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Revisiting the Chemistry of the Actinocenes $[(\eta^8\text{-}C_8H_8)_2An]$ (An = U, Th) with Neutral Lewis Bases. Access to the Bent Sandwich Complexes $[(\eta^8\text{-}C_8H_8)_2An(L)]$ with Thorium (L = py, 4,4′-bipy, *t*BuNC, R_4phen)

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Supporting Information

ABSTRACT: In stark contrast to uranocene, $(Cot)_2Th$ reacts with neutral mono- or bidentate Lewis bases to give the bent sandwich complexes $(Cot)_2Th(L)$ (L = py, 4,4′-bipy, *t*BuNC, phen, Me_4phen). DFT calculations in the gas phase show that, for both U and Th, formation of the bent compound $(Cot)_2An(L)$ should be facile, the linear and bent forms being close in energy.

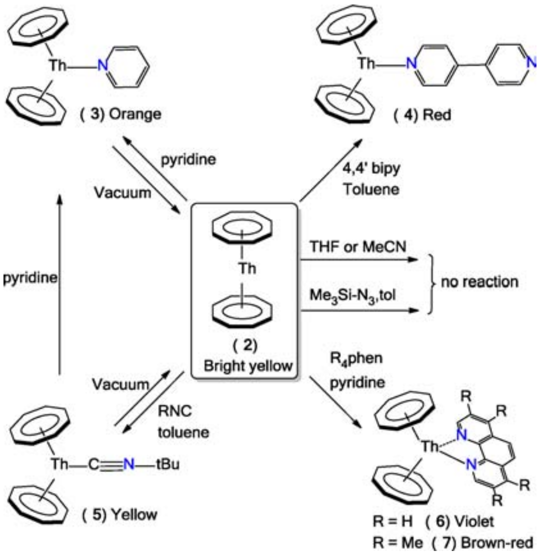
The discovery in 1968 of the uranium compound $(Cot)_2U$ (Cot = η^8-C_8H_8),[1] the first linear sandwich complex of an f element, was a milestone in the history of actinide chemistry. In addition to sparking considerable theoretical debates on the nature of the metal−ligand bond,[2] it boosted the development of organo 4f- and 5f-element chemistry, and this class of compounds rapidly expanded with formation of the tetravalent derivatives $(Cot)_2An$ (An = Th, Pa, Np, Pu),[2] $(Cot)_2Ce$,[3] and their trivalent analogues $[(\eta^8\text{-}C_8H_nR_{8-n})_2M_f]^-$ (M_f = Ln, U, Th, Pu).[4]

For 45 years, lots of work on $(Cot)_2U$ (**1**), the most studied compound, and on the 4f- and 5f-analogues $[(\eta^8\text{-}C_8H_8)_2M_f]^{q-}$ (q = 1,0) proved their poor reactivity. Moreover, the recurrent and often unwanted formation of **1** in a number of reactions in a variety of organic solvents, and the same symmetrical structure being found for the $(Cot)_2M_f$ complexes (M_f = Th, Pa, U, Np, Pu, Ce) and their trivalent derivatives (crystallized in THF or aromatic solvents only), suggested that these compounds were unable to coordinate ligands toward the formation of bent derivatives $[(Cot)_2M_f(L)]^{q-}$ (L = neutral or anionic ligand). This was interpreted as the result of the inaccessibility of the metal center to supplementary ligands due to the steric constraints imposed by the two cyclooctatetraenyl rings. This statement was however not really supported by clear and systematic studies of the interaction of $(Cot)_2M_f$ species with a variety of ligands, and recently we reported that $^-$CN, a strongly coordinating anion with small size, could act as an efficient wedge for bending the very stable uranocene into $[(Cot)_2U(CN)]^-$, the first bent bis(η^8-C_8H_8) compound.[4] This result prompted us to revisit and compare the behavior of $(Cot)_2An$ (An = Th, U) with anionic ligands[5] and neutral Lewis bases.[4] The choice of U^{4+} and Th^{4+} ions lies primarily on their similar radii ($r_{Th^{4+}} \sim r_{U^{4+}} + 0.05$ Å).[6] Because their metal−ligand bonding also exhibits substantial but different covalency,[7,8] it was expected that the more ionic Th−Cot bonding[7] should facilitate the mobility of the Cot ligand and make the coordination of ligands easier. At last, by analogy with the "$(\eta^5\text{-}C_5Me_5)_2U$" complexes, for which a decreasing number of 5f electrons permitted larger addition of ligands and a transition from bent to linear shape, the $5f^0$ thorocene should trap a ligand more easily than its paramagnetic $5f^2$ analogue.[9] Thus, $(Cot)_2Th$ seemed to us the most suitable candidate to the formation of targeted $(Cot)_2M_f(L)$ species.[10]

Here, we revisit the reactivity of the actinocenes $(Cot)_2U$ and $(Cot)_2Th$ toward neutral mono- or bidentate ligands (L = py, 4,4′-bipy, *t*BuNC, 1,10-phenanthroline (phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen)). We report the surprising facile formation of the Lewis base adducts $(Cot)_2Th(L)$ with bent geometry (Scheme 1).

$(Cot)_2Th$ (**2**) was obtained in good yield as a bright-yellow microcrystalline powder from the reaction of $ThCl_4(dme)_2$[11] and K_2Cot in THF, followed by extraction in toluene. Poorly soluble in THF, **2** was found much more soluble in pyridine,

Scheme 1. Reactions of Thorocene with Neutral Lewis Bases



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giving an orange solution displaying a ^{1}H NMR signal at δ 6.28 (δ 6.50 in THF).[7] These features suggested some interaction of **2** with the solvent, and crystallization from pyridine yielded orange crystals of $(Cot)_2Th(py)$ (**3**), the first Lewis base adduct of a $(Cot)_2An$ species and, after $[(Cot)_2U(CN)]^-$,[4] the second example of a bis(Cot) compound adopting the unusual bent geometry.[4,12] Complex **3** readily lost pyridine under vacuum to give back **2**. The less volatile 4,4′-bipy was then considered so as to obtain a more thermally stable derivative. Surprisingly, **2** and 4,4′-bipy in the 1:1 molar ratio reacted in the solid phase, and after condensation of toluene, THF or acetonitrile, the red-pink complex $(Cot)_2Th(4,4'\text{-bipy})$ (**4**) was readily formed. Upon heating at 90 °C in toluene, **4** was dissociated into the yellow thorocene, which gave back **4** upon cooling at room temperature. Compound **4** was isolated in 91% yield from acetonitrile after washing with toluene. Attempts at the bimetallic $(Cot)_2Th(4,4'\text{-bipy})Th(Cot)_2$ by addition of 0.5 equiv 4,4′-bipy to **2** in toluene were unsuccessful. After reflux of the suspension, slow cooling repeatedly afforded yellow and red microcrystals of **2** and **4**.

Strongly coordinating Lewis bases with a suitable size were targeted in order to get new $(Cot)_2Th(L)_2$ adducts. While $(Cot)_2Th$ was left unchanged in the presence of excess Me_3SiN_3 or MeCN in refluxing toluene, it was readily transformed into $(Cot)_2Th(CN\textit{t}Bu)$ (**5**) with *t*BuNC in either boiling THF or toluene. Under these refluxing conditions, pale-yellow crystals of **5** deposited almost quantitatively within 12 h. Although dissociation of *t*BuNC took place under vacuum, complex **5** was isolated after mild drying. Its IR spectrum displayed a characteristic vibration $\nu(C{\equiv}N)$ at 2176 cm^{-1} expectedly larger than that of free *t*BuNC (2136 cm^{-1}), indicating the absence of π-back-bonding. These values can be compared with that of 2181 cm^{-1} in $[Cp^*_2U(NMe_2)(CN\textit{t}Bu)_2]^+$.[13] The ^{1}H NMR spectrum and the color change of the suspension, from yellow to orange, confirmed the displacement of the *t*BuNC ligand in neat pyridine-d_5. Moreover, addition of only 1 equiv of pyridine onto a suspension of **5** in toluene-d_8 showed the presence of some released isonitrile. Because only one *t*BuNC molecule was coordinated in **5**, the use of the bidentate and sterically constrained phenanthroline and its much more soluble and strongly coordinating tetra-methyl derivative Me_4phen, was considered. Addition of phen or Me_4phen to **2** in pyridine immediately afforded dark-violet or dark-purple microcrystalline powders, respectively. After washing with toluene, complexes $(Cot)_2Th(L)$ (L = phen (**6**), Me_4phen (**7**)) were obtained in almost quantitative yields, and red crystals of **7** suitable for XRD were obtained by diffusion of Et_2O into a pyridine solution. Most of these complexes were characterized by X-ray crystallography, elemental analyses, and ^{1}HNMR spectroscopy (when sufficiently stable and soluble). In pyridine, the narrow NMR signal of the Cot ligand generally appeared in the δ 6.10−6.50 region, slightly distinct from the δ 6.67 value for the free dianion.

In striking contrast to **2**, the emerald-green complex $(Cot)_2U$ (**1**) did not coordinate pyridine and *t*BuNC as observed by ^{1}H NMR (δ(Cot) −37.7). Moreover, only crystals of **1** (as checked by X-ray crystallography) were recovered from boiling pyridine solutions or from refluxing THF or toluene solutions containing excess *t*BuNC. Upon mixing a 1:1 molar ratio of **1** and phen or the stronger coordinating Me_4phen in pyridine, lots of emerald-green deposits of $(Cot)_2U$ were recovered, and no change of color of the solution was observed. However the ^{1}H NMR spectrum of the soluble fraction showed the paramagnetic U−Cot signal shifted at −36.7 and −34.2, respectively suggesting some U−R_4phen interaction. Crystallization attempts by slowly cooling to room temperature a hot mixture of **1** and Me_4phen showed the starting materials to crystallize separately. The distinct behaviors of **1** and **2** certainly reflect stronger U−Cot bonding and/or the role of the two 5f electrons of U^{4+} which can disfavor coordination of ligands.[7,8]

The X-ray crystal structures of **3**−**5** and **7**·0.75py are shown in Figures 1 and 2, together with selected bond distances. The planarity of the 4,4′-bipy ligand in **4** may be the result of intermolecular π-stacking interactions between the pyridine rings of two neighboring complexes (centroid···centroid distance 3.75 Å, dihedral angle 2.0°; see Figure S1). Compounds **5** and **7** are the only organothorium complexes with isonitrile or phenanthroline ligands to have been crystallographically characterized. Complex **7** contains two independent molecules in the asymmetric unit which differ slightly by the position of the Me_4phen ligand. All these compounds display the coordination of a single monodentate or bidentate ligand between the two almost planar Cot ligands of the bent thorocene moiety. The Cg···Th···Cg angles (Cg = ring centroid) significantly deviate from linearity, with values of

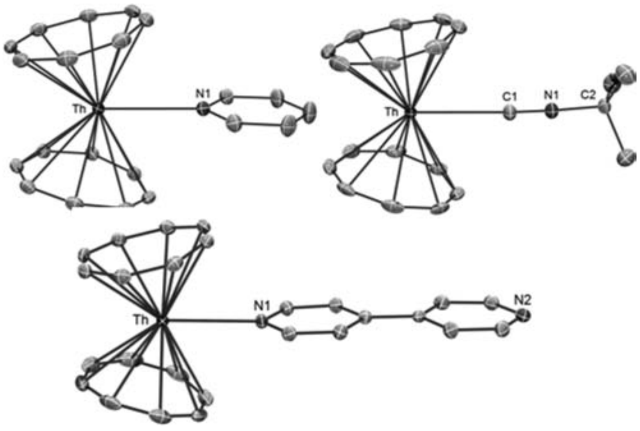

Figure 1. Views of $(Cot)_2Th(py)$ (**3**), $(Cot)_2Th(4,4'\text{-bipy})$ (**4**), and $(Cot)_2Th(\textit{t}BuNC)$ (**5**). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å): For **3**: Th−N1 2.733(2), <Th−C> 2.76(2), <Th···Cg> 2.07(2). For **4**: Th−N1 2.707(2), <Th−C> 2.76(2), <Th···Cg> 2.067(4). For **5**: Th−C1 2.713(4), N1−C1 1.151(5), <Th−C(Cot)> 2.77(2), <Th···Cg> 2.078(5).

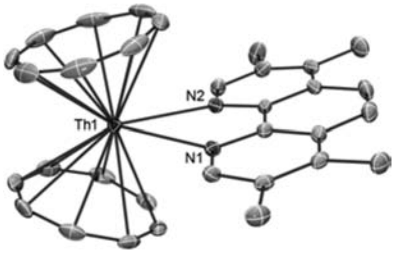

Figure 2. View of one of the two independent molecules in $(Cot)_2Th(Me_4phen)$ (**7**). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) (the corresponding values in the second molecule are in brackets): Th−N1 2.701(2) [2.692(2)], Th−N2 2.720(2) [2.680(2)], <Th−C> 2.81(4) [2.82(4)], <Th···Cg> 2.146(1) [2.155(4)].

153.9, 153.1, and 154.3° for **3**−**5**, respectively, and a lower value of 144.2° for the two molecules in **7**. If the smaller angle in **7** can be due to larger steric congestion, the other angles are quite identical to that found in $[(\mathrm{Cot})_2\mathrm{U(CN)}]^-$ (153.3°)[4] but strongly distinct from the bending angle of 168.7° in the bulky complex $(\eta^8\text{-}1,4\text{-}\{\mathrm{Ph_3Si}\}_2\mathrm{C_8H_6})_2\mathrm{U}$.[12] These Cg···Th···Cg angles can be compared with those found in the mixed-ring derivatives $(\mathrm{Cot})(\mathrm{Cp}^*)\mathrm{Th}(\mathrm{CH}\{\mathrm{SiMe_3}\}_2)$ (137.82°),[14] $\{(\mathrm{Cot})(\mathrm{Cp}^*)\mathrm{Th}\}_2(\mu\text{−}\eta^3\text{-}\eta^3\text{-}\mathrm{C_8H_8})$ (132.11°), and $(\mathrm{Cot})(\mathrm{Cp}^*)\mathrm{ThCl_2Mg}(t\mathrm{Bu})(\mathrm{THF})$ (137.04°),[15] which are quite lower because of the smaller congestion of the $\mathrm{C_5Me_5}$ versus the $\mathrm{C_8H_8}$ ring, and they are identical to the Cg···Sc···Cg angle (152.9°(3)) in the dinuclear compound $\mathrm{Li(THF)_2}(\mu\text{−}\eta^4\text{:}\eta^4\text{-}\mathrm{C_8H_8})\mathrm{Sc(Cot)}$,[16] where the bridging nonplanar $\mathrm{C_8H_8}$ ligand is η^4-coordinated to the metal centers.

The mean Th−C(Cot) distances in complexes **3**−**5** and **7** are, respectively, 2.76(2), 2.76(2), 2.77(2), and 2.81(4)/2.82(4) Å (for the two independent molecules), and they can be compared with that of 2.701(4) Å in the linear thorocene parent.[10] Considering that the increase by one unit in the coordination number increases the metal−ligand distance by ~0.05 Å, then the Th−C(Cot) bond lengths in the linear $(\mathrm{Cot})_2\mathrm{Th}$ and bent derivatives $(\mathrm{Cot})_2\mathrm{Th(L)}$ are quite similar, suggesting that the steric congestion in the latter complexes has little effect. A similar feature was recently observed in the bent and linear uranocenes.[12] The average Th−C(Cot) distances are also similar to those reported in some mono-Cot compounds, such as, e.g., in $(\mathrm{Cot})\mathrm{Th}(\mathrm{N}\{\mathrm{SiMe_3}\}_2)_2$[17] [2.75(2) Å], and they can be compared with that of 2.73(2) Å in the uranium complex $[(\mathrm{Cot})_2\mathrm{U(CN)}]^-$.

The Th−N(py) distances in **3** [2.733(2) Å] and **4** [2.707 (2) Å] are within the range [2.587−2.753 Å] found in the other pyridine-containing thorium compounds.[18−21] The Th−N(Me$_4$phen) bond lengths in **7**, which span a narrow range with a mean value of 2.698(15) Å, are slightly larger than those measured in the substituted phen complexes $\mathrm{Th(O_2CphenCO_2)_2(H_2O)_2}$ and $\mathrm{Th(HOCH_2PhenCH_2OH)(NO_3)_4}$, which vary from 2.628 to 2.658 Å.[22,23] The Th−C(*t*BuNC) distance in **5** [2.713(4)] can only be compared with those in a few uranium(IV) complexes, $(\mathrm{Cp})_3\mathrm{U(OTf)(CN}t\mathrm{Bu)}$ [2.59(2) Å],[24] $[(\mathrm{Cp}^*)_2\mathrm{U(NMe_2)(CN}t\mathrm{Bu)_2}]^+$ [2.58(1), 2.60(1) Å],[13] and $(1,3\text{-}\{\mathrm{Me_3Si}\}_2\mathrm{C_5H_3})_2\mathrm{UBr(CN}t\mathrm{Bu)_2}$ [2.662(7), 2.697(7) Å].[25] The differences in these bond lengths are likely related to the distinct coordination numbers, electronic charges and coordination environments.

DFT calculations were performed so as to inspect the electronic origins of these different coordination behaviors. Noticeably, the optimized geometries for complexes **3**−**6** are sensitive to the functional utilized, and while the popular B3LYP functional overestimates the Th−N bond length in the adducts by 0.11 Å, the geometries obtained with the dispersion corrected M06-2X functional are in excellent agreement with the X-ray structures (details in SI). The thermodynamics of the coordination of the explored neutral donors to **2** are well reproduced, and the coordination of Me$_4$phen leads to the strongest interaction (ΔE= −19.5 kcal/mol). As expected, the monodentate ligands py, *t*BuNC and 4,4′-bipy are more weakly bound to the $\mathrm{Th^{IV}}$ ion with interaction energies of −7.7, −5.6, and −5.6 kcal/mol, respectively. These values are consistent with the ease of removal of the py and *t*BuNC ligands upon exposure of complexes **3** and **5** to reduced pressure and the displacement of *t*BuNC by py in complex **5**. Nonetheless, very similar trends and values are also obtained within the analogous uranium complexes (see SI), and the DFT calculations failed to reproduce the different thermodynamic balances between the two actinide ions. Inspection of the An−py interaction in complexes $(\mathrm{Cot})_2\mathrm{An(py)}$ (An = Th, U) was carried out within the NBO framework. The An−N bond appears as a donor−acceptor interaction between the occupied lone pair of py (LP(N)) and a vacant orbital localized on the actinide(IV) ion (LP*(An)) (Figure 3). As depicted in Figure 3, the metal vacant orbital has a similar breakdown for both Th and U, with about 50% 6d and 25% 5f character. Though LP*(U) is lower in energy than LP*(Th), the overlap with the nitrogen lone pair is larger for thorium, as evaluated by the corresponding off-diagonal element of the Fock matrix $F_{\mathrm{LP(N)\text{-}LP^*(An)}}$. The resulting second-order perturbation energy ($E^{(2)}$) is somewhat greater for $\mathrm{Th^{IV}}$ than $\mathrm{U^{IV}}$ (78.2 vs 48.4 kcal/mol, respectively). In fact, while the Th−C and U−C bond lengths (2.78 and 2.73 Å, respectively) follow the contraction of the metal ionic radius (Δr_i = −0.05 Å), the computed U−N bond length of 2.74 Å is slightly more elongated than the distance expected from the Th−N distance in **3** (2.77 Å). This observation accounts for a lower An−N overlap in the $\mathrm{U^{IV}}$ complex. Nonetheless, the stronger and shorter metal−py interaction with $\mathrm{Th^{IV}}$ likely originates from stronger electrostatic interactions due to the higher acidity of thorium (q_Th = +1.51 vs q_U = +1.18).

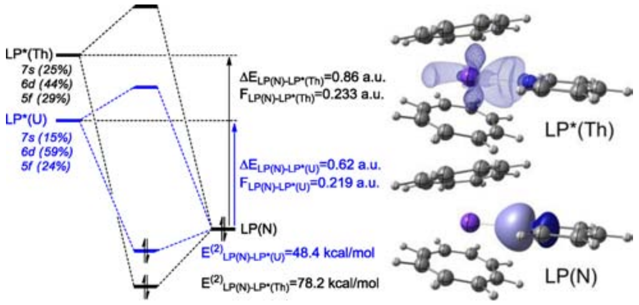

Figure 3. NBO analysis of the An−py interaction in **3** and $(\mathrm{Cot})_2\mathrm{U(py)}$, treated as a second-order perturbation.

This work describes the distinct behavior of $(\mathrm{Cot})_2\mathrm{An}$ (An = U, Th) with neutral Lewis bases L and clearly demonstrates the unique behavior of $(\mathrm{Cot})_2\mathrm{Th}$ which readily gave the first $(\mathrm{Cot})_2\mathrm{An(L)}$ complexes with bent geometry. Further work is in progress to extend the variety of $[(\mathrm{Cot})_2\mathrm{M_f(L)}]^{q-}$ ($\mathrm{M_f}$ = Th, U, and lanthanides) complexes with neutral and anionic ligands, with the aim to obtain novel species with interesting reactivity, to explore the limitations arising from steric effects, and to afford further experimental and theoretical information on their metal−ligand bonding.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterizations. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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