Actinide tetra-N-heterocyclic carbone ‘sandwiches’†

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Highly-symmetrical, thorium and uranium octakis-carbene ‘sandwich’ complexes have been prepared by ‘sandwicking’ the An(iv) cations between two anionic macrocyclic tetra-NHC ligands, one with sixteen atoms and the other with eighteen atoms. The complexes were characterized by a range of experimental methods and DFT calculations. X-ray crystallography confirms the geometry at the metal centre can be set by the size of the macrocyclic ring, leading to either square prismatic or square antiprismatic shapes; the geometry of the latter is retained in solution, which also undergoes reversible, electrochemical one-electron oxidation or reduction for the uranium variant. DFT calculations reveal a frontier orbital picture that is similar to thorocene and uranocene, in which the NHC ligands show almost exclusively σ-donation to the metal without π-backbonding.

Incorporation of a delocalized negative charge across a polynedate ligand backbone by inclusion of quaternary boron provides an alternative strategy. Scorpionate NHCs,† including bis- or tris-NHC borate ligands have yielded complexes with up to six coordinated NHCs per metal centre for both d- and more recently f-block cations (Fig. 1D and E).17–19 Coordinatively saturated hexa-NHC transition metal complexes (e.g. on iron) have demonstrated noteworthy electronic structure properties, spanning luminescence20,21 magnetic bistability,18 reactivity,22–26 and single molecule magnetism, often taking advantage of the impressive σ-donor strength of the NHC.27

We hypothesized that larger macrocyclic tetra-NHC ligands may be able to better stabilize complexes of the larger actinide cations.28–31 We (the Jenkins group) recently developed dianionic tetra-NHC complexes for catalysis and group transfer reactions of transition metals (Fig. 1F).34–39 We considered that the increased ionic radii of actinides versus transition metals could lead to actinide bis(NHC macrocycle) ‘sandwiches’, reminiscent of porphyrins, phthalocyanines, or even cycloctetraene (COT) sandwiches (e.g. (COT)₂M), and, more importantly, that the strong σ-donor capacity of the NHC ligand should impart unusual electronic structures on these complexes.40–43

In this manuscript, we report the first macrocyclic NHC – f-block complexes and the first octa-NHC complexes of any metal. Isostructural square-antiprismatic thorium and uranium complexes were prepared with a 16-membered-ring macrocycle ([(B₂Me₂,MeTC)₆]₄; Fig. 1F with n = 1), while an 18-membered-ring macrocycle ([(B₂Me₂,EtTC)₆]₄; Fig. 1F with n = 2) yields a square prismatic geometry uranium(iv) complex. DFT calculations show that the NHCs have considerable σ-donating character

Introduction

The development of N-heterocyclic carbene (NHC) ligands has transformed many fields of organometallic chemistry,3–4 but the revolutionary application of their unusually strongly σ-donating nature in transition metal chemistry has not crossed over as expected to actinides.5–7 An electrostatic mismatch often prevents straightforward ligation of neutral NHCs to f-block complexes8 so just a few weakly bound adducts have been reported, such as the U(nv) complex (Fig. 1A).9 We (the Arnold group) first developed chelating ligands with an anionic amido group to circumvent this problem (Fig. 1B).9 This general approach was later expanded to other f-block elements,10–14 including thorium (Fig. 1C).15

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which leads to significant ligand field splitting consistent with traditional COT actinide sandwich complexes.

Results and discussion

The synthesis of the octa-NHC actinide complexes is extremely challenging. For transition metal systems, we have typically deprotonated the 16-atom ring macrocyclic ligand $\left[ H_4(BMe_2,MeTC\textsuperscript{H}) \right] Br_2$ with $^n$BuLi at low temperature prior to adding a metal salt,\textsuperscript{34–39} but this methodology is unsuccessful with 5f salts, possibly due to lithium adduct formation.\textsuperscript{44} Other strong bases, such as NaCH\textsubscript{2}Ph in diethyl ether, led to degradation of $\left[ H_4(BMe_2,MeTC\textsuperscript{H}) \right] Br_2$. The key breakthrough was determining that MN(SiMe\textsubscript{3})\textsubscript{2} (M = Li, Na or K), deprotonated the most acidic protons in the ligands in ethereal solvents. Addition of eight equivalents of NaN(SiMe\textsubscript{3})\textsubscript{2} to two equivalents of $\left[ H_4(BMe_2,MeTC\textsuperscript{H}) \right] Br_2$ in DME at $-35 \, ^\circ\text{C}$ followed by UI\textsubscript{4}(1,4-dioxane)\textsubscript{2} gives an intense brown solution which is then heated to 50 $^\circ\text{C}$ to drive the deprotonation reaction to completion (Scheme 1). Room temperature reactions gave only very low yields of 1, which is consistent with our previous reports on iron complexes with this 16-atom macrocycle.\textsuperscript{34–36,38}

NMR spectra of crude reaction mixtures contain multiple sets of paramagnetic peaks as well as diamagnetic peaks attributed to degraded macrocycle, thus purification steps were critical to isolate $\left( BMe_2,MeTC\textsuperscript{H} \right)_2 U$ (1). After the reaction was completed, the DME was removed under vacuum, and HN(SiMe\textsubscript{3})\textsubscript{2} was then separated from the mixture by washing it away with hexanes. The resulting burgundy residue was dissolved in a 1 : 1 toluene/hexanes mixture and filtered over Celite, which left the resulting salt (NaI) and other impurities behind. This dark red coloured solution was crystallized by cooling at $-35 \, ^\circ\text{C}$ overnight which yielded pure $\left( BMe_2,MeTC\textsuperscript{H} \right)_2 U$ (1) as dark purple plates in 9.3% isolated yield (Scheme 1A).

Complex 1 is remarkably air and moisture stable and only very slowly degrades in air over months in the solid state; it appears to be indefinitely stable in an inert atmosphere at ambient temperature. The $^1H$ NMR spectrum of a CD\textsubscript{2}Cl\textsubscript{2} solution of complex 1 shows eight resonances (Fig. S1\textsuperscript{†}) ranging from 14.8 ppm to $-55.9 \, ppm$, which demonstrates that the H atoms in the methylene bridges are diastereotopic and that there are two distinct NHC environments. In every case that we have previously reported with similar macrocycles (excluding a chiral macrocycle),\textsuperscript{39} only one NHC environment is observed by $^1H$ NMR.\textsuperscript{14–16,38} This result suggests that the NHCs are locked into position in solution giving 1 relative $D_2$ symmetry. Heating the solution to 50 $^\circ\text{C}$ in CD\textsubscript{3}CN (Fig. S10\textsuperscript{†}) does not show any dynamic process or reduction in symmetry due to binding of an acetonitrile, which is consistent with the moisture stability of 1.

Several reactions were carried out to target binding a ninth ligand onto 1, e.g. with diphenyldiazomethane or tolyl azide (see ESI\textsuperscript{†}). However, all either showed no reaction at ambient temperatures, or decomposition of 1 at higher temperatures to decomposed ligand products and unidentified insoluble uranium decomposition products (see ESI\textsuperscript{†}).

By employing similar reaction conditions to 1, with an additional separation step on C\textsubscript{2}-terminated silica gel, we were able to isolate $\left( BMe_2,MeTC\textsuperscript{H} \right)_2 Th$ (2), albeit in 1% isolated crystalline yield (Scheme 1A). Complex 2 is colourless and stable in
air. Since \((\text{BMe}_2\text{MeTC})_2\text{Th}\) is diamagnetic, we were able to evaluate its NMR spectra in more detail than 1. The \(^1H\) NMR spectrum in CDCl\(_3\) of 2 shows eight resonances, implying that the relative \(D_2\) symmetry is the same as 1 [Fig. S7†]. Coupling \((J = 13\) Hz\) is observed between the diastereotopic protons on the methylene bridges. In concordance with the \(D_2\) symmetry, nine carbon resonances are observed in the \(^{13}C\) NMR spectrum, including the two resonances for the NHC carbene carbons at 210.1 and 207.6 ppm, respectively. The \(^{13}C\) resonances for the NHC carbens are consistent with the few other reported diamagnetic thorium NHC complexes.\(^{15,19}\)

We (the Jenkins group) and others have found significant differences in structure and reactivity between 16- and 18-atom ring macrocyclic tetra-NHC ligands. For example, a chromium complex prepared with the 16-atom macrocycle, \([\text{H}_4(\text{BMe}_2\text{MeTC})]\text{Cr}]_2\), yields a relatively stable Cr\(\text{n}\) dimer, \([(\text{BMe}_2\text{MeTC})\text{Cr}]_2\) with a chromium–chromium quadruple bond; however, switching to the 18-atom macrocycle, \([\text{H}_4(\text{BMe}_2\text{EtTC})]\text{Br}_2\), yields the highly unstable paramagnetic monomeric complex \((\text{BMe}_2\text{EtTC})\text{Cr}\). Similarly, iron complexes with 16-atom rings are more stable, but not catalytically active for aziridination, while 18-atom rings yield less stable complexes that perform that reaction.\(^{28,37,45,46}\) This trend of reduced stability for 18-atom rings translates to the actinide complexes here. Despite a wide variety of reaction conditions (see ESI†), we were only able to obtain a few single crystals of the uranium complex \((\text{BMe}_2\text{EtTC})_2\text{U}\) (3) [Scheme 1B]. Complex 3 is highly reactive towards air and thermally unstable, precluding further characterization. We also carried out reactions to synthesize the thorium analogue of 3, but were unable to isolate any product.

The solid state structure of \((\text{BMe}_2\text{MeTC})_2\text{U}\) (1) reveals a square anti-prismatic geometry about the uranium centre which is in accordance with the symmetry implied by the \(^1H\) NMR [Fig. 2A]. There are two separate NHC groups because one is opposite a methylene bridge and the other is opposite a \(\text{BMe}_2\) bridge. All of the U–C bonds are between 2.61 Å and 2.65 Å, which is consistent with previously characterized NHC–U bonds for tetravalent uranium.\(^{47-49}\) In the solid state, \((\text{BMe}_2\text{MeTC})_2\text{Th}\) (2) is isostructural to its uranium counterpart, giving a near perfect square anti-prismatic geometry [Fig. 2C]. The Th–C bonds are between 2.69 Å and 2.73 Å which is consistent with reported NHC complexes.\(^{15,19}\) Notably, the M–NHC bond lengths for both 1 and 2 are similar to the M–C bonds for ura-nocene (2.647(4) Å) and thorocene (2.701(4) Å).\(^{45,50}\)

As we observed with chromium complexes of \((\text{BMe}_2\text{MeTC})\text{Cr}\) and \((\text{BMe}_2\text{EtTC})\text{Cr}\), adding a single additional carbon atom to each bridge dramatically changes the structure and properties at each metal ion, so the structure of 3 was particularly noteworthy.\(^{9,15}\) In contrast to 1, complex 3 crystallizes in a higher symmetry space group \((F\text{cc}c)\) and 3 has a square prismatic geometry about the uranium atom with precise \(D_{3d}\) symmetry [Fig. 2C]. In this case, the borate bridges are opposite the ethylene bridge and not offset over the opposing NHC. Presumably, the additional steric demands of the extra carbon atoms cause this change in geometry. Complex 3 only has two unique U–C bonds that are 2.615(5) Å and 2.697(4) Å for C1 and C2, respectively.

Fig. 2 Solid state structures of (A) \((\text{BMe}_2\text{MeTC})_2\text{U}\), 1. (B) \((\text{BMe}_2\text{EtTC})_2\text{U}\), 2 (shown top down), and (C) \((\text{BMe}_2\text{EtTC})_2\text{Th}\), 3. Green, burgundy, blue, grey, and olive ellipsoids (50% probability) represent U, Th, C, and B atoms, respectively. H atoms and lattice solvent molecules are omitted for clarity.

Notably, cyclic voltammetry of 1 in CH\(_3\)CN with 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte reveals two reversible one-electron redox processes centred at 0.21 V and –2.46 V versus ferrocene that we assign as oxidation
bonding orbitals are lower in energy and between the HOMO
singly occupied) orbitals that are essentially exclusively f-

(COT)2U; COT compared their DFT calculations to the originals, uranocene depictions as 
actinide centre (see ESI structures and faithfully reproduced the geometry about each 
metal centre (Fig. 3). The orbitals that show NHC donation to 
the bonding. Finally, the HOMO orbital for 
with little d or f orbital character.

As complexes 1–3 represent a novel actinide ‘sandwich’, we 
compared their DFT calculations to the originals, uranocene ((COT)2U; COT = cyclooctatetraene) and thorocene ((COT)2Th). In particular, we wanted to determine if the strong σ-donation of the NHCs would lead to increased HOMO–LUMO gaps. For complexes 1 and 3, LUMO orbitals also maintain a high degree of f-character and the complexes each have a HOMO–LUMO gap of

~77 kcal mol\(^{-1}\). A comparison with (COT)\(_2\)U calculated using the same methodology as our NHC complexes shows a HOMO–LUMO gap of 88 kcal mol\(^{-1}\) (Table S9†), which is higher than previous calculations.\(^{33}\) Notably the general orbital picture is quite similar; the singly occupied HOMO orbitals, as well as the associated LUMO, LUMO+1, and LUMO+2 for 1 primarily show f-orbital character, similar to uranocene (Fig. S24 and S35†).\(^{33}\) Indeed, calculations for uranocene only show modest \(\pi\)-interactions in the HOMO–1 and HOMO–2 orbitals. Calculations for 2 show similar contours to 1, but without any populated f-electrons, the HOMO–LUMO gap expands to 101 kcal mol\(^{-1}\) (Fig. 3). Again, a comparison with (COT)\(_2\)Th calculated using the same methodology as our NHC complexes shows a HOMO–LUMO gap of 92.1 kcal mol\(^{-1}\) (Table S9†), which is consistent with previous calculated HOMO–LUMO gaps for (COT)\(_2\)Th.\(^{33}\) Complex 2 and (COT)\(_2\)Th are diamagnetic complexes, which allows for more accurate energy comparisons, so these results suggest that the eight \(\sigma\)-donor NHC ligand set has a stronger ligand field than the two \(\pi\)-aromatic, cyclooctatetraenyl ligand set.

**Conclusions**

We have synthesized the first octa-NHC metal complexes using the large An(IV) cation. The homoleptic ‘sandwich’ organometallic complexes are either square anti-prismatic (D\(_{2d}\) symmetry) or square prismatic (D\(_{2d}\) symmetry) depending on the size of the
macrocyclic ring. The $D_2$ symmetry is retained in solution as evidenced by multi-nuclear NMR studies. The size of the ring greatly influences the stability despite each uranium complex having similar U–C bond distances. The 16-atom ringed species are remarkably air-stable, while the 18-atom uranium complex is incredibly frail. DFT calculations show that the NHCs donate electron density through a σ pathway and strong donation leads to very large HOMO–LUMO gaps. These experimental results (including solid state structures and electrochemistry) show similarities between these complexes and the earlier reports on uranocene and thorocene. Finally, DFT calculations suggest similarities between these complexes and the earlier reports on corresponding complexes.

Author contributions

J. F. D. and R. W. F. K. performed the synthesis and characterized the compounds. D. A. P. and C. C. P. executed the theoretical calculations. J. F. D. and X. B. C. solved the X-ray structures of the compounds. J. F. D., D. A. P., P. L. A., and D. M. J. designed the project, analyzed the results, and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the University of Tennessee for supporting sabbatical work for J. F. D. and D. M. J. at the University of Edinburgh. The University of Tennessee also provided additional financial support for this work via the X-ray facility. This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme (grant agreement no 740311, P. L. A.). Additional discussion, analysis, and writing of this manuscript (P. L. A.) was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division at the Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231. Computational resources were provided by the North Texas Scientific Computing, a division under the of the CIO for UNT and UNT System. We thank the EPSRC for funding through the Centre for Doctoral Training in Critical Resource Catalysis, CRITICAT (EP/L016419/1, R. W. F. K.).

References

1 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, 510, 485–496.

2 T. Scattolin and S. P. Nolan, *Trends Chem.*, 2020, 2, 721–736.

3 H. V. Huynh, *Chem. Rev.*, 2018, 118, 9457–9492.

4 C. A. Smith, M. R. Narouz, P. A. Lumnis, I. Singh, A. Nazemi, C.-H. Li and C. M. Crudden, *Chem. Rev.*, 2019, 119, 4986–5056.

5 P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, 109, 3599–3611.

6 S. T. Liddle, *Angew. Chem., Int. Ed.*, 2015, 54, 8604–8641.

7 F. T. Edelmann, J. H. Farnaby, F. Jaroschik and B. Wilson, *Coord. Chem. Rev.*, 2019, 398, 113005.

8 W. J. Oldham Jr, S. M. Oldham, W. H. Smith, D. A. Costa, B. L. Scott and K. D. Abney, *Chem. Commun.*, 2001, 1348–1349.

9 S. A. Mungur, S. T. Liddle, C. Wilson, M. J. Sarsfield and P. L. Arnold, *Chem. Commun.*, 2004, 2738–2739.

10 P. L. Arnold, R. W. F. Kerr, C. Weetman, S. R. Docherty, J. Rieb, F. L. Cruickshank, K. Wang, C. Jandl, M. W. McMullan, A. Pöthig, F. E. Kühn and A. D. Smith, *Chem. Sci.*, 2018, 9, 8035–8045.

11 P. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, G. S. Nichol, R. Bellabarba and R. P. Tooze, *Dalton Trans.*, 2013, 42, 1333–1337.

12 P. L. Arnold, *Chem. Commun.*, 2011, 47, 9005–9010.

13 Z. R. Turner, R. Bellabarba, R. P. Tooze and P. L. Arnold, *J. Am. Chem. Soc.*, 2010, 132, 4030–4051.

14 P. L. Arnold, Z. R. Turner, N. Kaltsoyannis, P. Pelekanaki, R. M. Bellabarba and R. P. Tooze, *Chem.–Eur. J.*, 2010, 16, 9623–9629.

15 P. L. Arnold, T. Cadenbach, I. H. Marr, A. A. Fyne, N. L. Bell, R. Bellabarba, R. P. Tooze and J. B. Love, *Dalton Trans.*, 2014, 43, 14346–14358.

16 R. Pränkel, J. Kniczek, W. Ponikwar, H. Nöth, K. Polborn and W. P. Fehlhammer, *Inorg. Chim. Acta*, 2001, 312, 23–39.

17 C. Santini, M. Marinelli and M. Pellei, *Eur. J. Inorg. Chem.*, 2016, 2016, 2312–2331.

18 K. R. Meihaus, S. G. Minasian, W. W. Lukens, S. A. Kozimor, D. K. Shuh, T. Tyliszczak and J. R. Long, *J. Am. Chem. Soc.*, 2014, 136, 6056–6068.

19 M. E. Garner, S. Hohloch, L. Maron and J. Arnold, *Organometallics*, 2016, 35, 2915–2922.

20 N. W. Rosemann, P. Chábera, O. Prakash, S. Kaufhold, K. Wärmnark, A. Yartsev and P. Persson, *J. Am. Chem. Soc.*, 2020, 142, 8565–8569.

21 J. P. Harris, C. Reber, H. E. Colmer, T. A. Jackson, A. P. Forshaw, J. M. Smith, R. A. Kinney and J. Telser, *Can. J. Chem.*, 2017, 95, 547–552.

22 K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K-E. Bergquist, L. Hägström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Loomoth and K. Wärnmark, *Science*, 2019, 363, 249.

23 M. E. Garner, S. Hohloch, L. Maron and J. Arnold, *Angew. Chem.*, 2016, 128, 13993–13996.

24 M. E. Garner and J. Arnold, *Organometallics*, 2017, 36, 4511–4514.
