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Constructing cerium supramolecular wheels and encapsulating uranium with a Schiff-base calixpyrrole ligand**

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Abstract

Trinuclear, supramolecular wheel structures are formed spontaneously from the metallation of a Schiff-base-pyrrole macrocycle by Ce^{3+} cations, while the related actinide U^{3+} cation is instead oxidised to U^{4+} and encapsulated by the macrocyclic framework.

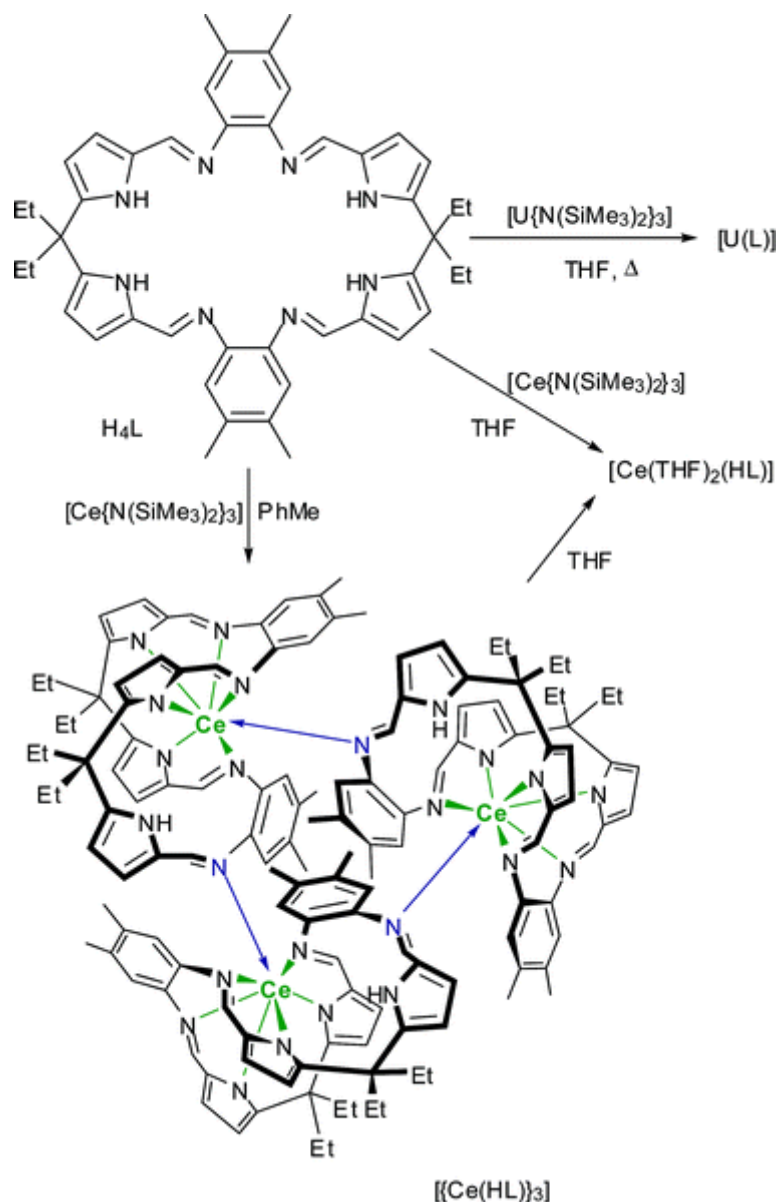
Introduction

The supramolecular chemistry of macrocycles is a burgeoning area of research that crosses traditional chemical, materials, and biochemical boundaries.¹ For example, the aggregation of metal porphyrins into stacks through exocyclic hydrogen-bonding interactions occurs in light-harvesting chlorosomal bacteriochlorophylls, and, as such, their mimics have potential application in optical devices and solar cells.² Furthermore, metal porphyrin complexes that incorporate exocyclic donor groups form the basis of a similar aggregation strategy in which capsular-shaped molecules are generated to provide unique, spatially-confined nanocavities suitable for catalytic reactions.³ Also, calixarenes, calixpyrroles, and their derivatives have been used extensively as hosts to recognise guest molecules.⁴ While the supramolecular chemistry of f-element macrocyclic compounds is less well developed,⁵ the design and synthesis of functional lanthanide edifices are of potential use in imaging applications that make use of their optical and magnetic properties and in the extraction and separation of the f-elements from nuclear waste streams.⁶ Furthermore, detailed spectroscopic and theoretical analyses of the electronic structures of directly related complexes of the lanthanides and actinides provide insight into the involvement of the f-orbitals in bonding.⁷

We reported recently that the octadentate Schiff-base-pyrrole macrocycle H_4L formed the uranyl Pacman complex $[\text{UO}_2(\text{THF})(\text{H}_2\text{L})]$,⁸ and that uniquely, the uranyl oxo-groups in this complex could be manipulated to interact with transition metals and to undergo reductive silylation.⁹ As such, we reasoned that *monometallic*, Ln^{3+} and An^{3+} complexes of H_4L , *i.e.* $[\text{MX}(\text{H}_2\text{L})]$, could provide a Pacman environment suitable for new reaction chemistry within the macrocyclic cleft. Herein, we report contrasting reactions between Ce^{3+} and U^{3+} amides and H_4L that lead to the construction of new, supramolecular wheels of Ce^{3+} and encapsulation of U^{4+} .

The reaction between $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and H_4L in non-coordinating solvents such as toluene does not form the expected amido complex $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}(\text{H}_2\text{L})]$, but instead complete protonolysis occurs to generate cleanly the orange trinuclear complex $[\{\text{Ce}(\text{HL})\}_3]$ in 70% isolated yield (Scheme 1).[†] The ^1H NMR spectrum of $[\{\text{Ce}(\text{HL})\}_3]$ in $[\text{D}_6]$ -benzene is extremely complex and contains a total of 87 resonances between ± 40 ppm that are consistent with a trinuclear structural arrangement in which each of the ligands is inequivalent (ESI, Fig. S1).[†] Addition of THF to this NMR sample collapses the ^1H NMR spectrum to a simpler 32-line

spectrum that is best assigned to the mononuclear adduct $[\text{Ce}(\text{THF})_2(\text{HL})]$ (ESI, Fig. S2).[†] Alternatively, this latter compound can be synthesised directly by the reaction between H_4L and the Ce^{III} amide in THF solvent.



Scheme 1. Transamination reactions of the Schiff-base calixpyrrole H_4L with Ce^{III} and U^{III} amido complexes.

The nuclearities of the Ce complexes were confirmed by X-ray crystallography (Fig. 1, left and middle, respectively).[‡] In the trinuclear compound $[\{\text{Ce}(\text{HL})\}_3]$ each cerium cation is seven coordinate with a distorted capped-octahedral geometry. This geometry has caused the macrocycle to distort and renders the imine nitrogen adjacent to the protonated pyrrole available for exocyclic bonding to the next Ce, which results in a trinuclear “wheel” supramolecule. Similar exogenous bonding has been seen in silver complexes of an S_2O_2

macrocycle, and results in the formation of the tetranuclear, cyclic complex $[\text{Ag}(\kappa^2\text{-}\mu\text{-S}_2\text{O}_2)(\text{ClO}_4)_2][\text{ClO}_4]_2$.¹⁰ In our case, the triangle made by the three Ce cations is equilateral (Ce–Ce–Ce angles 60.68°, 59.57°, 59.75°), with Ce^{***}Ce separations that average to 8.1 Å. Unlike in our related bimetallic transition metal Pacman compounds,¹¹ it is not instructive to describe a bite angle for L due to these bridging imine groups. The interconnecting Ce–N bonds are a little longer (2.658(4), 2.743(4) and 2.708(4) Å) than those which do not bridge (average 2.620 Å) and elongated compared to those reported in the literature (range 2.597(4) to 2.664(4) Å),¹² suggesting that this bond is relatively weak. The Ce–N(pyrrolide) distances vary widely, from 2.504(4) to 2.699(4) Å, and are at the long end of the known range.¹³

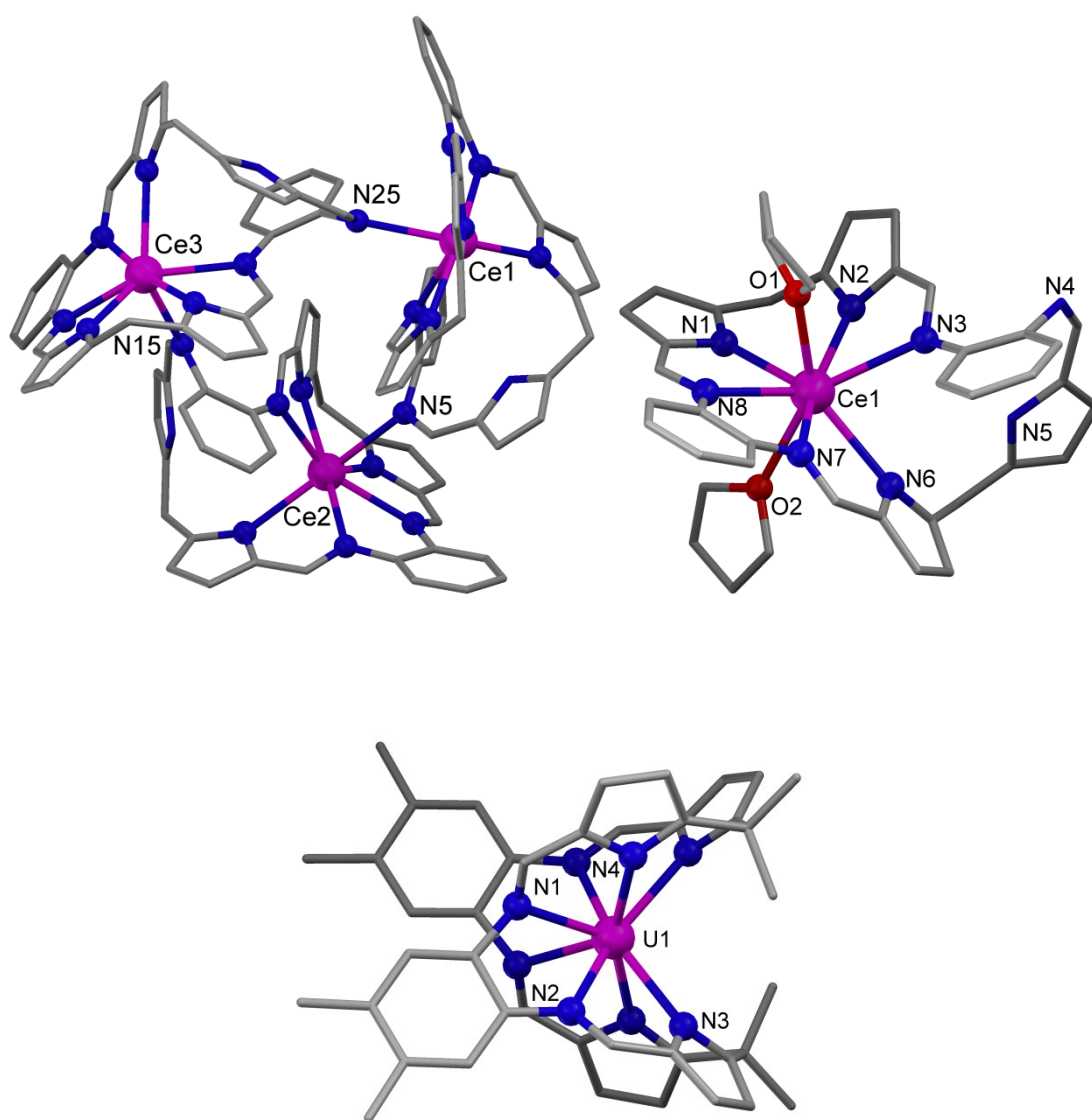


Figure 1. Ball-and-stick representations of the X-ray crystal structures of $[\{\text{Ce}(\text{HL})\}_3]$, $[\text{Ce}(\text{THF})_2(\text{HL})]$, and $[\text{U}(\text{L})]$. For clarity, all hydrogens, and selected aryl-CH₃ and *meso*-substituents have been omitted. Selected bond lengths (Å): $[\{\text{Ce}(\text{HL})\}_3]$ Ce1–N1 2.597(4), Ce1–N2 2.537(4), Ce1–N3 2.505(4), Ce1–N4 2.664(4),

Ce1–N7 2.641(4), Ce1–N8 2.617(4), Ce1–N25 2.658(4), Ce2–N5 2.743(4), Ce3–N15 2.708(4); [Ce(THF)₂(HL)] Ce1–O1 2.5451(16), Ce1–O2 2.6141(15), Ce1–N1 2.6386(18), Ce1–N2 2.5511(17), Ce1–N3 2.5624(18), Ce1–N4 2.7797(17), Ce1–N7 2.6781(18), Ce1–N8 2.5778(18); [U(L)] U1–N1 2.533(8), U1–N2 2.474(10), U1–N3 2.459(10), U1–N4 2.520(9).

In contrast, the cerium cation in [Ce(THF)₂(HL)] is 8-coordinate with a distorted square-antiprismatic geometry. One quadrant of the macrocycle is twisted from the Pacman shape to accommodate the additional THF molecules, with an angle of 41° formed between the two arene ‘hinges’ that are normally close to coplanar. This removes one imino N donor from the coordination sphere of the Ce^{III} and positions the single protonated pyrrole group further from the metal, allowing L to bind as a hexadentate ligand. Despite the position of the remaining N–H pointing towards the cavity, no close contacts that might suggest hydrogen-bonding interactions are present. The Ce–N(pyrrolide) and Ce–N(imine) bond distances are similar to those seen in [Ce(HL)]₃.

A similar reaction between the U^{III} amide [U{N(SiMe₃)₂}]₃ and H₄L in boiling THF was carried out, and results in a brick red solution from which the only product isolated is the U^{IV} complex [U(L)] in 80% yield, Scheme 1. Alternatively, during an attempt to synthesise [(UI)₂(L)] at elevated temperatures, a small quantity of crystalline [U(L)] was generated, presumably as a consequence of elimination of HI. The ¹H NMR spectrum of [U(L)] displays resonances between ±50 ppm that are consistent with a symmetric ligand environment, and this assignment is further corroborated by the X-ray crystal structure which shows that the macrocycle encapsulates the U^{IV} cation (Fig. 1, right).‡ To accommodate the U^{IV} cation the macrocycle is twisted laterally with an overall C₂-symmetry which is crystallographically enforced (*ca.* 35° angle between one arene hinge and an adjacent N₄-donor plane). This causes the two arene groups that normally adopt face-to-face π-stacking motifs in the related Pacman-shaped structures to slip past each other; even so, these aryl groups are still essentially coplanar (dihedral angle 6.7°). The U centre has a distorted square-antiprismatic geometry with U–N(pyrrolide) bond distances of 2.474(10) and 2.459(10) Å, similar to those found in uranium porphyrin complexes (range 2.35–2.59 Å),¹⁴ and U–N(imine) bond distances of 2.520(9) and 2.533(8) Å, similar to those in the very few examples reported for uranium(IV)–imine complexes (range 2.51–2.63 Å).¹⁵ From these data, it is clear that the U^{III} centre has undergone spontaneous oxidation and that due to the smaller size of U^{IV} compared to Ce^{III}, does not require extra THF in its coordination sphere. We presume that the N–H bond is cleaved homolytically by the U^{III} centre to eliminate dihydrogen with concomitant single electron oxidation of U^{III} to U^{IV}.¹⁶ Treatment of [U{N(SiMe₃)₂}]₃ with H₄L in THF at room temperature afforded a material that was identified by ¹H NMR spectroscopy as the silylamido complex [U{N(SiMe₃)₂}(H₂L)], but which always contains quantities of [U(L)]; as such, [U(L)] appears to be the thermodynamic sink of the system.

We have shown that in the absence of donor solvents, Ce^{III} complexes of the Schiff-base calixpyrrole H₄L undergo aggregation through exocyclic bond formation to generate the molecular trinuclear complex [Ce(HL)₃], while in contrast U^{III} undergoes a homolytic oxidation process that results in encapsulation of the U^{IV} cation within the macrocyclic framework. These complexes represent new structural motifs for this ligand and provide the basis for new supramolecular chemistry of the lanthanides and actinides.

Notes and references

[\ddagger] Syntheses: H₄L modification of literature procedure derived from diethylketone.¹⁷ Yellow solid in 70 % yield (39.0 g). Analysis. Found: C, 76.85; H, 7.20; N, 15.50% C₄₆H₅₂N₈ requires: C, 77.00; H, 7.30; N, 15.60.

[{Ce(HL)}₃] Orange crystalline solid in 70 % yield. Single crystals were grown from a saturated C₆D₆ solution. Analysis. Found: C, 64.77; H, 5.86; N, 13.02 %. C₁₃₈H₁₄₇N₂₄Ce₃ requires: C, 64.69; H, 5.86; N, 13.12.

[Ce(THF)₂(HL)] Yellow solid in 251 mg, 72 % yield. Single crystals were grown from a saturated THF solution at -20 °C. Analysis. Found: C, 65.20; H, 6.94; N, 10.85 % C₅₄H₆₅N₈O₂Ce requires: C, 64.97; H, 6.56; N, 11.22.

[U(L)] Red solid in 80 % yield. Two single crystal X-ray datasets were collected from different crystals. The first crystal was grown from a C₆D₆ solution that resulted from a reaction between two equivalents of UI₃ and H₄L which had been heated to 80 °C, while a second, poorer set derived from a crystal grown from a C₆D₆ solution of [U{N(SiMe₃)₂}(H₂L)] which had been heated to 80 °C; this latter dataset refined to an isomorphous structure. Analysis. Found: C, 57.93; H, 4.94; N, 11.84 % C₆₀H₅₂N₈U requires: C, 58.10; H, 5.09; N, 11.78. UV-vis (THF) $\lambda_{\text{max}} = 1112 \text{ nm}$ ($\epsilon = 78.27 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) $\mu_{\text{eff}} = 2.296 \mu_{\text{B}}$ in a C₆D₆ solution.

Crystal data. [{Ce(HL)}₃](C₆H₆)₁₀: C₁₉₈H₂₀₂N₂₄Ce₃, $M = 3343.24$, orange prism, $0.47 \times 0.35 \times 0.1 \text{ mm}^3$, triclinic, space group $P-1$, $a = 19.2737(5)$, $b = 20.1203(6)$, $c = 22.5956(5) \text{ \AA}$, $\alpha = 75.830(2)$, $\beta = 86.608(2)$, $\gamma = 83.598(2)$, $V = 8438.2(4)$, $R_{\text{int}} = 0.068$, $Z = 2$, $\rho(\text{calc}) = 1.314 \text{ g.cm}^{-3}$, $\mu = 0.857 \text{ mm}^{-1}$, $F(000) = 3474$, $T = 150(2) \text{ K}$, Bruker SMART APEX CCD area detector, graphite monochromated MoK α radiation, $R(F^2 > 2\sigma) = 0.0752$, $wR1 = 0.1397$, 46583 independent reflections [$2\theta = 30.55^\circ$] and 1950 parameters.

[Ce(THF)₂(HL)]: C₅₄H₆₅N₈CeO₂, $M = 998.26$, orange block, $0.54 \times 0.43 \times 0.34 \text{ mm}^3$, monoclinic, space group $P21/n$, $a = 23.4691(5)$, $b = 12.2848(2)$, $c = 23.6793(5) \text{ \AA}$, $\alpha = 90.00$, $\beta = 117.8990(10)$, $\gamma = 90.00$, $V = 6033.6(2)$, $R_{\text{int}} = 0.054$, $Z = 4$, $\rho(\text{calc}) = 1.099 \text{ g.cm}^{-3}$, $\mu = 0.794 \text{ mm}^{-1}$, $F(000) = 2076$, $T = 150(2) \text{ K}$, Bruker SMART APEX CCD area detector, graphite monochromated MoK α radiation, $R(F^2 > 2\sigma) = 0.0570$, $wR1 = 0.1053$, 16459 independent reflections [$2\theta = 30.55^\circ$] and 586 parameters.

[U(L)]: C₄₆H₄₈N₈U, $M = 950.95$, red needle, $0.30 \times 0.10 \times 0.01 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 15.1086(15)$, $b = 33.751(4)$, $c = 8.3453(8) \text{ \AA}$, $\beta = 110.747(6)$, $V = 4180.8(7)$, $R_{\text{int}} = 0.099$, $Z = 4$, $\rho(\text{calc}) = 1.511 \text{ g.cm}^{-3}$, $\mu = 3.924 \text{ mm}^{-1}$, $F(000) = 1888$, $T = 93(2) \text{ K}$, AFC8/Saturn 70, graphite monochromated MoK α radiation, $R(F^2 > 2\sigma) = 0.0828$, $wR1 = 0.1679$, 4285 independent reflections [$2\theta = 27.52^\circ$] and 269 parameters. All structures were solved using direct methods and refined using SHELXL in the WinGX software package.¹⁸ All non hydrogen atoms were refined anisotropically and hydrogen atoms were assigned idealized positions and were included in structure-factor calculations.

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