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# Bent thorocene complexes with the cyanide, azide and hydride ligands<sup>†</sup>

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Alexandre Hervé, Nicolas Garin, Pierre Thuéry, Michel Ephritikhine and Jean-Claude Berthet\*

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Reaction of the linear thorocene with NC<sup>-</sup>, N<sub>3</sub><sup>-</sup> and H<sup>-</sup> led to the bent derivatives  $[(Cot)_2Th(X)]^-$  (X = CN, N<sub>3</sub>) and the bimetallic  $[\{(Cot)_2Th\}_2(\mu-H)]^-$ , whereas only  $[(Cot)_2U(CN)]^-$  could be formed from  $(Cot)_2U$ .

Apart from the ubiquitous cyclopentadienyl ligands, the Cot dianion (Cot =  $\eta$ -C<sub>8</sub>H<sub>8</sub>) and its substituted derivatives have been particularly considered within the f-block since the discovery of uranocene, (Cot)<sub>2</sub>U (1).<sup>1</sup> Its report, after initial theoretical prediction,<sup>2</sup> gave a formidable impetus to the coordination chemistry of the f-elements.<sup>3</sup> Indeed, in addition to be viewed as the ferrocene analogue for the large f-elements, it was expected to open new chemical and theoretical vistas.<sup>3</sup> This enthusiasm, partly related to the ideal overlapping of the C<sub>8</sub> ring with the f-orbitals of these large ions should offer a better understanding of the metal<sub>f</sub>-ligand bonding and of the chemical specificities of the f-elements, and prompted formation of many (Cot)<sub>2</sub>M<sub>f</sub> (M<sub>f</sub> = Th, Pa, Np, Pu, Ce),<sup>3–5</sup> and [( $\eta^8$ -C<sub>8</sub>H<sub>n</sub>R<sub>8–n</sub>)<sub>2</sub>M<sub>f</sub>]<sup>-</sup> (M<sub>f</sub> = Ln, U, Th, Pu)<sup>1b,6,7</sup> sandwich complexes with unique *D*<sub>8b</sub> symmetry.

In contrast to the  $[(C_8H_8)_2Ln]^-$  anions which behave as ionic salts of  $(C_8H_8)^{2-}$  and show facile ligand mobility,<sup>8</sup>  $(Cot)_2M_f$  $(M_f = Ce, An)$  complexes of the  $M_f^{4+}$  cations are much less ionic and 1 is by far the most stable of them.<sup>1b,9,10</sup> Its remarkable stability compared to the Ce<sup>4+</sup> and Th<sup>4+</sup> analogues was theoretically explained by the greater covalency due to the larger involvement of 5f and 6d orbitals in the uranium–ligand bonding.<sup>4,10,11</sup>

The great stability of **1** was experimentally evidenced by a very poor reactivity, and its recurrent crystallization in the  $D_{8h}$  symmetry whatever the coordinating solvent. This inability to coordinate ligand was also explained by the strong U–Cot bonding and the inaccessibility of the metal centre embedded between the two Cot ligands. The thought that **1** cannot adopt a bent configuration insidiously widened to the other (Cot)<sub>2</sub>An species despite the thorium analogue (Cot)<sub>2</sub>Th (2)<sup>12</sup> was reported to have distinct physico-chemical properties from **1**. The greater sensitivity of **2** to solvolysis and its reputed more ionic Th–Cot bonding even caused initial doubt about the structural similarity of **1** and **2**.

The recent characterisation of the cyanido complex,  $[(Cot)_2U(CN)][NR_4]$ ,<sup>13</sup> demonstrated for the first time the possibility for  $(Cot)_2U$  to coordinate a ligand with a change in geometry from linear to bent. After the cyanide ion, a strongly coordinating ligand with adapted linear shape, it was of interest to consider other anions and to compare their behaviour towards uranocene and thorocene.

Here we report the distinct reactivity of  $(Cot)_2 U$  and  $(Cot)_2 Th$  with a variety of sodium salts Na\*X (X = CN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, H<sup>-</sup>; Na\* = Na(18-crown-6)), and the facile formation with thorium of mono or bimetallic products with unusual open sandwich structure (Scheme 1).

Addition of excess NaCN into a 1:1 solution of 18-crown-6 and 1 in pyridine gave, after 48 h at 90 °C, a dark-green solution from which the starting material (Cot)<sub>2</sub>U crystallized as emerald green platelets. The <sup>1</sup>H NMR spectrum showed however a U–Cot signal at  $\delta$  –32.4, shifted downfield in comparison with that of 1 ( $\delta$  –37.7), and attributed to [(Cot)<sub>2</sub>U(CN)][Na\*] (3),<sup>13</sup> the formation of which required harsher conditions than that of [(Cot)<sub>2</sub>U(CN)][NR4].<sup>13</sup> Similar treatment of (Cot)<sub>2</sub>Th gave a yellow-orange suspension after 20 h at room temperature (3 h in the <sup>1</sup>H NMR experiment), from which [(Cot)<sub>2</sub>Th(CN)][Na\*] (4) could be isolated in pure form after evaporation of the solvent and extraction in THF. Crystallization in



Scheme 1 Synthesis of the bent actinocene complexes 3-6.

CEA, IRAMIS, SIS2M, CNRS UMR 3299, CEA/Saclay, 91191 Gif-sur-Yvette, France. E-mail: jean-claude.berthet@cea.fr

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hot THF gave crystals suitable for X-ray diffraction,<sup>‡</sup> demonstrating that 4 has the expected bent sandwich geometry. In pyridine, complex 4 showed a <sup>1</sup>H NMR signal at  $\delta$  +6.60, shifted downfield relative to the  $\delta$  +6.28 resonance of 2. Its IR spectrum displays a strong  $\nu$ (CN) stretching frequency at 2108 cm<sup>-1</sup>, a value larger than 2073 cm<sup>-1</sup> for [(Cot)<sub>2</sub>U(CN)][NR<sub>4</sub>],<sup>13</sup> but close to the values found for bridging cyanide.<sup>14</sup> The easy synthesis of 4 incited us to compare the behaviour of 1 and 2 toward the anions  $N_3^-$  and H<sup>-</sup>, which have a suitable size and display weaker coordinating properties than cyanide. (Cot)<sub>2</sub>U neither reacted with Na\*N<sub>3</sub> in THF or pyridine, nor in the presence of Na\*H in THF; only crystals of 1 could be recovered from the green solution. In the latter case, a broad <sup>1</sup>H NMR Cot–U signal at  $\delta$  –35.8, shifted from that of 1, was observed from the lightly coloured solution. It might be related to the rapid equilibrium between 1 and its reduced counterpart, since no U-H signal could be detected between +360 and -60 ppm.

The reaction of 2 with Na\*X (X = N<sub>3</sub><sup>-</sup>, H<sup>-</sup>) followed a very distinct course, affording products that evidence the greater ability of thorocene to trap anions, in line with the lesser covalent Cot-Th bond character which favours the mobility of Cot around the metal centre.<sup>9</sup> The azido complex [(Cot)<sub>2</sub>Th(N<sub>3</sub>)][Na\*] (5) was thus easily obtained by refluxing 2 and NaN<sub>3</sub> in pyridine, in the presence of 1 equiv. of crown ether. After 24 h, the resulting orange suspension was evaporated to dryness and 5 was obtained pure with a yield of 62% (not optimized). The IR spectrum revealed the presence of the N<sub>3</sub> group with a characteristic intense  $\nu_{asym}(N_3)$  band at 2075 cm<sup>-1</sup>, which is in the range of values reported for a series of uranium azides.<sup>15</sup> Slow diffusion of Et<sub>2</sub>O into a pyridine solution of 5 gave yellow crystals suitable for X-ray diffraction, which revealed the monometallic structure of the complex.

Treatment of 2 with 6 equiv. of NaH and 1 equiv. of 18-crown-6 in THF was attempted to prepare either a hydride or the Th(III) species [(Cot)<sub>2</sub>Th]<sup>-</sup>. After 24 h at 20 °C, a yellow-green powder precipitated from the solution, and was separated from excess NaH by extraction in THF. The <sup>1</sup>H NMR spectrum in THF showed the Cot and hydride resonances at  $\delta$  6.30 and  $\delta$  13.4, respectively, in a 32:1 ratio, suggesting the formation of the unexpected bimetallic hydride  $[{(Cot)_2 Th}_2(\mu-H)]^-$ , which was confirmed by X-ray crystallography. Compound [{(Cot)<sub>2</sub>Th}<sub>2</sub>(µ-H)] [Na\*(THF)] (6[Na\*(THF)]) was isolated pure in good yield (85%). Its strong reactivity was evidenced by the immediate release of H<sub>2</sub> in the presence of HNEt<sub>3</sub>BPh<sub>4</sub> in THF, to give back 2 whereas it proved to be unstable in pyridine, splitting into 2 and an unidentified (Cot)<sub>2</sub>Th derivative in the 1:1 ratio. The <sup>1</sup>H NMR spectrum in pyridine revealed the presence of one residual THF molecule in the analytical sample. By analogy with the (RCp)<sub>3</sub>U series,<sup>16</sup> attempts to get the monometallic hydride [(Cot)2Th(H)][Na\*] by addition of excess NaH and 18-crown-6 in refluxing THF were unsuccessful. The Th-H resonance of the anion 6 is shifted upfield relative to the signal at  $\delta$  19.2 of the dimer  $\left[(C_5Me_5)_2ThH_2\right]_2{}^{17}$  and is within the range of  $\delta$  12.81–15.4 found for a series of  $(R_nC_5H_{5-n})_3$ ThH complexes.<sup>18</sup> Interestingly, in some attempts at the formation of  $[(Cot)_2Th^{III}][K^*]$  by reduction of 2 with a mixture of KC8 and 18-crown-6 in THF or toluene, reproducible crystallisation of the hydride  $[{(Cot)_2Th}_2(\mu-H)][K^*]$  (6[K\*]) was observed. In the absence of THF on K\*<sup>+</sup>, the K atom interacts with C=C bonds in the two Cot ligands (shortest  $K \cdots C$  distances 3.068(4) and 3.119(4) Å) (see ESI<sup>+</sup>).<sup>2</sup>



Fig. 1 Views of complexes 4 (left) and 5 (right) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): for 4: Th–C1 2.648(4), C1–N1 1.157(6), Na–N1 2.365(4), Th…Cg 2.09 and 2.10, Cg…Th…Cg 150. For 5: Th–N1 2.518(4), N1–N2 1.179(5), N2–N3 1.159(5), Na–N3 2.484(4), Th…Cg 2.10, Cg…Th…Cg 149, N1–N2–N3 178.3(5).

Views of 4 and 5 are shown in Fig. 1 and the anion  $[{(Cot)_2Th}_2(\mu-H)]^-$  of  $6[Na^*(THF)_2]$  is represented in Fig. 2.<sup>2</sup> These are unique examples of anionic bent actinocenes, with [(Cot)<sub>2</sub>U(CN)][NR<sub>4</sub>].<sup>13</sup> The CN<sup>-</sup> ligand in 4 is best refined with a Th–C rather than a Th–N linkage, in line with all the uranium cyanides,<sup>1,13,14,15c,19</sup> but in contrast to the only other thorium cyanide (<sup>t</sup>Bu<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Th(OSiMe)<sub>3</sub>(NC).<sup>20</sup> Complex 5 is the first structurally characterized thorium azide. The structural differences between the anions  $[(Cot)_2Th(X)]^-$  (CN, N<sub>3</sub>) and  $[(Cot)_2U(CN)]^$ arise from the interaction of the sodium atom, bound to the crown ether, with the terminal nitrogen atom of the cyanide or the 1,3-coordinated azide. The structure of  $[{(Cot)_2 Th}_2(\mu-H)]^-$  resembles that of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThH<sub>2</sub>]<sub>2</sub>,<sup>17</sup> and comprises a H<sup>-</sup> anion located on a two-fold axis of symmetry in 6[Na\*(THF)2]; the [Na\*(THF)2] counter-cation, which also admits two-fold symmetry, bridges two identical bent (Cot)<sub>2</sub>Th fragments which interlock in an almost perpendicular position. The Cot ring centroids around the Th...Th core are at the apexes of a distorted tetrahedron and the two planes containing the Th and H1 atoms and the two ring centroids in each (Cot)<sub>2</sub>Th fragment intersect with dihedral angles of 83.7° in 6[Na\*(THF)<sub>2</sub>] and 89.8° in 6[K\*].

The carbon atoms of the C<sub>8</sub> rings in **4–6** are planar with a rms deviation of 0.050 Å at most. The Cg···Th···Cg angles (Cg = ring centroid) significantly deviate from linearity, with values of 150°, 149° and 148–149° in **4**, **5** and **6**, respectively, and can be compared with the angle found in  $[(Cot)_2U(CN)]^-$  (153°).<sup>13</sup>



**Fig. 2** View of the anion of  $[((Cot)_2Th]_2(\mu-H)][Na^{(THF)_2}]$ , **6[Na^{(THF)\_2}]**, with 30% probability displacement ellipsoids. Hydrogen atoms are omitted, except for H1. Symmetry code: i = 1 - x, -y, z. Selected bond lengths (Å) and angles (°): Th–H1 2.323(7), Th···Cg 2.09 and 2.10, Cg···Th···Cg 148.

These angles are quite similar denoting a weak steric pressure in the hydride **6**.

The mean Th–C(Cot) distances in the two 11-coordinate complexes 4 and 5 are identical and equal to 2.78(2) Å, a value larger than 2.701(4) Å in the linear 10-coordinate thorocene.<sup>12</sup> This difference reflects the distinct charges and coordination numbers of the complexes. These distances are also similar to those reported in some mono-Cot compounds,<sup>21</sup> such as  $[(Cot)ThCl_2(THF)_2]$  (2.72(2) Å)<sup>21*a*</sup> or  $[(Cot)Th(N{SiMe_3}_2)_2]$  (2.75(2) Å),<sup>21*b*</sup> and can be compared with the average U–C(Cot) distance in  $[(Cot)_2U(CN)]^-$  (2.73(2) Å), the latter smaller distance being due to the ionic radius of U<sup>4+</sup> being smaller than that of Th<sup>4+</sup> by *ca*. 0.05 Å.<sup>22</sup> The Th–C(Cot) distances in 6 are quite similar to those in 4 and 5, averaging 2.77(3) Å in 6[Na\*(THF)\_2] and 2.79(3) Å in 6[K\*]. All the Th…Cg distances are in the narrow range of 2.09–2.12 Å.

The Th–C<sub>cyanide</sub> distance of 2.648(4) Å is close to 2.626(4) Å in  $[(Cot)_2U(CN)]^-$ , whereas the Th–N<sub>azide</sub> bond length of 2.518(4) Å can be compared with U–N<sub>azide</sub> distances which span the range 2.219(6)–2.564(12) Å<sup>15b,c</sup> and to the Th–NC bond length of 2.454(4) Å in (<sup>t</sup>Bu<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Th(OSiMe)<sub>3</sub>(NC).<sup>20</sup>

The Th–H1 distances (2.323(7) Å in **6[Na\*(THF)**<sub>2</sub>] (2.26 and 2.34 Å in **6[K\*]**) can be compared to values reported in the literature, which vary within a large range depending on whether the hydride is terminal or bridging [1.99(5)–2.6(1) Å]. The present values are however close to those in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ThH (2.33(13) Å)<sup>18b</sup> and in [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThH<sub>2</sub>]<sub>2</sub> [2.03(1) (terminal); 2.29(3) (bridging) Å].<sup>17</sup>

In summary, comparison of the reactivity of the actinocenes (Cot)<sub>2</sub>An towards the addition of a variety of anions evidences distinct chemical behaviour between Th and U. Both 1 and 2 trap the cyanide ion, but only thorocene reacts with the weaker ligands  $N_3^-$  and H<sup>-</sup>. The monometallic complexes [(Cot)<sub>2</sub>Th(X)]<sup>-</sup> are obtained with  $CN^-$  and  $N_3^-$ , while an unexpected bimetallic complex is formed with H<sup>-</sup>. All these species show a unique bent thorocene fragment. These results clearly dismiss the long-held belief that actinocenes are poorly reactive species and are devoid of any coordinating ability, and they demonstrate that at least one attainable coordination site remains on the actinide centre. That thorocene is much more reactive than uranocene is also clearly evidenced here despite the lower Lewis basicity of the Th<sup>4+</sup> ion.<sup>23</sup> This may originate from the reputedly less covalent Cot-Th bonding which favours the mobility of  $\cot^{2-}$  on the metal centre and makes easier the bending of the  $(Cot)_2$ Th fragment upon interaction of a ligand.

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### Notes and references

<sup>‡</sup> Crystallographic data. Crystal data for 4: C<sub>29</sub>H<sub>40</sub>NNaO<sub>6</sub>Th, *M* = 753.65, orthorhombic, space group *Pna*2<sub>1</sub>, *a* = 16.9230(6), *b* = 12.8262(4), *c* = 13.4858(4) Å, *V* = 2927.20(16) Å<sup>3</sup>, *Z* = 4. Refinement of 344 parameters on 8618 independent reflections out of 68 974 measured reflections (*R*<sub>int</sub> = 0.022) led to *R*<sub>1</sub> = 0.027, w*R*<sub>2</sub> = 0.064,  $\Delta\rho_{min} = -1.07$ ,  $\Delta\rho_{max} = 0.95$  eÅ<sup>-3</sup>, Flack parameter 0.487(7). Crystal data for 5: C<sub>28</sub>H<sub>40</sub>N<sub>3</sub>NaO<sub>6</sub>Th, *M* = 769.66, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.7844(4), *b* = 19.3693(6), *c* = 13.0254(4) Å, *β* = 115.214(2)°, *V* = 2918.11(16) Å<sup>3</sup>, *Z* = 4. Refinement of 352 parameters on 8909 independent reflections out of 123 806 measured reflections (*R*<sub>int</sub> = 0.034) led to *R*<sub>1</sub> = 0.035, w*R*<sub>2</sub> = 0.091,  $\Delta\rho_{min} = -1.43$ ,  $\Delta\rho_{max} = 2.70$  eÅ<sup>-3</sup>. Crystal data for **6**[Na\*(THF)<sub>2</sub>]: C<sub>52</sub>H<sub>73</sub>NaO<sub>8</sub>Th<sub>2</sub>, *M* = 1313.17, tetragonal, space group *P*4<sub>21</sub>*c*,

*a* = 15.2646(3), *c* = 22.1864(8) Å, *V* = 5169.6(3) Å<sup>3</sup>, *Z* = 4. Refinement of 287 parameters on 7863 independent reflections out of 123 984 measured reflections ( $R_{int} = 0.037$ ) led to  $R_1 = 0.031$ ,  $wR_2 = 0.061$ ,  $\Delta \rho_{min} = -1.62$ ,  $\Delta \rho_{max} = 0.50$  e Å<sup>-3</sup>, Flack parameter 0.491(7). Crystal data for **6[K\*]**: C<sub>44</sub>H<sub>57</sub>KO<sub>6</sub>Th<sub>2</sub>, *M* = 1185.08, monoclinic, space group *C2/c*, *a* = 37.0796(18), *b* = 9.8234(3), *c* = 25.6897(13) Å, *β* = 118.992(2)°, *V* = 8184.8(6) Å<sup>3</sup>, *Z* = 8. Refinement of 478 parameters on 12 469 independent reflections out of 148 463 measured reflections ( $R_{int} = 0.072$ ) led to  $R_1 = 0.036$ ,  $wR_2 = 0.053$ ,  $\Delta \rho_{min} = -1.41$ ,  $\Delta \rho_{max} = 0.93$  e Å<sup>-3</sup>.

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