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# Synthesis and Structures of Tris(cyclononatetraenyl) Rare-Earth Complexes $[\text{Ln}(\text{C}_9\text{H}_9)(3)]$ ( $\text{Ln} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho},$ $\text{Er}, \text{Tm}$ )

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# Synthesis and Structure of Tris-cyclononatetraenyl Rare Earth Complexes $[\text{Ln}(\text{C}_9\text{H}_9)_3]$ ( $\text{Ln} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ )

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**ABSTRACT:** The article reports the synthesis and structural characterization of a series of  $\text{Ln}(\text{C}_9\text{H}_9)_3$  complexes with the cyclononatetraenyl (Cnt,  $\text{C}_9\text{H}_9$ ) ligand ( $\text{Ln} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ ). The Yb and Sm complexes were not obtained and the reaction of the potassium salt of the Cnt ligand with trivalent halides salts of the corresponding metals led to the known bis-Cnt sandwich compounds,  $\text{Ln}(\text{C}_9\text{H}_9)_2$ . The X-ray diffraction studies on the trivalent complexes show that the Cnt ligand is significantly bent in order to accommodate the large size of the ligand while keeping the aromaticity. When the size of the lanthanide ion decreases, the ligand does not switch away but swings over the metal ion in order to maximize the electrostatic interactions. The  $^1\text{H}$  NMR and the UV-Visible spectroscopies were recorded as well as the solid-state magnetism. The UV-Visible spectroscopy highlights a remarkable charge-transfer band in the Tm complex while ligand-based transitions are principally observed with all other metal ions. The magnetic behavior of the series agrees with trivalent lanthanides ions and the computations at the CASSCF level confirm the trivalent electronic structure.

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## INTRODUCTION

Organometallic complexes of lanthanide provide interesting alternatives to coordination compounds because of the versatility of the ligands that are used, allowing unusual structural geometries and reactivities.<sup>1-2</sup> The most common ligands are the cyclopentadienyl (Cp)<sup>3-4</sup> and the cyclooctatetraenyl (Cot)<sup>5-6</sup> ligands and all the analogues obtained by the easy substitution of the hydrogen atoms by various groups, which can vary the bulk and the electronic properties.<sup>7-9</sup> Historically, the first organolanthanide complexes reported were the  $\text{LnCp}_3$  complexes<sup>10</sup> short after the discovery of the  $\pi$ -bonding mode of the Cp ligand.<sup>11</sup> In this particular example, the authors reported several physical properties including the room temperature magnetic susceptibility<sup>12</sup> and also mentioned the probable ionic bonding of the ligand because the fast methathesis in presence of iron(II).<sup>12</sup>

The great success of the Cp ligand is easily explained by its versatility: the variety of chemical groups provides a rich chemistry,<sup>1</sup> the steric bulk provides kinetic stability and the electronic tunability provides multiple applications. The increasing recent interest in magnetism and single-ion magnets<sup>13</sup> questions about the need of additional geometries around f-elements in order to better tune the magnetic performances.<sup>14</sup> Thus, the symmetry and overall geometry is starting to play a bigger role in the design of such complexes.<sup>14</sup> The recent report of record-breaking single-ion magnets molecules based on substituted Cp ligands<sup>15-18</sup> is witness of this topical interest: the linear geometry of

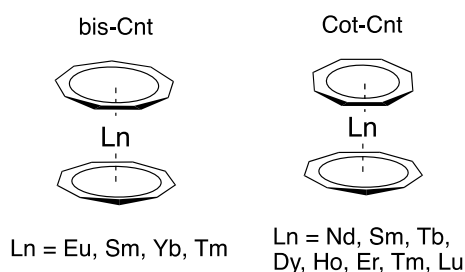
the complex is crucial in the development of high-performance single molecules magnets (SMMs) of Dy,<sup>14</sup> while limited axial density contribution is suitable for Er SMMs.<sup>19-21</sup> In other words, small bulky Cp ligands are suitable for Dy,<sup>15</sup> while larger Cot ligands better suit Er, for example.<sup>22-23</sup> Our group has extended this strategy for the development of SMMs of divalent Tm, a  $f^{13}$  metal ion, with the large aromatic Cot ligand.<sup>24</sup>

Another important finding is the report of intermediate valent states<sup>25</sup> occurring in these complexes, mostly for Yb and Ce, including the iconic  $\text{Yb}(\text{Cp})_3$ <sup>26</sup> and  $\text{Ce}(\text{Cot})_2$ .<sup>27</sup> In these compounds, the net valency of the metal center is not integer but intermediate and the ground and excited states can be described as a linear combination of several configurations, in which the valence is different. In these compounds, the relative energy of the ligand  $\pi$  and  $\pi^*$  orbitals compared to that of the f-orbitals plays an important role,<sup>28</sup> as well as the symmetry argument,<sup>29-31</sup> allowing or not the formation of open-shell singlet states.

The chemistry of large aromatic ligands was recently incremented by some of us and other groups, by the use of the cyclononatetraenyl (Cnt) ligand,  $\text{C}_9\text{H}_9$ , a Hückel aromatic monoanionic ligand (Chart 1). The Cnt ligand was synthesized in the 1960's<sup>32-33</sup> but is only scarcely used in combination with metals because of rather facile rearrangement to dihydroindene,<sup>34</sup> a bicyclic isomer. Nevertheless, the Cnt ligand proved to be very well adapted to large metal ion such as Ba.<sup>35</sup> Recently, a series of linear sandwich complexes of divalent lanthanide ions was reported by some of us<sup>36</sup> while the heteroleptic Er complex with the

Cot ligand was reported as a SMM.<sup>23</sup> The analysis of the heteroleptic Ln(Cot)(Cnt) series of the late lanthanide ions highlighted that the Cnt ligand may vary its coordination mode on lanthanides, depending on their size.<sup>37</sup> A particular attention was given to the great flexibility of the ligand, which is able to bend, moving away from the cationic charge of the metal without necessarily breaking the aromaticity. This interesting behavior is an important feature for any of the future reactivity studies with this ligand, while its electronics may significantly differ from the classical Cp ligand. Thus, this article reports the synthesis and characterization of a series of trivalent Ln(Cnt)<sub>3</sub> complexes and nicely highlight the bending flexibility of the ligand as well as the different electronics than that of the Cp ligand.

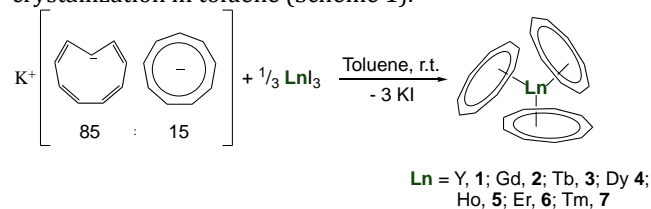
**Chart 1.** Known complexes of lanthanides with the Cnt ligand.



## RESULTS AND DISCUSSION

### Synthesis and solid-state structure.

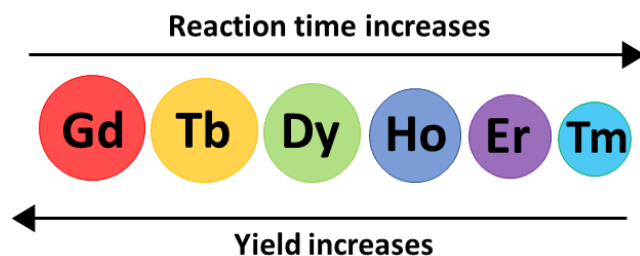
Potassium cyclononatetraenyl (KCnt) has two accessible isomers, namely, the *cis*- and *trans*-isomers, for *cis,cis,cis,cis*- cyclononatetraenyl and *cis,cis,cis,trans*-cyclononatetraenyl, respectively. In its *cis*-form all the carbon atoms are located in the same plane and the charge is delocalized over the all cycle. In the *trans*-form, one carbon atom is moved inside the ring, and the negative charge is thus mainly localized on this position (Scheme 1). For the synthesis of lanthanide complexes from halides, it is better to use an isomer mixture because of higher solubility, as demonstrated earlier.<sup>36,37</sup> The recrystallization of KCnt from diethyl ether gives a ratio of *trans*:*cis*-isomer up to 85:15. This mixture of isomers has been used in all the syntheses described in this work. The reaction of KCnt with lanthanide iodides in toluene yielded the series of complexes with general formula Ln(Cnt)<sub>3</sub>·tol (Ln = Y, **1**, Gd, **2**; Tb, **3**; Dy, **4**; Ho, **5**; Er, **6**) and Ln(Cnt)<sub>3</sub> (Ln = Tm, **7**) after crystallization in toluene (Scheme 1).



**Scheme 1.** Syntheses of Ln(Cnt)<sub>3</sub> **1-7**.

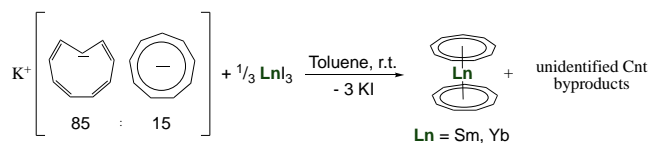
It should be noted that a molar ratio 3:1 is not strictly essential. The desired products can be obtained with 2:1

and 1:1 ratios of the starting products with lower yields, indicating the strong stabilization of the 3:1 complex in toluene and facile redistribution. Additionally, the KI side product is not greatly soluble in toluene, which simplify the purification. However, the non-polar nature of toluene makes the reaction completion time rather long, particularly for the late lanthanides with the smallest ionic radii, which required a few weeks of stirring to get acceptable yield (Figure 1). The reactions were performed at room temperature in order to allow the smooth isomerization of the Cnt ligand. At higher temperature, this isomerization is more difficult to control<sup>38</sup> as noted in a previous and more recent work.<sup>37</sup>



**Figure 1.** Dependence of the reaction time and yield on the ionic radii.

Thus, for Y, Gd, Tb, Dy (**1-4**), the reactions are completed within 3-4 days, while Ho-Er (**5, 6**) required 2-3 weeks and Tm (**7**) needed minimum 6 weeks to obtain a reasonable amount of the product. Interestingly, in the case of SmI<sub>3</sub>(THF)<sub>x</sub> and YbI<sub>3</sub>(THF)<sub>y</sub> (x = 4, y = 3), the reaction with three equivalents of KCnt led to the formation of the previously reported bis(cyclononatetraenyl) [Ln(Cnt)<sub>2</sub>] (Scheme 2).<sup>36</sup> Performing the reaction in the presence of soft oxidants such as AgI, FeCl<sub>3</sub> did not yield the desired Sm(Cnt)<sub>3</sub> and Yb(Cnt)<sub>3</sub>. This spontaneous reduction is rather interesting and is reminiscent from the steric induced reduction (SIR) that was proposed by Evans at the end of the 1990's.<sup>39</sup> The question here is whether this case only relies on the sterics of the complexes or if there is a possible electronic contribution to this reduction since most examples are known with very bulky Cp substituents.



**Scheme 2.** Reaction of KCnt with Yb and Sm; formation of Ln(Cnt)<sub>2</sub> (Ln = Yb, Sm).

Thus, several points are important noting. First, several smaller elements than Sm are stable,<sup>40</sup> meaning that the sterics is only one of the possible contributions; the redox potential of the final product must be affordable to allow reduction. A series of Cp\*<sub>3</sub>Ln complexes with smaller lanthanides (Ln = Tb, Dy, Ho, Er) were obtained by a mechanochemical method to avoid C-H bond activation, which occurs when the crowded complexes react with aromatic solvents (benzene and toluene).

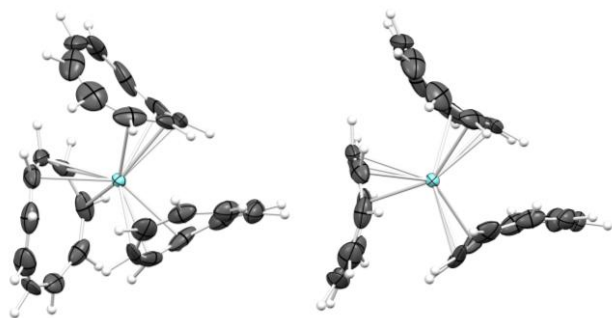
**Table 1.** Main structural parameters for **1-7**.

	Y	Gd	Tb	Dy	Ho	Er	Tm
Ln-C(closest)	2.58(1)	2.63(2)	2.61(2)	2.58(3)	2.59(2)	2.56(1)	2.54(1)
Ln-C(farthest)	4.40(18)	4.41(18)	4.40(19)	4.41(18)	4.42(18)	4.43(18)	4.48(3)
Ln-C <sup>9</sup> (average) <sup>a</sup>	3.35(7)	3.38(9)	3.37(10)	3.37(10)	3.37(10)	3.37(11)	3.40(3)
Ln-C <sup>4</sup> (average) <sup>b</sup>	<b>2.69(14)</b>	<b>2.73(12)</b>	<b>2.71(13)</b>	<b>2.70(14)</b>	<b>2.69(14)</b>	<b>2.69(15)</b>	<b>2.67(16)</b>

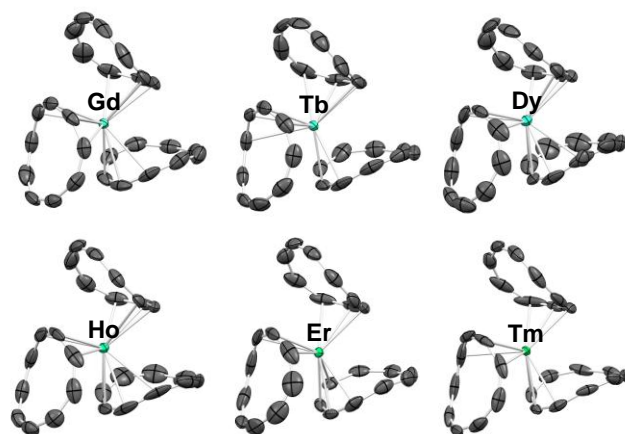
a) average of the nine carbon atoms in the Cnt ring b) average of the four closest carbon atoms in the Cnt ring

Second, the redox potential of the Cnt<sub>2</sub>Ln complexes was estimated higher than that of the Cp\*<sub>2</sub>Ln, indicating that the spontaneous reduction is thus facilitated by the redox potential of the final divalent product. Third, it is noticeable that the electronic structure of the Cp<sub>3</sub>Ln analogues of Eu and Yb ions have multiconfigurational intermediate valence states and Denning *et al.* estimated the charge transfer extent for Cp<sub>3</sub>Yb. It means that, while these complexes are stable, partial formal electronic reduction occurs. Thus, if any charge transfer is a first step before a possible complete reduction, it is worth to look at the fate of the next reducible lanthanides after Yb and Sm, that is Tm. Several hints will be detailed in the next paragraphs.

The crystals of the Ln(Cnt)<sub>3</sub> were easily obtained after concentration of the filtered toluene solution by reducing the temperature to -35°C. All the complexes, except Tm(Cnt)<sub>3</sub>, crystallized with one solvent molecule, which could be easily removed by washing with pentane and further drying under reduce pressure. Complexes were sparingly soluble in diethyl ether and crystalized without solvent, similarly to Tm(Cnt)<sub>3</sub>. For example, the crystal structures of Tb(Cnt)<sub>3</sub> was also obtained in this way (Figure S12). The IR spectra of complexes in the 4000–600 cm<sup>-1</sup> range confirmed the presence of an organic ligand with weak broad bands at 3010–3000 cm<sup>-1</sup> that were attributed to the ν(C–H) of the Cnt ring (Figure S13).

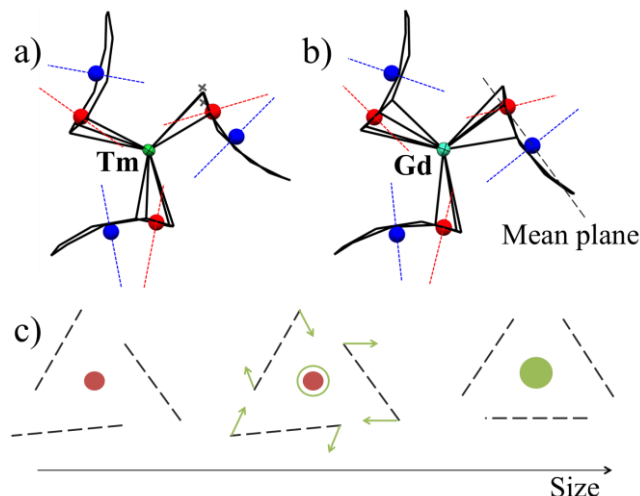
**Figure 2.** Structure of the Y(Cnt)<sub>3</sub> complex, **1**.

X-ray analysis revealed that the complexes of Gd–Er and Y (**1-6**) are isostructural (Figure 2 and 3) and crystallized in the orthorhombic system *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group with one toluene molecule. The Tm(Cnt)<sub>3</sub> complex crystallized in *P*-1 space group. All Cnt rings are crystallographically distinct.

**Figure 3.** Structures of the Ln(Cnt)<sub>3</sub> complexes (Ln = Gd, **2**; Tb, **3**; Dy, **4**; Ho, **5**; Er, **6**; Tm, **7**).

All structures have similar coordination mode of the Cnt ligand, which coordinate in an apparent η<sup>4</sup>-fashion. Although the ligand remains aromatic, with no significant alternation of the C–C bond distances and no significant distortion of the C sp<sup>2</sup> hybridization, it is clearly noticeable that the ligand bends rather strongly with a mean deviation from planarity (dashed line, Figure 4c) of 0.19(9) Å for **2** and 0.17(9) for **7**. Additionally, because of the size of the ligand, the centroids formed by the nine carbon atoms (blue, Figure 4a,b) of the Cnt ligand are away from the metallic coordination (blue lines, Figure 4). Nonetheless, the centroids formed by the four closest carbon atoms (red, Figure 4a,b) are also away from the later (red lines, Figure 4), indicating an intermediate situation. It is now rather interesting to follow the evolution along the series. First the shortest Ln–C bond range from 2.63(2) Å in **2**, which is the largest lanthanide ion to 2.54(1) Å in **7**, which is the smallest. The evolution thus nicely follows the lanthanide contraction of ionic radii (see Table 1). Additionally, the L–C average distance of C1–C4 also nicely follows this evolution. However, this trend is less clear with the farthest carbon atom distance because the esd (estimated standard deviations) on the mean distance is large. Likewise, the average Ln–C distance on all carbon atoms is rather similar in all compounds. This can be explained by a dynamic coordination of the Cnt ligand: an increased size of the atom logically pushes away the closest carbon atoms but also allows accommodating more density from the farthest carbon atoms, which are then getting closer. Thus, the overall breathing movement of the Cnt in the tris-Cnt

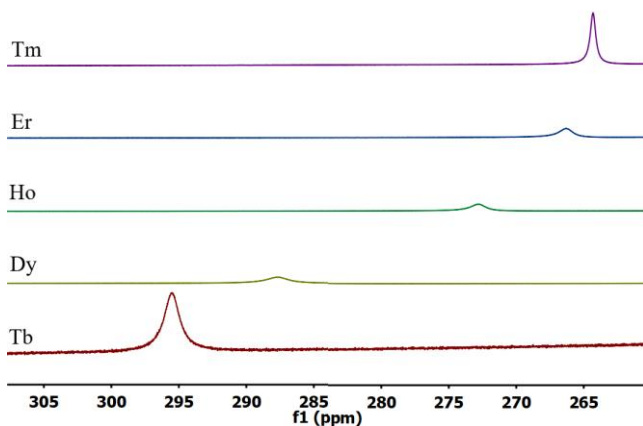
compounds is not a linear shift but rather a pivot of the overall ligand (Figure 4c).



**Figure 4.** Schematic representation of the structural parameters of **7** (a), and **2** (b) and of the pivot movement with increasing size (c). The blue balls are for the C9 centroids, red for the C4 centroids. Orange and green balls represent the Ln atom, which size increases and the arrow the movement of the Cnt ligand (see text for description).

**Solution structure.** All the complexes remain stable in solvents such as benzene, toluene and diethyl ether. The lability of the Cnt ligand prevented us to use good coordinating solvents, such as THF, for the studies to ensure the Cnt coordination. The  $^1\text{H}$  NMR spectra in  $\text{C}_6\text{D}_6$  for all complexes (except Gd) show similar trends. For the diamagnetic  $\text{Y}(\text{Cnt})_3$  complex, **1**, a sole singlet related to the Cnt ligand at 6.27 ppm was observed (Figure S1). The lower value of chemical shift in **1** compared with starting KCnt (6.94 ppm) can be explained by its coordination. Because of the electronic nature of  $\text{Gd}(\text{Cnt})_3$ , **2**, the  $^1\text{H}$  NMR remained silent. However, all the other paramagnetic complexes, **3-7**, could be analyzed by this technique (Figure 5).

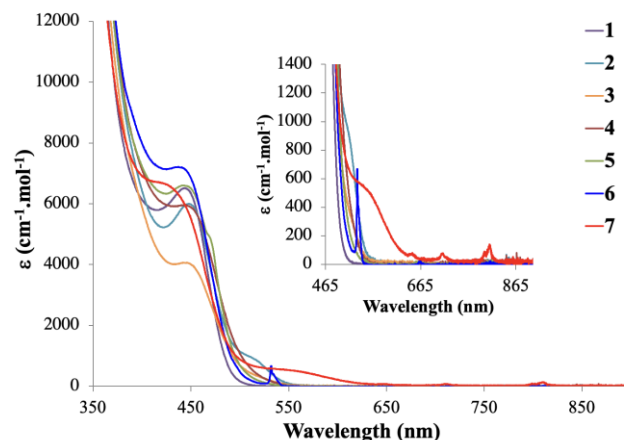
Within the series, one singlet was observed at 295, 287, 273, 266, 264 ppm for **3** to **7**, respectively. Variable-temperature (VT) NMR of **1** showed no decoalescence of the singlet in the  $-80$  to  $+80$  °C temperature range, indicating no significant modification in its coordination environment.



**Figure 5.**  $^1\text{H}$  NMR spectra of **2-7** recorded in toluene- $d_8$ .

UV-visible absorption spectra for all the complexes in toluene solution are shown in Figure 6. All compounds possess a strong absorption in UV region with a band in the visible area. This band has a maximum in rather small wavelength range (439-447 nm). This characteristic is typical for a ligand  $\pi$  to  $\pi^*$  transition. Note that the starting *cis-cis-cis* KCnt salt absorbs only in the UV with bands at 252, 318, and 325 nm in THF solution and the solution is very pale yellow.<sup>32</sup>

It is noteworthy that the UV spectra of  $\text{Er}(\text{Cnt})_3$ , **6** and  $\text{Tm}(\text{Cnt})_3$ , **7**, exhibit low intensive bands at 532 and 787 nm, for **6** and **7**, respectively (Figure 6). These bands may be assigned to the hypersensitive transitions  $^2\text{H}_{11/2} \leftarrow ^4\text{I}_{15/2}$  at 532 nm for **6** and  $^3\text{H}_4 \leftarrow ^3\text{H}_6$  at 810 nm for **7**.<sup>41-42</sup> For **5** (Ho), **2** (Gd) and **7** (Tm) an additional band (shoulder) is present at 470, 530 and 610 nm, respectively. In the Tm case, this band is rather interesting since the  $\epsilon$  value is around  $500 \text{ cm}^{-1}\text{M}^{-1}$  in agreement with charge-transfer bands.

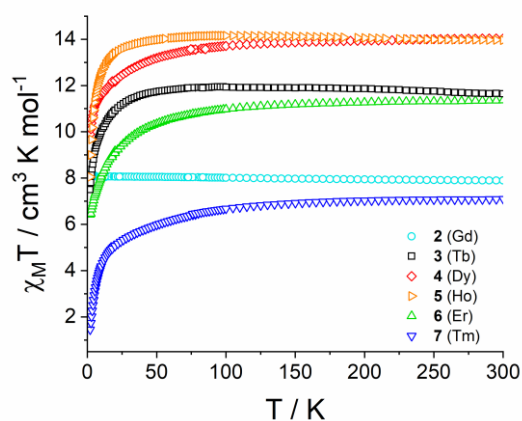


**Figure 6.** Normalized UV-Vis spectra of **1-7** (Concentrations in toluene;  $1.4 \cdot 10^{-4}$  M, **1**;  $7.0 \cdot 10^{-5}$  M, **2**;  $1.0 \cdot 10^{-4}$  M, **3**;  $6.2 \cdot 10^{-5}$  M, **4**;  $1.2 \cdot 10^{-4}$  M, **5**;  $1.2 \cdot 10^{-4}$  M, **6**;  $1.4 \cdot 10^{-4}$  M, **7**)

As mentioned above all the tris-Cnt complexes are not stable in presence of air. Thus, when the UV-cuvettes were opened and left for few seconds, an immediate color change arised from bright orange (yellow for **1**) to intensive blue-violet. In the UV-Vis spectra, an absorption bands appeared around 600 nm with a shoulder at around 540 nm. (Figure S2). No hypersensitive transitions for **6** and **7** were observed in the oxidized products.

**Magnetic data.** Magnetic data were carried out on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet (Figure 7). In order to preserve the magnetization in linear regime as a function of the external field  $H$  ( $\chi_M = M/H$ ), the magnetization data were collected with an external magnetic field of 200 Oe in the temperature range of 1.9–20 K, of 2000 Oe in the temperature range of 18–80 K and of 10000 Oe in the temperature range of 76–300 K. The experimental magnetic susceptibility data are corrected for the diamagnetism and sample holder. Due to possible crystallite reorientation issues and because of the instability of the compounds in air, **3** and **7** were pelletized

in inert atmosphere glovebox and sealed into NMR tubes before the measurements. Magnetic susceptibility data for the complexes **2-7** are presented in Figure 6. The values at room temperature of 7.9, 11.6, 14.0, 14.0, 11.3 and 7.1  $\text{cm}^3 \text{K mol}^{-1}$  for **2-7** respectively are in good agreement with the calculated Curie constants for the ground state, which is 7.88  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^8S_{7/2}$  multiplet of  $\text{Gd}^{\text{III}}$ , **2** ( $g_J=2$ ), 11.82  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^7F_6$  multiplet of  $\text{Tb}^{\text{III}}$ , **3** ( $g_J=3/2$ ), 14.17  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^6H_{15/2}$  multiplet of  $\text{Dy}^{\text{III}}$ , **4** ( $g_J=4/3$ ), 14.07  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^5I_8$  multiplet of  $\text{Ho}^{\text{III}}$ , **5** ( $g_J=5/4$ ), 11.48  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^4I_{15/2}$  multiplet of  $\text{Er}^{\text{III}}$ , **6** ( $g_J=6/5$ ), and 7.15  $\text{cm}^3 \text{K mol}^{-1}$  for a  $^3H_6$  multiplet of  $\text{Tm}^{\text{III}}$ , **7** ( $g_J=7/6$ ).  $\chi_{\text{M}}T$  decreases for **3-7** on cooling, which means that the degeneracy of the ground state multiplet is removed by the crystal field for all compounds. In contrast,  $\chi_{\text{M}}T$  remains constant for spin-only compound **2**. In absence of external dc field, the relaxation of the magnetic moment does not slow down, meaning that **2-7** do not behave as Single-Molecule Magnets in zero field.



**Figure 7.** Temperature dependent  $\chi_{\text{M}}T$  values for **2-7**.

**Computational studies.** Ab initio computations based on X-ray diffraction structures were done at the SA-CASSCF/RASSI-SO level for **3-7** (computational methods in supplementary information). The calculated wave-functions energies and g-tensors for ground and excited states of **3-7** are presented in Tables S1, S3, S5-S7.

The two smallest ions, terbium and dysprosium, present a calculated ground state of almost pure  $m_j=\pm 6$  (98%) and  $m_j=\pm 15/2$  (89%) respectively, unlike the other systems. The holmium system, **5**, shows highly mixed ground state of  $m_j=\pm 7$  (40%) and  $m_j=\pm 8$  (30%), and the erbium-based complex, **6**, also presents a ground state mixed between  $m_j=\pm 15/2$  (50%) and  $m_j=\pm 9/2$  (23%). In the thulium system, **7**, the crystal-field leads the non-Kramers ion's ground state to be distinctly non-degenerated, and slightly mixed, with one state  $m_j=\pm 6$  (78%) and the other  $m_j=\pm 6$  (88%) at 6  $\text{cm}^{-1}$ , which indicates that the magnetic anisotropy of this compound is not completely axial. The  $2J+1$  states overall splitting is small for each ion, with all excited states within 117, 177, 168, 186 and 172  $\text{cm}^{-1}$  for **3-7**, respectively. Their first excited state are likewise found low in energy, from 5.7  $\text{cm}^{-1}$  for  $\text{Tm}(\text{Cnt})_3$  to 56  $\text{cm}^{-1}$  for  $\text{Dy}(\text{Cnt})_3$ , and all possess clearly mixed configurations.

The small overall splitting and the absence of significant gap between ground state and first excited state, allied to the important mixing of the  $m_j$  states rationalize well the experimental measured fast decrease of  $\chi_{\text{M}}T$  on cooling below 50 K and the absence of Single-Molecule Magnet behavior for **3-7**. Those data suggest that the three Cnt ligands form an almost spherical-shaped crystal field.

Computations at the CASPT2/RASSI-SO level were carried out to attempt to better describe the ground state and the first excited states by taking into account dynamical correlation. The CASPT2 wave-functions and computed energies are presented in Tables S2, S4 and S8 and the computed magnetic susceptibility and magnetization are presented in Figures S3-S4. The CASPT2 computations for the Er and Ho did not converge on reliable results, and thus will not be discussed here. For **3, 4** and **7**, the overall splitting is bigger than the CASSCF computed one, with all excited states within 140, 219, and 264  $\text{cm}^{-1}$  respectively. The nature of the ground state remains relatively similar with an increased mixing for **3** and **4**, while it is strongly different for **7** with  $m_j=\pm 5$  (62%) and  $m_j=\pm 5$  (33%) instead of  $m_j=\pm 6$  (78%) and  $m_j=\pm 6$  (88%). The excited states are strongly mixed, and the first excited multiplets are close to the ground states. The modification of the nature of the ground state allied with the increasing of the overall splitting and the energetical proximity between the ground and the first excited states lead to a better description of the experimental data.

**Conclusions.** In conclusion, this article presents the synthesis of a series of trivalent tris-Cnt complexes of the late lanthanide ions. The large Cnt ligand strongly bends in order to adapt to the size of the metal ion and evolves along the series by swinging over the latter in order to accommodate the maximum electronic density. The Sm and Yb complexes have not been prepared because the reaction of trivalent Sm and Yb halides with the potassium salt of the Cnt led to the known bis-Cnt complexes of divalent oxidation state. This spontaneous reduction reactivity has been already reported in the literature with large organometallic ligands and an electronic contribution was proposed to explain this reactivity. The complexes have strong charge transfer bands in the visible and the Tm and Er complexes exhibit hypertensive f-f transitions. The magnetic data were recorded and rationalized on the basis of computations at the CASSCF/RASSI-SO or CASPT2/RASSI-SO levels. The overall density provided by the multiple hapticity of the large Cnt ligands suggests an almost spherical crystal field. This structural study validates that the use of the large monoanionic Cnt ligand will provide significantly different structures and reactivity than the classical Cp and Cot ligand.

## EXPERIMENTAL SECTION

**General considerations.** All the reactions were performed using standard Schlenk-line techniques and in Ar-filled gloveboxes (MBraun). All glassware was dried at 100°C overnight before use. All solvents were dried over Na, degassed and transferred under reduced pressure in a cold flask. KCnt salt was prepared according to reported procedures of the literature<sup>32-33</sup> and recrystallized from diethyl ether to obtained the *trans*-form in a 85:15 ratio.<sup>36</sup>  $\text{LnI}_3$  salts were purchased from Aldrich and Alfa Aesar. NMR spectra were recorded in 5 mm tubes adapted with a

J. Young valve on Bruker 300 MHz Avance III spectrometers. Chemical shifts are expressed relative to TMS in ppm. Visible spectra were recorded in the 300–1000 nm range at room temperature on an Agilent Cary 60 Spectrometer in 10 mm quartz cuvettes in toluene. The solvent background was corrected. Elemental Analyses were done at the Mikroanalytischer Labor Pascher. The EA samples were dried under reduced pressure in order to remove the remaining solvents molecules. Several elemental analyses showed significant differences on the C mass percentage although they were tried multiple times. It is possible that these differences may be due to the high reactivity of the complexes and the possible formation of highly refractory Ln carbides.

**X-ray crystallography.** Single crystals of **1-7** were coated in Paratone-N oil and mounted on a Kapton loop on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD detector and a graphite Mo-K $\alpha$  monochromator (Nonius, Delft, Netherlands). All data were measured at 150 K under a nitrogen stream and a refinement method was used for solving the structure. The structure solution and the refinement were achieved with the Olex software.<sup>43</sup> Figures of the compound structure were obtained using the MERCURY softwares.<sup>44</sup> The hydrogen atoms were included in the geometrically calculated position and refined. Crystallographic data and refinement statistics are given in Table S9.

**Syntheses.** *Preparation of Tris(cyclononatetraenyl)yttrium (1).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and YI<sub>3</sub> (47.0 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 3–4 days until the color of the solution became intense yellow. After the insoluble remains were filtered, a yellow filtrate was concentrated and left at -35 °C. Large yellow crystals were obtained in few hours and were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of **1** can be obtained by further concentration of the filtrate. Total yield: 15 mg (34%). IR (ATR): 3006 (w), 2920 (w), 783 (s), 658 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz,  $\delta$ /ppm): 6.27 (s, 27H). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Y: C, 73.64; H, 6.14. Found: C, 73.14; H, 6.20.

*Preparation of Tris(cyclononatetraenyl)gadolinium (2).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and GdI<sub>3</sub> (53.8 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 3 days until the color of the solution became intense orange. After the insoluble remains were filtered, the orange filtrate was concentrated and left at -35 °C. Large orange crystals were obtained in few hours and were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of the filtrate. Total yield: 19 mg (37%). IR (ATR): 3006 (w), 2930 (w), 779 (s), 653 (s). The <sup>1</sup>H NMR in C<sub>6</sub>D<sub>6</sub>, 300 MHz remains silent. Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Gd: C, 63.78; H, 5.31. Found: C, 62.00; H, 5.24.

*Preparation of Tris(cyclononatetraenyl)terbium (3).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and TbI<sub>3</sub> (54.0 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 4 days until the color of the solution became intense orange. After the insoluble remains were filtered, an orange filtrate was concentrated and left at -35 °C. Large orange crystals were obtained in few hours and were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of the filtrate. Total yield: 19 mg (37%). IR (ATR): 3002 (w), 2924 (w), 779 (s), 653 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz,  $\delta$ /ppm): 295.5 (s). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Tb: C, 63.53; H, 5.29. Found: C, 62.68; H, 5.31.

*Preparation of Tris(cyclononatetraenyl)dysprosium (4).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and DyI<sub>3</sub> (54.3 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 4 days until the color of the solution became intense orange. After the insoluble remains were filtered, an orange filtrate was concentrated and left at -35 °C. Large orange

crystals were obtained in few hours and were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of the filtrate. Total yield: 17 mg (33%). IR (ATR): 3002 (w), 2924 (w), 779 (s), 653 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz,  $\delta$ /ppm): 287.5 (s). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Dy: C, 63.04; H, 5.25. Found: C, 61.61; H, 5.20.

*Preparation of Tris(cyclononatetraenyl)holmium (5).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and HoI<sub>3</sub> (54.6 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 14 days minimum until the color of the solution became intense orange. After the insoluble remains were filtered, an orange filtrate was concentrated and left at -35 °C. Large orange crystals were obtained in few hours and they were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of filtrate. Total yield: 11 mg (21%). IR (ATR): 3002 (w), 2924 (w), 779 (s), 658 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz,  $\delta$ /ppm): 273.0 (s). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Ho: C, 62.79; H, 5.23. Found: C, 62.31; H, 5.26.

*Preparation of Tris(cyclononatetraenyl)erbium (6).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and ErI<sub>3</sub> (54.8 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 21 days minimum until the color of the solution became intense orange. After the insoluble remains were filtered, an orange filtrate was concentrated and left at -35 °C. Large orange crystals were obtained in few hours and they were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of filtrate. Total yield: 12 mg (23%). IR (ATR): 3011 (w), 2944 (w), 779 (s), 653 (s). <sup>1</sup>H NMR (tol-D<sub>8</sub>, 300 MHz,  $\delta$ /ppm): 266.5 (s). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Er: C, 62.55; H, 5.21. Found: C, 62.00; H, 5.24.

*Preparation of Tris(cyclononatetraenyl)thulium (7).* 6 mL of toluene was added to a solid mixture of KCnt (47.1 mg, 300  $\mu$ mol) and ErI<sub>3</sub> (54.8 mg, 100  $\mu$ mol) prepared in a glass vial. The mixture was stirred during 40 days minimum until the color of the solution became intense orange-brown. After the insoluble remains were filtered, a brown filtrate was concentrated and left at -35 °C. Large brown crystals were obtained in few hours and they were filtered and washed with pentane, dried and stored at -35 °C. Additional amount of product can be obtained by further concentration of filtrate. Total yield: 8 mg (15%). IR (ATR): 3006 (w), 2924 (w), 779 (s), 653 (s). <sup>1</sup>H NMR (tol-D<sub>8</sub>, 300 MHz,  $\delta$ /ppm): 264.3 (s). Elemental analysis: calcd. for C<sub>27</sub>H<sub>27</sub>Tm: C, 62.31; H, 5.19. Found: C, 61.55; H, 5.19.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. <sup>1</sup>H NMR, magnetic and crystallographic data with structures deposited at the CCDC with #2113686-2113693 for **1-8**, respectively.

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The authors declare no competing financial interests.

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**Table of Content Graphics.**

