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Cyclopentadienyl capped thorium(IV) porphyrinoid complex

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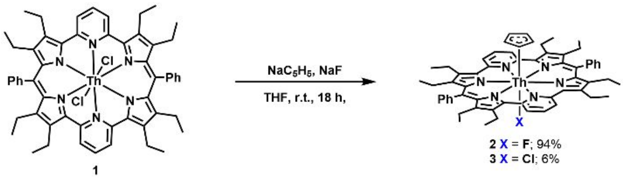
The reaction between Th(IV) dipyriamethyrin dichloride and sodium cyclopentadienyl (Cp) results in the formation of a cyclopentadienyl capped thorium dipyriamethyrin complex, which to our knowledge represents the first expanded porphyrin *f*-element Cp complex.

Introduction

Organometallic complexes provide unique frameworks for codifying fundamental reactivity across the periodic table. They have found widespread use, for instance, in the context of both inorganic and organic syntheses and in a wide range of applications. Metal arene complexes have attracted particular interest due to their diverse coordination chemistry, including an ability to form chelation structures with varying denticities via the pi-system or as sigma complexes.

Early work with ferrocene shed light on the distinctive properties associated with the cyclopentadienyl (Cp) anion in comparison to pnictogen, chalcogen, and halogen based ligands.[1-5,18] Continued exploration into Cp and related arene ligand frameworks has led to breakthroughs in organometallic reactivity, including the generation of sophisticated catalysts such as the those used for alkene metathesis.[6-7,16-17] In the past few years, substituted Cp systems have allowed advances in heavy element coordination chemistry. Notably, alklylated Cp moieties have been used to prepare a range of novel molecular *f*-element complexes, including several where the metal is in the uncommon +2 oxidation state.[8-9] On the other hand, reports on heteroleptic actinide complexes with unsubstituted cyclopentadienyl anions remain limited. This study was undertaken in part to close this knowledge gap. As detailed below we have found that the axial chloride anion in the thorium(IV)dipyriamethyrin-Cl_2 (**1**), an *f*-element expanded porphyrinoid complex, can be converted to Th-[dipyriamethyrin](F)(Cp) complex **2**. To our knowledge this system constitutes the first porphyrinoid *f*-element complex stabilized with an unsubstituted cyclopentadienyl anion.



Scheme 1. The reaction between complex 1 and sodium cyclopentadienyl and the corresponding formation of complex **2**.

Complex **2** was prepared by treating complex **1** with sodium cyclopentadienyl (Cp) in a glass scintillation vial (Scheme 1). Comprehensive analyses using single crystal X-ray diffraction and ^{1}H NMR spectroscopy, revealed a single substitution of an axial chloride atom for a cyclopentadienyl anion. Interestingly, during the reaction, the other chloride atom initially present in complex **1**, was replaced by a fluoride anion, despite the apparent absence of an external fluoride source within the experiment. This result was, at first blush, surprising. However, a replicate experiment returned an identical structure. A possible explanation for the observed incorporation of the F^- anion as the second axial ligand involves the intermediate formation of a cationic Th(IV)(dipyriamethyrin)(Cp)$^+$ complex that then reacts with fluoride ions present in the scintillation glass vials. Like many glasses, scintillation glass is known to contain fluoride. We thus suggest that the putative cationic intermediate extracts fluoride anions from the glass surface.[10] Carrying out the reaction with NaF also yielded complex **2**. No evidence for formation of a difluorinated complex was observed (Scheme 1). Dark red crystals suitable for X-ray diffraction analysis were grown via the slow evaporation of **2** from hexanes: THF (20:1, v: v) (Figure 1).

The resulting structure revealed that complex **2** contained a single η^5-cyclopentadienyl ligand coordinated to a Th(IV) centre at one of the axial positions. The cyclopentadienyl anion, although positioned above the Th(IV) cation, is slightly off-centre. Bond distances between this Cp anion and the Th(IV)

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cation range between 2.827 Å and 2.895. Å. The centroid of the Cp ring is located 2.600 Å away from the Th(IV) cation, forming an angle of 94.29° as defined by the $Cp_{centroid}$-Th-F_{axial} plane. Analysis of the Cp anion itself revealed two congruent C_{Cp}-C_{Cp} bonds measuring 1.406 Å. The remaining three bond lengths fall in the 1.385-1.389 Å range. These values point to an average bond that a slightly shorter than that observed in ferrocene (averaging around 1.40 Å).

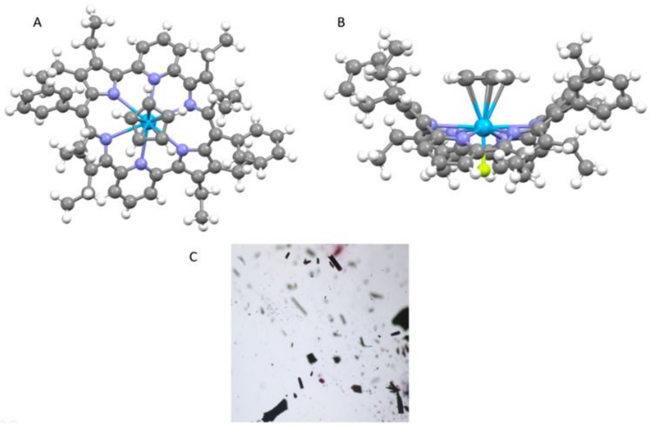
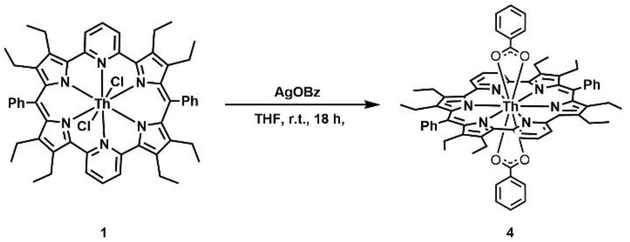


Figure 1. Single crystal X-ray diffraction analyses of complex **2**. A) Top view B) side view and C) picture of the crystals.

The thorium centre is complexed within the dipyriamethyrin core. Th(IV)-$N_{pyrrine}$ bonds are asymmetric with bond distances of 2.689 Å and 2.729 Å. In complex **2**, the Th(IV)-$N_{pyrrole}$ bond lengths range from 2.731 Å to 2.809 Å. These bond distances are all longer than their counterparts in complex **1**. Despite these variations, the quintessential buckled geometry of the core porphyrinoid structure in **2** is retained. Detailed analysis of the metal-fluoride bond in the single crystal structure of **2** revealed a subtle thermal ellipsoid displacement. This displacement is interpreted in terms of a complex that compromises approximately 94% $F^–$ and 6% $Cl^–$. The inferred dominant species Th-[dipyriamethyrin](F)(Cp) (**2**) is characterized by a Th-F bond distance of 2.235 Å.

UV-vis spectral analyses revealed the formation of a new peak at 428 nm (ε = 2500 M^{-1} cm $^{-1}$) (Figure 2). A modest bathochromic shift was seen for the Q-like band (λ_{max} = 568 nm; 8800 M^{-1} cm^{-1}) relative to complex **1** (λ_{max} = 560 nm). Nonetheless, the UV-vis spectrum of **2** proved qualitatively similar to that of complex **1**. This consistency leads us to suggest that the axial substitution associated with the conversion of **1** to **2** causes no gross changes to the core electronic configuration of the system.



Scheme 2. Reaction between complex **1** and silver benzoate leading to complex **4**.

The ^{1}H NMR spectrum of complex **2**, recorded in THF-d_8, displayed characteristics of a diamagnetic Th(IV) entity. Noteworthy spectral features include proton resonances attributed to the cyclopentadienyl anion that are observed at 6.50, 6.40, and 5.70 ppm with a cumulative integration corresponding to five protons. The peak multiplicity seen for the cyclopentadienyl group is attributed to an inherent asymmetry stemming from its coordination to the Th(IV) cation. This asymmetry matches what was observed in the solid-state (*vide supra*). Slight upfield shifts were observed in all the peaks corresponding to the phenyl protons, which resonate between 7.57 and 7.42 ppm. The differences relative to **1** are, however, minor. Again, this was taken as evidence that there is not a gross change in the overall electronic structure of the system. Attempts at recording the ^{19}F NMR spectrum revealed no discernible signals. Therefore, we conclude that complex **2** may exhibit different behaviour in solution than in the solid state.

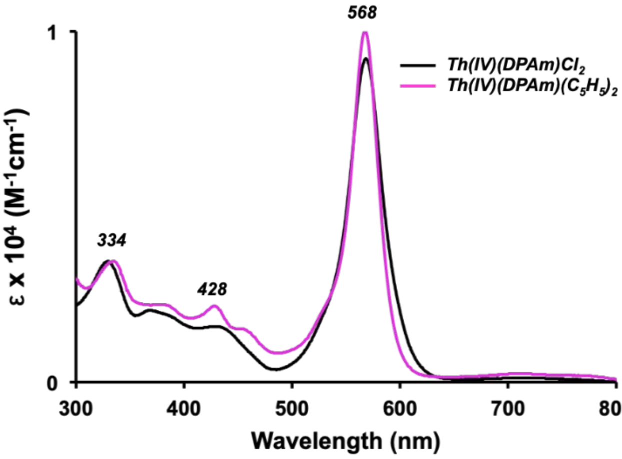


Figure 2. Overlaid UV-Vis spectra of complexes **1** (black line) and **2** (magenta line)

Subsequently, computational calculations were carried out on the fluoride and chloride ligated complexes **2** and **3** (Th-[dipyriamethyrin](X)(Cp); X = F or Cl) . In complex **2**, the more compact fluoride anion is calculated to form a shorter bond with the Th(IV) cation (2.09 Å), whereas in the chloride derivative, **3**, the Th(IV)-Cl bond length is considerably longer at 2.62 Å. In contrast, the bonds between the Cp anion and Th(IV) cation remained consistent, with Th(VI)-Cp bond distances of 2.61 Å and 2.63 Å being calculated for complexes **2** and **3**, respectively. Computational calculations into the complexation energy revealed that formation of the $F^–$ complex **2** is energetically more favourable than the corresponding $Cl^–$ derivative **3**. Complex **2** was calculated to be 59.49 kcal/mol more stable than its counterpart **3**. This difference in stability may reflect the smaller ionic radius of the fluoride ion as compared to the chloride anion, allowing for a tighter fit under the saddle of the porphyrinoid core. The higher charge density of the $F^–$ anion may also help account for why complex **2** was obtained rather than the corresponding chloride analogue **3**, notwithstanding the presence of chloride ligands in the starting complex, **1**.

We were also keen to explore whether complex **1** would allow access to additional actinide complexes involving more conventional axial ligands. With this latter goal in mind, we explored the reaction between the thorium(IV) complex **1** and silver benzoate. Unlike the reaction with NaCp, this led to the formation of new bis-benzoate thorium(IV) complex **4** (Scheme 2). A single crystal X-ray diffraction analysis revealed that the overall structure retained the saddle-like conformation seen in the starting dichloride complex **1**. For instance, a torsion angle of 169.95° is seen around the mean plane of the pyrrolic nitrogen atoms (Figure X). The bond distance between the metal cation and dipyriamethyrin ligand was similar to what was seen in complex **2**. In complex **4**, Th-N$_{pyridine}$ bond distances of 2.645 Å and 2.661 Å are observed, whereas the Th-N$_{pyrrole}$ bond distances range from 2.587 – 2.646 Å. Complex **4** is characterized by slightly shorter Th-N$_{pyridine}$ and Th-N$_{pyrrole}$ bonds compared to complex **2** (for which bond distances of 2.683 and 2.614-2.646 Å are observed).

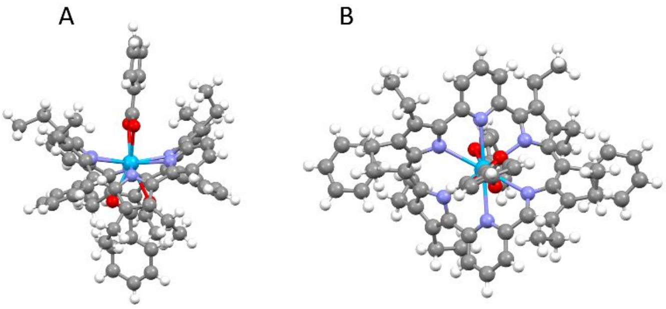


Figure 3. Single crystal X-ray structure of complex **4**. A) side view B) top view.

Bonding analysis of complexes **2** and **4** allowed us to gain insight into how axial modification leads to changes in bonding for the in plane-expanded porphyrin. Passing from the strongly basic cyclopentadienyl anion to the weakly basic benzoate resulted in a shortening of the separation between the thorium and the porphyrinoid core. Average bond distances between the Th(IV)- N$_{pyrrole}$ were shorter for the benzoate complex **4** (2.645 Å) in comparison to the Cp complex **2** (2.729 Å). The shortening of these bonds is taken as an indication that weakening the axial ligand -Th(IV) bonding leads to a strengthening of the in-plane porphyrinoid-bound Th(IV) actinide cation interactions. This inference is consistent with previously reported results that showed that replacement of an axial chloride ligand by a O-tetramethylsilane axial ligand results in a change to the in-plane porphyrinoid-metal bonding, specifically an increase in the bond covalency between the in-plane porphyrin and the actinide cation.[15]

Conclusion

In summary, we have synthesized and characterized what is to the best of our knowledge the first expanded porphyrin *f*-element Cp complex. The present study thus underscores how judiciously selected expanded porphyrins can be used to access to new *f*-element complexes, including those using ligands, such as unsubstituted cyclopentadienyl anions, that have hitherto been all but unexplored in the context of heavy element research.

Author Contributions

DNM and JTB contributed equally.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ The authors declare no competing financial interest. X-ray crystal structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) by making references to file numbers 2288552- 2288553.

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