Dalton
Transactions

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2019, **48**, 10782

Received 11th April 2019,
Accepted 4th June 2019

DOI: 10.1039/c9dt01553a

rsc.li/dalton

The experimental determination of Th(IV)/Th(III) redox potentials in organometallic thorium complexes†‡

Christopher J. Inman and F. Geoffrey N. Cloke *

The first Th^{IV}/Th^{III} redox couple values have been determined experimentally using cyclic voltammetry (CV), which has been facilitated by the use of [$^n Bu_4N$][BPh_4] as a supporting electrolyte in THF. Th(IV) and Th(III) metallocene compounds have been studied and their redox couple values are in the range of −2.96 V to −3.32 V *vs* $FeCp_2^{+/0}$.

Well-defined molecular complexes of thorium primarily exist in the +4 oxidation state, with only nine crystallographically authenticated examples of Th(III) in the literature to date.[1] Recent successes in the isolation of low-valent thorium complexes and their subsequent use in the reductive transformations of small molecules prompted us to investigate their electrochemical behaviour.[2] There is a paucity of such studies with the often referenced values for the estimated Th^{IV}/Th^{III} redox couple of −3.0 and −3.7 V *vs.* SHE (standard hydrogen electrode) dating back to the 1970s and 1980s based on extrapolation from atomic spectroscopy and theoretical calculations, but never from direct experimental measurement.[3] In the absence of $E_{1/2}$ values for the Th^{IV}/Th^{III} redox couple, such potentials have been indirectly estimated by the reaction of Th(III) complexes with substrates of known $E_{1/2}$ values.[2d] This method offers an qualitative way to gauge the minimum value of the redox potential, but it has obvious limitations, such as the effects of the steric properties of the substrates. In this paper we present cyclic voltammetry (CV) studies that provide a direct experimental measurement of the Th^{IV}/Th^{III} redox couple in several complexes.

The scarcity of CV studies on the Th^{IV}/Th^{III} redox couple is associated with the rarity of thorium complexes in the +3 oxidation state, the incompatibility such complexes have with common electrolytes such as [$^n Bu_4N$][PF_6], as well as the Th^{IV}/Th^{III} couple likely being one of the most negative redox potentials ever measured using cyclic voltammetry, and is therefore expectedly challenging to measure.[4] For instance, we have previously observed that $ThCOT^{TIPS2}Cp^{\star}Cl$ (COT^{TIPS2} = 1,4-{Si^iPr_3}$_2C_8H_6$ and Cp* = C_5Me_5) exhibits an irreversible reduction wave at −3.33 V *vs.* $FeCp_2^{+/0}$ in [$^n Bu_4N$][PF_6]/THF but decomposes over several cycles.[5]

To increase analyte stability the more inert electrolyte, [$^n Bu_4N$][$B(C_6F_5)_4$], was screened. Our group and others have had success using this electrolyte with uranium complexes which are stable on the electrochemical timescale over many cycles.[6] Unfortunately, this was not the case when this electrolyte was used in CV studies of $ThCp_3^{TMS2}Cl$ (Fig. S3‡), therefore a different electrolyte was required.

Due to the highly reactive nature of Th^{III} we postulated that a fluoride-free electrolyte could be used to increase current response and stability of the analyte. Arnold *et al.* reported the use of [$^n Bu_4N$][BPh_4] to successfully study electrochemical processes in uranium compounds.[7] We decided to test the viability of [$^n Bu_4N$][BPh_4] as an electrolyte for Th(III) and indeed it proved highly compatible. For example, a sample of $ThCp_3^{TMS2}$ (Cp_3^{TMS2} = 1,3-{1,3-$SiMe_3$}$_2C_5H_3$) in 0.05 M [$^n Bu_4N$][BPh_4]/THF was stable over a 24 hours period. Therefore, we decided to use this electrolyte going forward for the investigation of the Th^{IV}/Th^{III} redox couple using CV. Gratifyingly, it allowed us to study several Th(IV) compounds, some of which are precursors to known Th(III) complexes, as well as an authentic Th(III) complex (Chart 1). A full list of voltammograms and electrochemical parameters is given in the ESI.‡

The cyclic voltammogram of $ThCp_3^{TMS2}$ (Fig. 1, top) features a quasi-reversible redox process at −2.96 V *vs.* $FeCp_2^{+/0}$ which is in excellent agreement with voltammograms obtained for $ThCp_3^{TMS2}Cl$ (Fig. 1, bottom) that display a process at −2.96 V *vs.* $FeCp_2^{+/0}$.[8–10] Scanning oxidatively for $ThCp_3^{TMS2}$ and reductively for $ThCp_3^{TMS2}Cl$ gives a similar process and therefore provides evidence that this is indeed a genuine Th^{IV}/Th^{III} process.

Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK. E-mail: f.g.cloke@sussex.ac.uk

† Dedicated to Robin Perutz in celebration of his 70th birthday and wishing him many more.

‡ Electronic supplementary information (ESI) available: Full experimental and cyclic voltammetry. See DOI: 10.1039/c9dt01553a

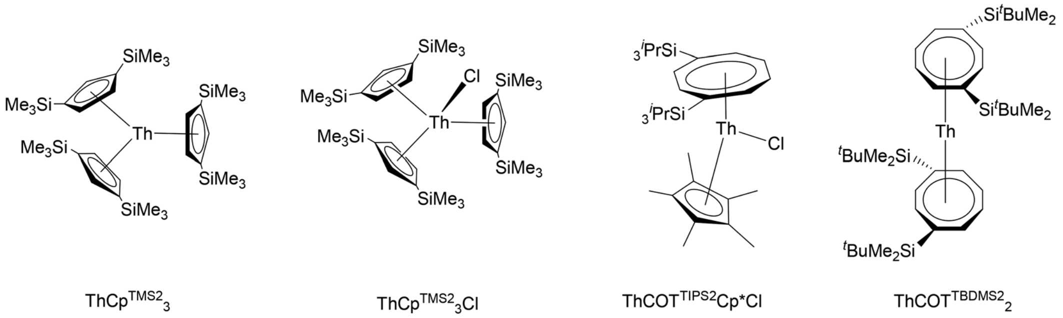

Chart 1 Thorium compounds included in this electrochemical study.

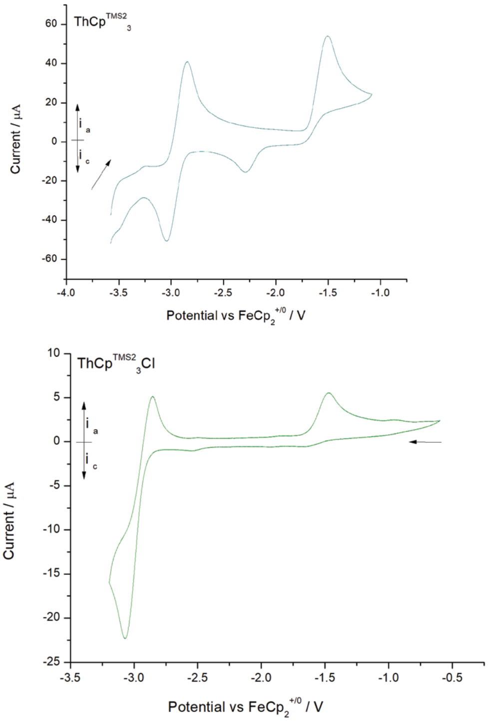

Fig. 1 Voltammogram for ThCp$_3^{TMS2}$ (1 cycle, 8.72 mM, 200 mV s^{-1} scan rate) (top) and ThCp$_3^{TMS2}$Cl (1 cycle, 3.19 mM, 200 mV s^{-1} scan rate) (bottom) in 0.05 M [^{n}Bu$_4$N][BPh$_4$]/THF. The arrows indicate sweep direction of the experiment. See Tables S1 and S2‡ for parameters of these voltammograms.

The voltammogram of ThCOT$_2^{TBDMS2}$ (COT^{TBDM2} = 1,4-{Si^{t}BuMe$_2$}$_2$C$_8$H$_6$) features a process at −3.23 V *vs.* FeCp$_2^{+/0}$ (Fig. 2).[11]

ThCOT^{TIPS2}Cp*Cl displays a quasi-reversible process at −3.32 V *vs.* FeCp$_2^{+/0}$ (Fig. 3)[12] and is in good agreement with the irreversible reduction we previously reported for this compound,[5] suggesting that the use of [^{n}Bu$_4$N][BPh$_4$] as an electrolyte results in more favorable electrochemical behavior. As might be anticipated, the presence of the electron donating Cp* (as compared with *e.g.* Cp^{TMS2}) leads to the most negative redox potential in the compounds studied here.

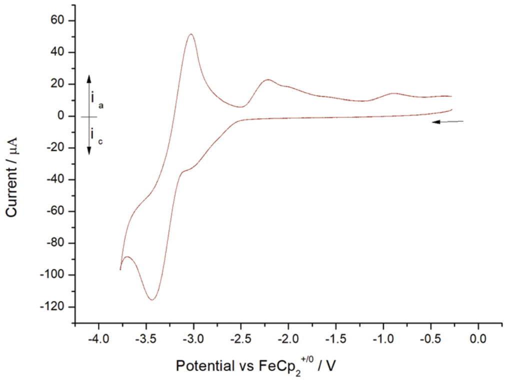

Fig. 2 Voltammogram (1 cycle) for 7.25 mM ThCOT$_2^{TBDMS2}$ in 0.05 M [^{n}Bu$_4$N][BPh$_4$]/THF, scan rate 200 mV s^{-1}. See Table S3‡ for parameters of these voltammograms.

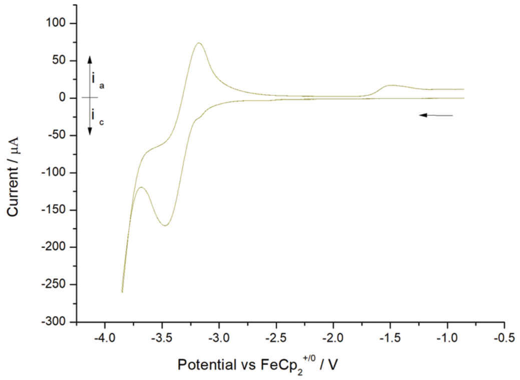

Fig. 3 Voltammogram (1 cycle) for 11 mM ThCOT^{TIPS2}Cp*Cl in 0.05 M [^{n}Bu$_4$N][BPh4]/THF, scan rate 200 mV s^{-1}. See Table S4‡ for parameters of these voltammograms.

In conclusion we report the first measured values for the Th^{IV}/Th^{III} redox couple using cyclic voltammetry, in an organic solvent using a commercially available electrolyte. Table 1 summarizes the results obtained from CV for the compounds depicted in Chart 1. As can be seen they all display processes between −2.96 and −3.32 V *vs.* FeCp$_2^{+/0}$ which we assign to the Th^{IV}/Th^{III} redox couple and are indicative of extremely redu-

Table 1 Thorium compounds and their Th^{IV}/Th^{III} reduction potential values. Additional parameters for these processes are also given. The parameters below are from voltammograms in Fig. 1–3. See respective figures for analyte concentration

Compound	Potential *vs.* $FeCp_2^{+/0}$/V	$\lvert i_{pa}/i_{pc} \rvert$	ΔE_{pp}/mV
$ThCp_3^{TMS2}Cl$[1a]	−2.96	0.95	210
$ThCp_3^{TMS2}$ [1a]	−2.96	1.17	210
$ThCOT_2^{TBDMS2}$ [1b]	−3.23	1.13	420
$ThCOT^{TIPS2}Cp^{*}Cl$[5]	−3.32	0.82	280

$\Delta E_{pp} = \lvert E_{pc} - E_{pa} \rvert$, 200 mV s^{-1} scan rate.

cing metal centres.[2d] This study underlines the importance of choice in electrolyte and will further our understanding of the reactivity of the Th(III) oxidation state, and suggests that electrochemical studies of even lower oxidation states (*i.e.* Th(II), U(II)) might be feasible.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank EPSRC (EP/M023885/1) for financial support and a studentship (C. J. I.). We would also like to thank Professor Greg Wildgoose (University of East Anglia), Dr Alexander Kilpatrick (Humboldt-Universität zu Berlin) and Professor Inke Siewert (Georg-August University Göttingen) for invaluable discussions and acknowledge Dr Nikolaos Tsoureas (University of Sussex) for experimental guidance and support.

Notes and references

1 (*a*) P. C. Blake, M. F. Lappert, J. L. Atwood and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1148–1149; (*b*) J. S. Parry, F. G. N. Cloke, S. J. Coles and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1999, **121**, 6867–6871; (*c*) P. C. Blake, N. M. Edelstein, P. B. Hitchcock, W. K. Kot, M. F. Lappert, G. V. Shalimoff and S. Tian, *J. Organomet. Chem.*, 2001, **636**, 124–129; (*d*) J. R. Walensky, R. L. Martin, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2010, **49**, 1743–1749; (*e*) N. A. Siladke, C. L. Webster, J. R. Walensky, M. K. Takase, J. W. Ziller, D. J. Grant, L. Gagliardi and W. J. Evans, *Organometallics*, 2013, **32**, 6522–6531; (*f*) R. R. Langeslay, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2016, **138**, 4036–4045; (*g*) A. Formanuik, A. M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes and D. P. Mills, *Nat. Chem.*, 2017, **9**, 578; (*h*) R. R. Langeslay, G. P. Chen, C. J. Windorff, A. K. Chan, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2017, **139**, 3387–3398; (*i*) A. B. Altman, A. C. Brown, G. Rao, T. D. Lohrey, R. D. Britt, L. Maron, S. G. Minasian, D. K. Shuh and J. Arnold, *Chem. Sci.*, 2018, **9**, 4317–4324.

2 (*a*) F. Ortu, A. Formanuik, J. R. Innes and D. P. Mills, *Dalton Trans.*, 2016, **45**, 7537–7549; (*b*) A. Formanuik, F. Ortu, C. J. Inman, A. Kerridge, L. Castro, L. Maron and D. P. Mills, *Chem. – Eur. J.*, 2016, **22**, 17976–17979; (*c*) A. Formanuik, F. Ortu, R. Beekmeyer, A. Kerridge, R. W. Adams and D. P. Mills, *Dalton Trans.*, 2016, **45**, 2390–2393; (*d*) A. Formanuik, F. Ortu, J. Liu, L. E. Nodaraki, F. Tuna, A. Kerridge and D. P. Mills, *Chem. – Eur. J.*, 2017, **23**, 2290–2293.

3 (*a*) L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, 1973, **77**, 1528–1539; (*b*) S. G. Bratsch and J. J. Lagowski, *J. Phys. Chem.*, 1986, **90**, 307–312.

4 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

5 Z. E. Button, J. A. Higgins, M. Suvova, F. G. N. Cloke and S. Mark Roe, *Dalton Trans.*, 2015, **44**, 2588–2596.

6 (*a*) N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777–3788; (*b*) C. J. Inman, A. S. P. Frey, A. F. R. Kilpatrick, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2017, **36**, 4539–4545; (*c*) D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez and J. L. Kiplinger, *Organometallics*, 2004, **23**, 5142–5153; (*d*) E. J. Schelter, D. E. Morris, B. L. Scott and J. L. Kiplinger, *Chem. Commun.*, 2007, 1029–1031.

7 (*a*) J. A. L. Wells, M. L. Seymour, M. Suvova and P. L. Arnold, *Dalton Trans.*, 2016, **45**, 16026–16032; (*b*) J. A. Hlina, J. R. Pankhurst, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2016, **138**, 3333–3345.

8 These two compounds also feature a process at *ca.* −1.4 V *vs.* $FeCp_2^{+/0}$ which we attribute to a ligand based process based on comparisons with other reports in the literature (see ref. 6*b*–*d*). A process at *ca.* −2.20 V *vs.* $FeCp_2^{+/0}$ is also observed in $ThCp_3^{TMS2}$ when scanning oxidatively. This process is not observed when scanning in the opposite direction and cannot be assigned with any certainty.

9 Linear dependence of i_{pa} versus (scan rate)$^{1/2}$ (Fig. S6‡) for the Th^{IV}/Th^{III} redox couple in the voltammogram of $ThCp_3^{TMS2}Cl$ indicates the process is diffusion controlled and the observed increase in ΔE_{pp} with increasing scan rate is consistent with quasi-reversible electron-transfer kinetics.

10 R. G. Compton and C. E. Banks, *Understanding Voltammetry*, Imperial College Press, London, 2011.

11 A process at −0.88 V *vs.* $FeCp_2^{+/0}$ was also observed which cannot be assigned with any certainty. A minor process is also observed at *ca.* −3 V *vs.* $FeCp_2^{+/0}$. This process is not observed when a smaller scan window is used (Fig. S7‡).

12 Linear dependence of i_{pa} versus (scan rate)$^{1/2}$ (Fig. S10‡) for the Th^{IV}/Th^{III} redox couple in the voltammogram of $ThCOT^{TIPS2}Cp^{*}Cl$ indicates the process is diffusion controlled and the observed increase in ΔE_{pp} with increasing scan rate is consistent with quasi-reversible electron-transfer kinetics. $ThCOT^{TIPS2}Cp^{*}Cl$ exhibits an irreversible process at −1.50 V *vs.* $FeCp_2^{+/0}$ which we assign as a ligand-based process based on literature (see ref. 6*b*–*d*).