

## Synthesis and characterization of a tetrathiafulvalene-salphen actinide complex†

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A new tetrathiafulvalene-salphen uranyl complex has been prepared. The system was designed to study the electronic coupling between actinides and a redox active ligand framework. Theoretical and experimental methods – including DFT calculations, single crystal X-ray analysis, cyclic voltammetry, NMR and IR spectroscopies – were used to characterize this new uranyl complex.

A large number of complexes based on organic donor tetrathiafulvalene (TTF) ligands and 3d transition metal centers are known.<sup>1</sup> Complementing studies of these systems are recent efforts to develop TTF-containing complexes of the lanthanide cations.<sup>2</sup> To the best of our knowledge this work has not been extended to the actinide series.

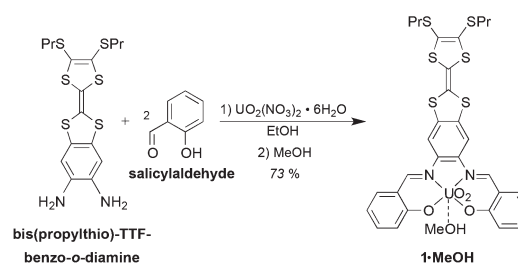
Early actinides are typically characterized by more radially extended and accessible f orbitals compared to the lanthanides. Accordingly, substitution of a lanthanide ion for an actinide in a redox active ligand framework offers an opportunity to enhance electronic communication between the ligand and the coordinated metal.<sup>3</sup> Here, we report a uranyl complex (**1**) based on a TTF-functionalized *N,N'*-phenylenebis(salicylideneimine) analogue (*i.e.*, <sup>TTF</sup>salphenH<sub>2</sub>). Although complex **1** contains a diamagnetic ion, characterizing the interactions between UO<sub>2</sub><sup>2+</sup> and the TTF-ligand represents a crucial first step towards subsequent experiments involving paramagnetic actinyls. Complex **1** was analyzed using a combination of theoretical, electrochemical, and spectroscopic methods. Taken in concert, these studies support the notion that communication between an actinyl cation and a redox active ligand can be achieved. They thus set the stage for more

technically challenging studies involving related species such as the PuO<sub>2</sub><sup>2+</sup> cation.

The present strategy for obtaining actinide complexes based on TTF-functionalized ligands involves coordinating a uranyl cation to an *N,N'*-phenylenebis(salicylideneimine) salphen-type ligand, specifically the known TTF-salphen dianion (<sup>TTF</sup>salphen<sup>2-</sup>).<sup>4</sup> The TTF part of the <sup>TTF</sup>salphen<sup>2-</sup> dianion is redox active and capable of two reversible one-electron oxidations, while the salphen portion of the ligand provides a tetradentate binding site extensively used in actinide science for stabilizing multiple uranium oxidation states (U<sup>4+</sup>, UO<sub>2</sub><sup>1+</sup>, UO<sub>2</sub><sup>2+</sup>).<sup>3f,5</sup> Complex **1** was thus deemed attractive as a platform for examining electronic coupling effects involving actinide elements and redox active ligands.

The synthesis of complex **1** is shown in Scheme 1. Briefly, reacting bis(propylthio)-TTF-benzo-*o*-diamine<sup>6</sup> with salicylaldehyde and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in ethanol provided complex **1** as a red solid in 73% yield.† The <sup>1</sup>H NMR spectrum of this new product was consistent with the uranyl center being complexed by the <sup>TTF</sup>salphen<sup>2-</sup> ligand (see ESI†).<sup>4</sup> Complex **1** (as its methanol complex) was unambiguously characterized in the solid-state *via* an X-ray crystallographic analysis. Suitable crystals for the analysis were obtained by slow evaporation of a solution of complex **1** in a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (Fig. 1).†

The ligand geometry around the uranium ion in **1**·MeOH is best described as pentagonal bipyramidal. It resembles previous structures of TTF-unsubstituted complexes, *i.e.*

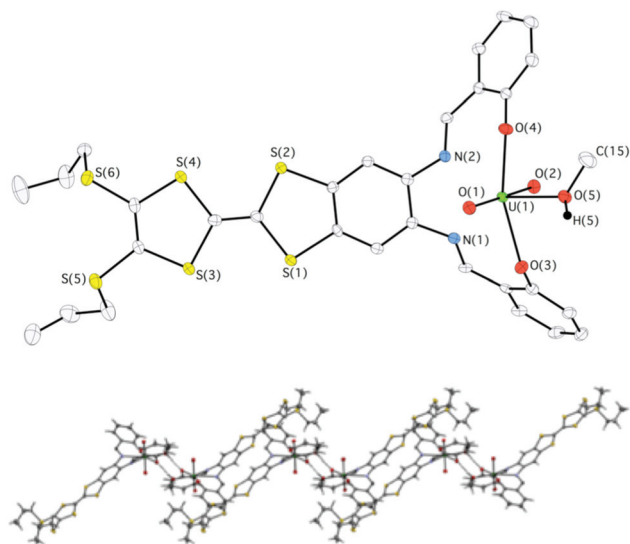
Scheme 1 Synthesis of complex **1**·MeOH.

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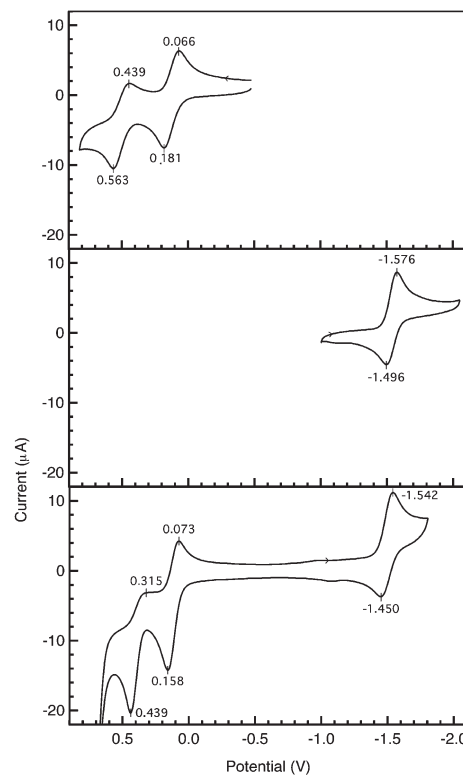


**Fig. 1** *Top*, A thermal ellipsoid plot of **1**-MeOH with the thermal ellipsoids drawn at the 35% probability level. *Bottom*, A thermal ellipsoid plot showing the extended structure of **1**-MeOH (U, green; S, yellow; O, red; C, grey; and H, white). All hydrogen atoms positions were idealized.

(salphen)UO<sub>2</sub>(L) (L = neutral ligand) reported by Bandoli *et al.* and Ikeda *et al.*<sup>5</sup> The uranyl U–O distances in **1**-MeOH are 1.780(2) and 1.776(2) Å, and consistent with previous uranyl complexes.<sup>5</sup> The axial uranyl U–O distances in **1**-MeOH are much shorter than the average equatorial U–O(salphen) distance (2.281 Å;  $\sigma = 0.056$  Å). The equatorial U–N(imine) distances in (TTFsalphen)UO<sub>2</sub>(HOME) are 2.544(3) and 2.531(3) Å. In this regard, both equatorial U–O and U–N distances in complex **1** are similar to unfunctionalized uranyl salphen complexes previously reported.<sup>5a,b</sup>

The extended structure of **1**-MeOH is unique in comparison to other uranyl salphen complexes. To the best of our knowledge, previous solid state structures of uranyl salphen complexes that contained a solvent molecule occupying the fifth site in the uranyl equatorial plane were monomeric and devoid of any intermolecular interactions. In contrast, the extended structure of **1**-MeOH is best described as a one dimensional chain (Fig. 1). For example, the short 2.615(3) Å (HOME)H...O(TTFsalphen)<sup>2-</sup> distance seen in the extended structure is consistent with hydrogen-bonding interactions between the methanol ligands and the salphen phenoxide subunits present in adjacent **1**-MeOH complexes. The TTF subunits of the TTFsalphen<sup>2-</sup> ligands were also seen to stack with eclipsed overlapping  $\pi$ -faces (Fig. 1). The shortest observed distance between the ligand planes is 3.581(4) Å. However, due to the head-to-tail arrangement of the individual ligands, no short S...S intermolecular contacts were observed.

Electrochemical analyses of **1**-MeOH and controls were carried out using cyclic voltammetry (CV). Fig. 2 compares the CV of **1**-MeOH with a similar (salphen)UO<sub>2</sub>(DMSO) (in 10% DMSO/CH<sub>2</sub>Cl<sub>2</sub>) – which does not contain a redox active salphen ligand – and the free-ligand, TTFsalphenH<sub>2</sub> (in CH<sub>2</sub>Cl<sub>2</sub>). In the voltammogram of the free ligand, two waves



**Fig. 2** Cyclic voltammogram of TTFsalphenH<sub>2</sub> (*top*, CH<sub>2</sub>Cl<sub>2</sub>), (salphen)UO<sub>2</sub>(EtOH) (*middle*, DMSO (10%)/CH<sub>2</sub>Cl<sub>2</sub>), and **1**-MeOH (*bottom*, DMSO (10%)/CH<sub>2</sub>Cl<sub>2</sub>). The measurements were performed using a glassy carbon working and a Pt counter electrode at a scan rate of 50 mV s<sup>-1</sup> with TBA-PF<sub>6</sub> as the supporting electrolyte. Potentials are referenced to (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe/(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sup>1+</sup>.

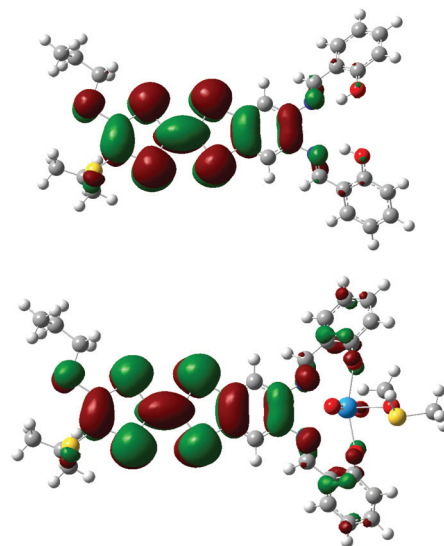
were observed with  $E_{1/2}$  values of 0.124 V and 0.501 V and whose peak potential separations ( $E_p$ ) are 0.115 V and 0.124 V, respectively. Hence, these waves were attributed to successive and quasireversible TTF/TTF<sup>•+</sup> and TTF<sup>•+</sup>/TTF<sup>2+</sup> oxidations. As expected based on previous reports,<sup>5b</sup> the CV of (salphen)UO<sub>2</sub>(DMSO) contained a single wave at -1.536 V ( $E_p = 0.080$  V) attributable to the quasireversible UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>1+</sup> one electron reduction. An additional weak uncoupled oxidation peak was also observed near -1.1 V that has previously been attributed to the dissociation of a coordinated DMSO ligand from the electrochemical reduction product (salphen)UO<sub>2</sub>(DMSO).<sup>5b</sup> The CV of **1**-MeOH displayed four redox processes, Fig. 2. When scanned in the negative direction, a quasireversible single electron redox process was observed at -1.496 V ( $E_p = 0.092$  V) that was attributed to the single electron UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>1+</sup> redox process. For comparison, these values were slightly cathodically shifted in comparison to those for (salphen)UO<sub>2</sub>(DMSO), a finding that reflects the presence of a more extended  $\pi$ -system in the case of TTFsalphen<sup>2-</sup> system. As observed for (salphen)UO<sub>2</sub>(DMSO), a weak uncoupled oxidation peak near -1.1 V was also observed, which likely arose from the dissociation of coordinated DMSO.<sup>5b</sup> When scanned in the positive direction, a quasireversible single-electron oxidation at 0.116 V ( $E_p = 0.85$  V) and a second non-reversible single-electron oxidation process at 0.377 V ( $E_p = 0.124$  V) were

observed. These waves, based on their similarity to the free ligand, were assigned to a quasireversible oxidation of the TTF moiety in  $\text{TTFsalphen}^{2-}$  to the corresponding radical cation followed by a second non-reversible oxidation to the dication. Overall, comparisons between  $\mathbf{1}\cdot\text{MeOH}$  with  $\text{TTFsalphenH}_2$  and  $(\text{salphen})\text{UO}_2(\text{DMSO})$ , provide support for the notion that coordination of  $\text{TTFsalphen}^{2-}$  to  $\text{UO}_2^{2+}$  subtly affects the  $\text{UO}_2^{2+}/\text{UO}_2^{1+}$  and  $\text{TTF}/\text{TTF}^{\cdot+}$  redox potential while changing the reversibility of the  $\text{TTF}^{\cdot+}/\text{TTF}^{2+}$  couple.

To understand better the electrochemical behavior of  $\mathbf{1}\cdot\text{MeOH}$  in comparison to simpler  $(\text{salphen})\text{UO}_2(\text{DMSO})$  and  $\text{TTFsalphenH}_2$ , DFT calculations were carried out on  $\mathbf{1}\cdot\text{MeOH}$ ,  $(\text{salphen})\text{UO}_2(\text{DMSO})$ , and  $\text{TTFsalphenH}_2$ , as well as their corresponding one- and two-electron oxidation and reduction products (*cf.* ESI<sup>†</sup>). These calculations are consistent with the numerous theoretical studies that have been conducted on  $\text{AnO}_2^{2+}$ , and the predicted structures are in good agreement with the bond distances and angles for  $\text{TTFsalphenH}_2$ ,<sup>4</sup>  $\text{H}_2\text{salphen}$ ,  $(\text{salphen})\text{UO}_2(\text{DMSO})$ ,<sup>4,5a,b</sup> and  $\mathbf{1}\cdot\text{MeOH}$ .

The ground state DFT calculations offer insight into the trends observed experimentally, especially in regards to the TTF oxidation potentials for  $\text{TTFsalphenH}_2$  and  $\mathbf{1}\cdot\text{DMSO}$ . We note that analogous comparisons cannot be made experimentally since a common solvent that provided reversible  $\text{TTF}/\text{TTF}^{\cdot+}$  redox processes for both compounds could not be identified. The calculations indicate coordination of  $\text{UO}_2^{2+}$  to  $\text{TTFsalphenH}_2$  serves to shift cathodically the  $\text{TTF}/\text{TTF}^{\cdot+}$  oxidation potentials. A large 0.166 eV shift was calculated under vacuum, intermediate 0.063 eV shift was observed in  $\text{CH}_2\text{Cl}_2$ , and only a small change (0.006 eV) found in DMSO. While the magnitude of these changes were calculated to be highly dependent on the dielectric medium, the overall trend toward cathodically shifted oxidation potentials appears to result from more appreciable delocalization of the radical cation in  $\mathbf{1}\cdot\text{DMSO}^{\cdot+}$  over the  $\pi$ -system of the salphen fragment as compared to the free  $\text{TTFsalphenH}_2^{\cdot+}$  ligand. This conclusion was reached through comparison of the natural orbitals corresponding that to the Kohn–Sham singly occupied molecular orbitals in Fig. 3.

In summary, the first TTF-actinide complex,  $\mathbf{1}\cdot\text{MeOH}$ , has been synthesized and fully characterized. The accessibility of the organic, TTF-centered radical cation, as well as stable reduction to form the corresponding  $\text{UO}_2^{1+}$  complex, was borne out *via* cyclic voltammetry analyses. These studies provide support for the conclusion that  $\mathbf{1}\cdot\text{MeOH}$  exhibits redox activity mediated by both the organic ligand and inorganic actinyl unit. Computational studies also provide support for the conclusion that the extended  $\pi$ -system of the  $(\text{TTFsalphen})\text{-UO}_2(\text{DMSO})$  complex contributes to stabilization of both the pentavalent  $\text{UO}_2^{1+}$  cation – in comparison to  $(\text{salphen})\text{-UO}_2(\text{DMSO})$  – as well as to stabilization of the radical cation, in comparison to the free  $\text{TTFsalphenH}_2$  ligand. We thus propose that complexes, such as  $\mathbf{1}\cdot\text{MeOH}$ , that contain a rigid redox-active organic TTF group linked to 5f metals warrant further study. They may allow for the creation of dual property materials involving *inter alia* complexation and both redox-



**Fig. 3** The natural orbitals corresponding to the SOMOs for  $\text{TTFsalphenH}_2^{\cdot+}$  (top) and  $\mathbf{1}\cdot\text{MeOH}^{\cdot+}$  (bottom); electron density cutoff = 0.02 (a.u.).

based modulation and electrochemical “sensing” of particular actinide cations. More broadly, redox-active actinyl complexes, of which the present system serves as a vanguard, could provide insights into the electronic and magnetic properties of the actinide cations.

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## Notes and references

† Selected data for **1**:  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  9.62 (s, N=CH, 2H), 7.84 (d,  $J = 8.6$  Hz, 2H), 7.72 (s, Ar-H, 2H), 7.64 (t,  $J = 7.5, 7.59$  Hz, 2H), 7.29 (d,  $J = 8.3$  Hz, 2H), 6.79 (t,  $J = 7.3, 7.48$  Hz, 2H), 2.82 (t,  $J = 7.1$  Hz,  $-\text{S}-\text{CH}_2\text{CH}_2\text{CH}_3$ , 4H), 1.61 (m,  $J = 7.10, 7.47$  Hz,  $-\text{S}-\text{CH}_2\text{CH}_2\text{CH}_3$ , 4H), 0.92 (t,  $J = 7.4$  Hz,  $-\text{S}-\text{CH}_2\text{CH}_2\text{CH}_3$ , 6H) ppm;  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  171.21, 166.62, 146.32, 137.08, 136.41, 128.25, 124.96, 121.36, 118.12, 114.13, 112.16, 111.05, 38.33, 23.39, 13.10 ppm. Calc. (%) C 39.56; H, 3.21; N, 2.97; S, 20.45. Exp. (%) C, 39.18; H, 3.34; N, 2.96; S, 20.01.

- (a) D. Lorcy, N. Bellec, M. Fourmigue and N. Avarvari, *Coord. Chem. Rev.*, 2009, **35**, 1398; (b) M. Shatruk and L. Ray, *Dalton Trans.*, 2010, **39**, 11105; (c) F. Pointillart, S. Golhen, O. Candor and L. Ouahab, *Dalton Trans.*, 2013, **42**, 149.

- 2 (a) S. Faulkner, B. P. Burton-Pye, T. Khan, L. R. Martin, S. D. Wray and P. J. Skabara, *Chem. Commun.*, 2002, 1668; (b) S. J. A. Pope, B. P. Burton-Dye, R. Berridge, T. Khan, P. J. Skabara and S. Faulkner, *Dalton Trans.*, 2006, 2907; (c) G. Cosquer, F. Pointillart, Y. Le Gal, S. Golhen, O. Cador and L. Ouahab, *Chem.–Eur. J.*, 2011, **17**, 12502; (d) F. Pointillart, Y. Le Gal, S. Golhen, O. Cador and L. Ouahab, *Chem.–Eur. J.*, 2011, **17**, 10397.
- 3 For examples of actinides bound to redox-active ligands see: (a) T. Arliguie, M. Fourmiguè and M. Ephritikhine, *Organometallics*, 2000, **19**, 109; (b) M. J. Monreal and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2010, **132**, 7676; (c) P. L. Diaconescu, P. L. Arnold, T. A. Baker, D. J. Mindiola and C. C. Cummins, *J. Am. Chem. Soc.*, 2000, **122**, 6108; (d) S. J. Kraft, P. E. Fanwick and S. C. Bart, *Inorg. Chem.*, 2010, **49**, 1103; (e) E. J. Schelter, R. L. Wu, B. L. Scott, J. D. Thompson, T. Cantat, K. D. John, E. R. Batista, D. E. Morris and J. L. Kiplinger, *Inorg. Chem.*, 2010, **49**, 924; (f) C. Camp, V. Mougél, P. Horeglad, J. Pécaut and M. Mazzanti, *J. Am. Chem. Soc.*, 2010, **132**, 17374.
- 4 C. Jia, S. X. Liu, T. D. Keene, A. Neels, V. Mereacre, A. K. Powell and S. Decurtins, *Inorg. Chem.*, 2008, **48**, 3452.
- 5 (a) G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *J. Chem. Soc. D*, 1971, 1330; (b) K. Mizuoka, S.-Y. Kim, M. Hasegawa, T. Hoshi, G. Uchiyama and Y. Ikeda, *Inorg. Chem.*, 2003, **42**, 1031; (c) K. Takao and Y. Ikeda, *Inorg. Chem.*, 2007, **46**, 1550.
- 6 C. Jia, S. X. Liu, C. Tanner, C. Leiggenger, A. Neels, L. Sanguinet, E. Levillian, S. Leutwyler and S. Decurtins, *Chem.–Eur. J.*, 2007, **13**, 3804.