $[\text{UO}_2\text{-salbipy-DMF}]$ complex in the gas-phase is predicted, but the inclusion of solvation effects via the CPCM solvation model has transformed the partial-metal reduction into a complete metal reduction. Although the solvation effects are included using a single point energy calculations, their effect is very significant.

The replacement of mono-dentate H_2O ligand present in the equatorial plane of the $[\text{UO}_2\text{-(saloph1-5)-H}_2\text{O}]$ complexes by the acetonitrile ligand has a marginal effect of ~ 0.013 eV on the predicted RFEs. Hence, the mono-dentate ligand exchange reactions are confirmed to have no significant impact on the computed RFEs.

The neutral uranyl complexes investigated here can easily be reduced to their anionic states, this is evident from the predicted electronic and solvation effects which are both found to thermodynamically favour the reduction process in non-aqueous solutions. For the cationic complexes, the electronic effects are the predominating effects over the solvation effects; the negative free energy predicted for the electronic effects make overall the reduction process as thermodynamically favourable in non-aqueous solutions.

In summary, reduction potentials of uranyl complexes in non-aqueous solutions can be predicted within ~0.1-0.2 eV of experimental values. Although, isodesmic method takes an edge over the direct method, choosing a reference complex and the reduction potential of that complex should have been determined at the same experimental conditions to the others of interest. Electronic structure, furthermore, should be the same as that of the complexes of interest with respect to the reference complex. If we fail to take the above mentioned points into account may introduce systematic errors to the computed results and the agreements with experimental results are envisaged to be poor. Thus, care should be taken to select a reference isodesmic complex. Considering the direct method, determination of absolute potential of reference electrode is imperative, otherwise, deviations from experiments are expected. Our research will serve as a database for the uranyl reduction potentials determined in non-aqueous solutions. Moreover, this is beneficial for those who tries to stabilize the unstable uranyl(V) by modifying the ligand properties and interested in understanding the fate of the movement of uranium in environment. As a consequence, stabilization can be fine-tuned and the presence f^1 state may show interesting single molecular magnet behaviors.

5. Conflicts of Interest

There are no conflicts to declare.

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Figures

$\text{L} = \text{DMSO}, \text{DMF}; \text{R}_1, \text{R}_2 = \text{H}, \text{CH}_3, \text{CF}_3, \text{C}(\text{CH}_3)_3 \text{ and Ph}.$

Figure 1. Structural isomers of the bis β -diketonate uranyl(VI) complexes.

Figure 2. The radial distribution function, $g(r)$, (a) and its integral (b) as a function of the uranium-DMSO oxygen distance.

Figure 3. (a) A snap-shot image of uranyl-DMSO cluster from MD simulations, the second coordination sphere DMSO molecules are shown as wire frame and (b) The B3LYP/B1 level of theory optimized uranyl-DMSO explicit cluster model $[\text{UO}_2(\text{DMSO})_{5.7}\text{DMSO}]^{2+}$ and the explicit DMSO molecules are shown in tube format.

Figure 4. Plot of calculated uranyl(VI/V) REFs (Calc. ΔG_{red} includes the correction of Fc/Fc^+ ref. 0.60 eV) at the B3LYP/B2(CPCM/UAKS)//B3LYP/B1 level of theory against the experimental REFs (Expt. ΔG_{red}) (Anomalies are excluded).

Figure 5. The LUMO (left) and HOMO (right) orbitals of the $[\text{U}^{\text{VO}}_2(\text{AP1})]^-$ complex.

Figure 6. Mean unsigned errors (MUEs) for the predicted RFEs of investigated uranyl complexes at the B3LYP/B2(CPCM/UAKS)//B3LYP/B1 level of theory.

Figure 7. Mean unsigned errors (MUEs) for the predicted RFEs of investigated uranyl complexes at the DFT level using empirically estimated Fc/Fc⁺ reference couples.

Figure 8. Mean unsigned errors (MUEs) for the predicted reduction free energies (RFEs) of investigated uranyl complexes at the DFT level using the Isodesmic reaction scheme (for the data see Table 6).

Figure 9. Plot of the $\Delta G_{\text{red(s)}}^{\text{VI/V}}$, $\Delta G_{\text{red(g)}}^{\text{VI/V}}$ and $\Delta\Delta G_{\text{solv}}$ of the β -diketonate uranyl complexes predicted in DMSO (eV).

Figure 10. Plot of the $\Delta G^{\text{VI/V}}_{\text{red(s)}}$, $\Delta G^{\text{VI/V}}_{\text{red(g)}}$ and $\Delta\Delta G_{\text{solv}}$ of the cationic $[\text{UO}_2(\text{Py})_5]^{2+/+}$, $[\text{UO}_2(\text{DMF})_5]^{2+/+}$, $[\text{UO}_2(\text{ACN})_5]^{2+/+}$, $[\text{UO}_2(\text{DMSO})_5]^{2+/+}$, $[\text{UO}_2-(\text{L4+DP})]^{1+/0}$, $[\text{UO}_2-(\text{L4+M})]^{+/0}$ and $[\text{UO}_2\text{-saloph-tBu}_2\text{-Py-K}]^{+/0}$ complexes (eV).

Tables

Table 1. Relative energies calculated for the structural isomers of unsymmetrical β -diketonate uranyl(VI) complexes in gas-phase (kcal/mol).

Complexes	L= DMSO			L= DMF		
	cis-a	cis-b	trans	cis-a	cis-b	trans
$[\text{UO}_2-(\text{tfacac})_2\text{-L}]$	4.90	0	0.68	-	-	-
$[\text{UO}_2-(\text{ba})_2\text{-L}]$	0.80	0	0.36	-	-	-
$[\text{UO}_2-(\text{btfacac})_2\text{-L}]$	3.82	0	0.67	4.72	0	2.09
$[\text{UO}_2-(\text{ttfacac})_2\text{-L}]$	3.41	0	0.75	3.76	0	2.39
$[\text{UO}_2-(\text{fod})_2\text{-L}]$	-	-	-	5.07	0	0.58

Table 2. Computationally predicted and empirically estimated absolute potentials of the Fc/Fc^+ electrode in non-aqueous solutions and the corresponding R^2 values for the E^0_{abs} vs. E^0_{expt} plots (eV).

	COSMO-RS ^b	B3LYP/B2//B3LYP/B1				M06/B2//B3LYP/B1			
		Emp. Fc/Fc^+	Calc. Fc/Fc^+	$^a\Delta E^0$	R^2	Emp. Fc/Fc^+	Calc. Fc/Fc^+	$^a\Delta E^0$	R^2
DMSO	5.043	5.202	4.415	0.787	0.69	5.494	4.734	0.760	0.62
DMF	-	5.390	4.450	0.940	0.87	5.778	4.751	1.027	0.85
DCM	-	5.491	4.583	0.908	0.68	5.663	4.904	0.759	0.64
Acetonitrile	4.988	5.239	4.524	0.715	0.56	5.246	4.749	0.497	0.58

Py	-	6.287	4.979	1.308	0.89	6.540	4.510	2.030	0.65
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^a ΔE^0 is the difference between the calculated and empirically estimated Fc/Fc^+ potentials, ^b from ref ⁸³.

Table 3. The calculated uranyl(VI/V) RFEs of the $[\text{UO}_2\text{-(AP1-3)}]$ complexes reported by Shamov *et al.* ⁵⁶ compared with experimental and predicted RFEs from our study (eV).

Complexes	Expt. ΔG_{red}	^a Expt. ΔG_{red}	^b ΔG_{red}	^c ΔG_{red}	^d ΔG_{red}	^e ΔG_{red}	^f ΔG_{red}
$[\text{UO}_2\text{-AP1}]^{0/1-}$	0.850	1.530	1.200	0.890	1.461	1.151	1.836
$[\text{UO}_2\text{-AP2}]^{0/1-}$	1.020	1.700	1.660	1.350	1.377	1.067	1.752
$[\text{UO}_2\text{-AP3}]^{0/1-}$	0.960	1.640	1.550	1.240	1.277	0.967	1.652
MUE	-	-	0.527	0.217	0.428	0.118	0.123 (0.803) ^g

^a $\Delta G_{\text{red}}^{\text{Expt.}} + 0.68$ eV (see the text for more explanation) -Expt. from ref ⁷³; ^b from Shamov *et al.* ⁵⁶ and no spin-orbit correction is included; ^c from Shamov *et al.* ⁵⁶ and spin-orbit correction of -0.31 eV is included; ^d from our work and no spin-orbit correction is included; ^e from our work, spin-orbit correction of -0.31 eV is included; ^f from our work, the RFEs are predicted using the isodesmic reference complex, $[\text{UO}_2\text{-salddt}]^{0/1-}$; ^g the MUE value calculated with respect to the experiment without the correction.

Table 4. The calculated MUEs (eV) for the predicted uranyl(VI/V) RFEs of the uranyl complexes at the DFT level, the effect of spin-orbit coupling (SOC) and the effect of reference electrode correction on the MUEs of the predicted RFEs and the dielectric constants of the non-aqueous solvents.

	ϵ	B3LYP/B2(CPCM)//B3LYP/B1				M06/B2(CPCM)//B3LYP/B1			
		ΔG_{red}	ΔG_{red} + SOC	ΔG_{red}^+ ref.c*	ΔG_{red}^+ SOC + ref.c*	ΔG_{red}	ΔG_{red} + SOC	ΔG_{red}^+ ref.c**	ΔG_{red}^+ SOC + ref.c**
DMSO	46.826	0.641	0.951	0.115	0.352	0.649	0.959	0.371	0.674
DMF	37.219	0.610	0.920	0.108	0.320	0.651	0.961	0.366	0.676
DCM	8.930	0.385	0.695	0.231	0.181	0.321	0.597	0.152	0.342
Acetonitrile	35.680	0.484	0.794	0.146	0.194	0.559	0.869	0.274	0.584
Py	12.970	0.385	0.695	0.255	0.165	1.147	1.457	0.862	1.172
Overall		0.527	0.837	0.162	0.266	0.656	0.960	0.396	0.681

* The reference electrode correction for the B3LYP functional is 0.60 eV.

** The reference electrode correction for the M06 functional is 0.285 eV.

Table 5. The calculated MUEs (eV) for the predicted uranyl(VI/V) RFEs of the uranyl complexes using the empirically estimated Fc/Fc^+ reference couples.

	B3LYP/B2(CPCM)//B3LYP/B1		M06/B2(CPCM)//B3LYP/B1	
	ΔG_{red}	$\Delta G_{\text{red}} + \text{SOC}$	ΔG_{red}	$\Delta G_{\text{red}} + \text{SOC}$
DMSO	0.206	0.185	0.187	0.233
DMF	0.330	0.105	0.376	0.123
DCM	0.523	0.229	0.472	0.197

Acetonitrile	0.232	0.094	0.083	0.372
Py	0.923	0.613	0.883	0.573
Overall	0.406	0.239	0.372	0.280

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Table 6. The calculated MUEs (eV) for the predicted uranyl(VI/V) RFEs of the uranyl complexes using the Isodesmic reaction scheme.

	B3LYP/B2(CPCM)//B3LYP/B1		M06/B2(CPCM)//B3LYP/B1	
	MUEs		MUEs	
	ID1	ID2	ID3	ID4
DMSO	0.278	0.103 ^a	0.418	0.226 ^a
DMF	0.165	0.165	0.294	0.294
DCM	0.156	0.156	0.174	0.174
CAN	0.100	0.100	0.133	0.133
Py	0.434	0.115 ^{**}	0.410	0.195 ^{**}
Overall	0.240	0.125[*]	0.316	0.211[*]

^{*} Where the reference potential used for the $[\text{UO}_2-(\text{Py})_5]^{2+/+}$ is **[−0.46 eV]** and for the uranyl-DMSO complex explicit cluster model used.

^{**} Where the reference potential used for the $[\text{UO}_2-(\text{Py})_5]^{2+/+}$ is **[−0.46 eV]**

^a For the uranyl-DMSO complex explicit cluster model used.

Table 7. The calculated $\Delta G_{\text{red(s)}}^{\text{VI/V}}$, $\Delta G_{\text{red(g)}}^{\text{VI/V}}$ and $\Delta\Delta G_{\text{solv}}$ of the β -diketonate uranyl complexes in DMSO solution (eV).

Complexes	$\Delta G_{\text{red(g)}}^{\text{VI/V}}$	$\Delta\Delta G_{\text{solv}}$	$\Delta G_{\text{red(s)}}^{\text{VI/V}}$
$[\text{UO}_2(\text{dpm})_2\text{-DMSO}]^{0/-}$	-1.590	-1.587	-3.177
$[\text{UO}_2(\text{acac})_2\text{-DMSO}]^{0/-}$	-1.672	-1.917	-3.589
$[\text{UO}_2(\text{ba})_2\text{-DMSO}]^{0/-}$	-1.894	-1.733	-3.627
$[\text{UO}_2(\text{dbm})_2\text{-DMSO}]^{0/-}$	-2.049	-1.651	-3.700
$[\text{UO}_2(\text{tfacac})_2\text{-DMSO}]^{0/-}$	-2.241	-1.664	-3.905
$[\text{UO}_2(\text{ttfacac})_2\text{-DMSO}]^{0/-}$	-2.398	-1.586	-3.984
$[\text{UO}_2(\text{btfacac})_2\text{-DMSO}]^{0/-}$	-2.420	-1.580	-4.000
$[\text{UO}_2(\text{hfacac})_2\text{-DMSO}]^{0/-}$	-2.917	-1.484	-4.401

214x146mm (150 x 150 DPI)