First homoleptic rare earth metal complexes with doubly-reduced dibenzocyclooctatetraene

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First Homoleptic Rare Earth Metal Complexes with Doubly-Reduced Dibenzocyclooctatetraene

By

James C. Mahoney

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ABSTRACT

A set of novel complexes of rare earth elements, M(III) = Y, La, Gd, Tb, and Dy, with the doubly-reduced dibenzo[a,e]cyclooctatetraene (DBCOT) anion has been synthesized and crystallographically characterized for the first time. Preparation of new complexes has been accomplished through the ligand-metathesis reaction of M(III) triiodides with K₂(DBCOT) in THF at ambient conditions. Subsequent crystallization via slow solvent evaporation afforded single crystals of good quality. X-ray diffraction technique confirmed that all complexes are isomorphous and conform to the [M(DBCOT)(THF)₄][M(DBCOT)₂] composition. In their crystal structures, the monoanionic double-decker sandwiches, [M(DBCOT)₂]⁻, weakly interact with the cationic counterparts, [M(DBCOT)(THF)₄]⁺. In both parts, the DBCOT²⁻ anions exhibit η⁸-coordination to metal centers with the M–C(DBCOT) bond length distances following the trends in ionic radii for the rare earth metals. In addition to single-crystal X-ray diffraction, all products have been characterized using UV-vis and IR spectroscopic methods. The complexes of diamagnetic Y(III) and La(III) have also been characterized by ¹H NMR spectroscopy. This new family represents the first structurally characterized homoleptic complexes of lanthanides with the doubly-reduced DBCOT²⁻ anions, opening up broad investigation of their properties and applications.
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Chapter 1: Introduction

The structures and properties of cyclooctatetraene (COT) and its aromatic dianion (COT$^{2−}$) are of special importance in organometallic chemistry. The addition of two electrons to boat-shaped COT is accompanied by aromatization and planarization of the COT$^{2−}$ core (Scheme 1). The first chemical reduction of COT to afford COT$^{2−}$ anion was reported back in 1960.\textsuperscript{1} This was followed by the discovery of uranocene, [U(COT)$_2$], representing the first complex of COT$^{2−}$ and an $f$-block element reported in 1968 by Streitwieser and Mueller-Westerhoff.\textsuperscript{2} Since then, the organometallic complexes of lanthanides with cyclooctatetraenyl dianions (COT$^{2−}$) have been the subjects of extensive research and found a variety of applications ranging from catalysis to optical and magnetic materials.\textsuperscript{3-6} In addition, the controlled modification of the COT rings has been broadly utilized in order to increase bulkiness and to tune properties of Ln–COT complexes.\textsuperscript{7-9} Due to a large number of unpaired $4f$-electrons of lanthanides,\textsuperscript{10} the main frontier of these studies has been recently shifted to single-molecule magnets (SMMs).\textsuperscript{11-13}

Scheme 1. Reduction of COT to COT$^{2−}$.

Homometallic Ln–COT complexes have been found to exhibit several major structural types, depending on the Ln:COT ratio and the oxidation state of the lanthanide ion. For example, Ln(IV)–COT complexes form a double-decker sandwich structure (A, Scheme 2) of the [Ln(COT)$_2$] composition. The known product of this type is [Ce(COT)$_2$] which was synthesized
and structurally characterized in 1976. The Ln(III)–COT complexes have been studied more extensively and the structural variations are based on the ratio of Ln(III):COT. The Ln(III)–COT complexes with a 1:1 ratio can form the halide-bridged dimeric structures (B) and also exist as mononuclear piano stool complexes (C). The first dimeric complex of type B was reported in 1971. Since then the series has been expanded allowing for some interesting magnetic studies. In 1989, the first piano-stool complex was reported followed by a second example in 2008. The Ln(III)–COT complexes can also form homometallic triple-decker sandwich architectures. The first triple-decker sandwich, [Nd₂(COT)₃(THF)₂] (D), was synthesized and characterized in 1972. In 2019, this series has been expanded in our group to include two new [M₂(COT)₃(THF)₂] members with M = Y and La.

\[ \textbf{Scheme 2. Homometallic Ln–COT complexes.} \]

In addition to homometallic complexes, several heterometallic Ln–COT products have been synthesized and crystallographically characterized. The Ln(II) metal ions tend to form a COT-based sandwich with two M(I) cations coordinating to the sandwich exterior (E, Scheme 3).
The first crystal structure of this type was published in 1985\textsuperscript{25} followed by the family expansion and extensive magnetic studies.\textsuperscript{5,26,27} Similarly, heterometallic Ln(III)–COT complexes form the double-decker sandwich structures with a coordinated or solvent-separated M(I) cation (F).\textsuperscript{28-30} In 1991, a mixed metal product featuring alternating Ln(III) and M(I) metal centers separated by COT\textsuperscript{2–} rings (G) has been reported.\textsuperscript{31} This series was further expanded in 2014\textsuperscript{32} and 2021\textsuperscript{27} along with magnetic property studies. In 2022, a series of heterotrimetallic COT-based triple-decker aggregates (H) has been prepared and crystallographically characterized in our group, accompanied by a comprehensive investigation of magnetic properties coupled with calculations.\textsuperscript{33}

\begin{center}
\includegraphics[width=\textwidth]{Scheme3.png}
\end{center}

Scheme 3. Heterometallic Ln–COT complexes.

Fusion of the COT core with additional aromatic groups has been broadly used to access new π-expanded polycyclic hydrocarbons with a central eight-membered ring.\textsuperscript{34-36} For example, fusion of two six-membered rings to the COT core at the $a$ and $e$ positions affords sym-dibenzo[$a,e$]cyclooctatetraene (DBCOT). Like COT, DBCOT can readily accept two electrons upon chemical reduction to form an aromatic and planarized dianion (Scheme 4).\textsuperscript{37} Moreover, DBCOT was also shown to exhibit rich coordination chemistry in its neutral state.
In 1969, the coordination abilities of DBCOT with Cr(CO)$_3$ and Mo(CO)$_3$ were investigated using spectroscopic methods, resulting in the formation of the first organometallic complexes of DBCOT. Using $^1$H NMR spectroscopy, Cr(CO)$_3$ groups were found to $\eta^6$-coordinate $\text{syn}$ to the benzene rings of DBCOT (I) while Mo(CO)$_3$ was found to $\eta^4$-coordinate to the $\pi$-bonds of the central COT ring (J, Scheme 5).$^{38}$ In 2000, the structure of [(anti-Cr(CO)$_3$)$_2$(DBCOT)] was reported and indicated that DBCOT is flattened somewhat when complexed in this manner (K).$^{39}$ In 2005, complexes of Ir(I) and Rh(I) $\eta^4$-coordinated to $^8$DBCOT were studied and showed potential as catalysts in hydrogenation with H$_2$ as well as in transfer hydrogenation reactions.$^{40}$ The dinuclear chloride-bridged complexes of Ir(I) and Rh(I) with DBCOT, namely [Ir(DBCOT)(μ-Cl)$_2$] and [Rh(DBCOT)(μ-Cl)$_2$] (L), were reported in 2008. Both featured $\eta^4$-coordination of the metal centers to the central ring of DBCOT.$^{41}$ The Ir(I)-DBCOT complexes were further investigated as catalysts and showed potential for catalysis in air.$^{42,43}$ In 2009, the strained-ring DBCOT complexes with $\eta^2$-coordination of Ni(0) were synthesized and crystallographically characterized.$^{44}$

**Scheme 4.** Reduction of DBCOT to DBCOT$^{2-}$. 

![Scheme 4](image-url)
Like COT, DBCOT has been proven to also obey the Hückel’s rule and to form an aromatic eight-membered ring upon two-electron acquisition. This was first accomplished in 1965 via electrochemical and chemical reduction reactions with Li, Na, and K metals in THF, using NMR and EPR spectroscopy for in situ product characterization.\textsuperscript{37} Several additional electrochemical studies with characterization of the electronic states of DBCOT upon reduction have followed.\textsuperscript{45,46} In 1996, the first crystal structure of the doubly-reduced DBCOT has been reported in the form of its complex with lithium(I) ions, [Li$_2$(DBCOT)(TMEDA)$_2$] (M, Scheme 6).\textsuperscript{47} This was not only the first structure which featured a DBCOT$^{2-}$ anion, but also the first structure that displayed $\eta^8$-coordination to the central eight-membered ring.

**Scheme 5.** Transition metal complexes with neutral DBCOT.
Very recently, a broad investigation of chemical reduction behavior of DBCOT with all Group 1 metals has been carried out in THF. Several crystal structures featuring DBCOT$^{2-}$ anions with Li(I), Na(I), K(I), Rb(I), and Cs(I) counterions have been reported in 2020. Notably, the use of different secondary coordinating agents has allowed to fine-tune the metal binding and solid-state packing for the series. It also allowed the isolation of the first “naked” DBCOT$^{2-}$ anion lacking any metal ion π-interactions in the solid-state, which clearly demonstrated planarization of the ligand core upon two-electron acquisition. Additionally, the electron density localization on the central eight-membered ring of DBCOT$^{2-}$ anion has been revealed computationally, consistent with the primary metal coordination site observed crystallographically. Importantly, several alkali metal salts of DBCOT$^{2-}$ isolated in this study did not require the use of secondary coordinating agents, thus affording effective ligand-transfer reagents to be utilized in future synthesis involving transition or rare earth metals.

In 2020, the crystal structure of [KY(DBCOT)$_2$(THF)$_2$] has been reported as part of a thesis which contained the first rare earth metal, Y(III), coordinated to the DBCOT$^{2-}$ anion. In 2022, the first Ln–DBCOT complex has been crystallographically characterized as [K(crypt-
While this has been a significant accomplishment, the crystal structure of this heteroleptic complex exhibited $\eta^2$-coordination of Dy(III) ion to the central ring of DBCOT$^{2-}$ (N, Scheme 6). Importantly, the applicability of the new material as a SMM has been tested and the complex was found to have SMM characteristics.$^{50}$ To this date, no crystallographically confirmed examples of Ln–DBCOT complexes featuring $\eta^8$-coordination have been reported.

Therefore, we have chosen to focus on design synthesis of homoleptic Ln–DBCOT complexes and selected several rare earth metals for this work, namely M(III) (M = Y, La, Gd, Tb, and Dy). In this thesis, we present a novel series of organometallic complexes of the formula [M(DBCOT)(THF)$_4^+$][M(DBCOT)$_2^-$] and report their preparation and full characterization, using X-ray diffraction and spectroscopic techniques.
Chapter 2: Results and Discussion

Synthesis and Characterization

All products were synthesized by reacting K₂DBCOT with rare earth metal iodides, MI₃, at room temperature in THF under inert atmosphere (Scheme 7). Black K₂DBCOT powder was prepared using the previously developed procedure and dried prior to use. Overall, five new complexes have been synthesized with M = Y, La, Gd, Tb, and Dy (See the Experimental Section for more details). The products were crystallized via slow solvent evaporation at elevated temperatures in the sealed L-shaped glass ampules. After 7-14 days, orange or brown block-shaped crystals have deposited in moderate yields. The X-ray crystallography (vide infra) revealed that all products have the \([M(DBCOT)(THF)_{4}^+][M(DBCOT)_2^-]\) composition.

\[
\begin{align*}
2 \text{ MI}_3 & \underset{\text{THF, 25 °C, 48 h}}{\xrightarrow{3 \text{ K}_2\text{DBCOT}}} \text{M}_2(\text{DBCOT})_3(\text{THF})_4 \\
\end{align*}
\]

Scheme 7. Preparation of new complexes: 1-Y, 2-La, 3-Gd, 4-Tb, and 5-Dy.

The purity of bulk products was determined via X-ray powder diffraction for 3-Gd, 4-Tb, and 5-Dy (See Figures S5, S6, and S7 in the Experimental Section) and \(^1\)H NMR spectroscopy for 1-Y and 2-La.

In the \(^1\)H NMR spectrum of 1-Y, two sets of signals with a ratio of 1:2 for DBCOT\(^{2-}\) anions that correspond to both the cationic and anionic moieties can be identified. Signals of the cationic moiety, [Y(DBCOT)(THF)\(_{4}^+\)], appear as multiplets at 6.81 ppm and 7.84 ppm with a singlet at 7.42 ppm (Figure 1). Compared to the doubly-reduced DBCOT\(^{2-}\) species generated with K metal, the proton signals in the cationic part of 1-Y show a similar pattern but are more deshielded,
spreading over a narrower range (6.81–7.84 ppm vs. 6.19–7.87 ppm in K$_2$DBCOT). For the anionic sandwich [Y(DBCOT)$_2$], the corresponding signals appear as multiplets at 6.65 ppm and 7.40 ppm along with a singlet at 6.34 ppm (Figure 1). These values are comparable to those reported by Bloch for [K(DME)$_2$Y(DME)(DBCOT)$_2$]. The proton signals of the terminal six-membered rings show smaller variations (6.65–7.40 ppm vs. 7.01–7.10 ppm in K$_2$DBCOT), but that of the central eight-membered ring is much more shielded (6.34 ppm vs. 7.17 ppm in K$_2$DBCOT).

**Figure 1.** $^1$H NMR spectrum of 1-Y in THF-$d_8$ at 25 °C (aromatic region) with chemical shifts marked red and blue for the cationic and anionic moieties.

In contrast, the $^1$H NMR spectrum of 2-La shows two broad peaks at room temperature. Only as the temperature drops below –20 °C, the proton signals of DBCOT$^{2−}$ start to appear and can be assigned to the cationic and anionic moieties (Figure 2). Signals corresponding to the
cationic moiety, [La(DBCOT)(THF)]^+], appear as broad peaks at 6.70 ppm and 7.81 ppm, along with a singlet at 7.23 ppm. Compared to 1-Y, the proton signals corresponding to [La(DBCOT)(THF)]^+ are slightly upfield shifted. For the anionic sandwich [La(DBCOT)_2^-], the corresponding signals are slightly downfield shifted in comparison to 1-Y and appear as multiplets at 6.59 ppm and 7.51 ppm, along with a singlet at 6.41 ppm (Figure 2).

Figure 2. ^1H NMR spectrum of 2-La in THF-d_8 at −60 °C (aromatic region) with chemical shifts marked red and blue for cationic and anionic parts.

In addition, all products were also characterized using UV-Vis and IR spectroscopy (See Figures S1 and S4, respectively). UV-Vis spectra of crystals dissolved in THF show two major absorption bands centered at 307 nm and 322 nm. The IR spectra are similar for the series with
major bands around 710 cm\(^{-1}\), 760 cm\(^{-1}\), 805 cm\(^{-1}\), 825 cm\(^{-1}\), and 845 cm\(^{-1}\) and THF peaks around 1000 cm\(^{-1}\) and 1140 cm\(^{-1}\).

**X-ray Crystallographic Studies**

Upon reaction of K\(_2\)DBCOT with MI\(_3\) (M = Y, La, Gd, Tb, Dy) in THF at room temperature, followed by slow evaporation of solvent, orange or brown block-shaped crystals of good quality have been isolated. The single crystal X-ray diffraction revealed that all crystals conform to the same \(\text{C}_{2\text{v}}\) space group with \(Z = 4\) (See Table S4 in the Experimental Section). The unit cell volume of \(\text{1-Y}\) of 5068.3(4) Å\(^3\) is notably smaller compared to 5120.5(6) Å\(^3\), 5093.0(8) Å\(^3\), and 5051.6(5) Å\(^3\) for \(\text{3-Gd}, \text{4-Tb}, \text{and 5-Dy}\), respectively. In comparison with \(\text{1-Y}\), the volume of \(\text{2-La}\) of 5267.7(9) Å\(^3\) is significantly larger. It can be noted here that multiple crystals of \(\text{2-La}\) have been checked and all were very weakly diffracting, thus precluding their structural description below.

The X-ray crystallographic characterization revealed the formation of a new structural type of the \([\text{M(DBCOT})(\text{THF})_4]^+][\text{M(DBCOT)}_2^-]\) composition. As all complexes are isostructural, we select here \(\text{1-Y}\) for detailed structural discussion and then use it for comparison with complexes of lanthanides, \(\text{3-Gd}, \text{4-Tb}, \text{and 5-Dy}\), followed by analysis of the trends for the whole series.

The ORTEP drawing of the asymmetric unit is shown in Figure 3. The M2 and M3 metal atoms in the cationic moieties have half occupancies due to sitting on a \(\text{2_1}\) screw axis.
**Figure 3.** The asymmetric unit of \([\text{M}_2(\text{DBCOT})_3(\text{THF})_4]\) drawn with thermal ellipsoids at the 45% level. The color scheme used: C grey, H white, O red, M cyan.

In the crystal structure of 1-Y (Figure 4), one Y(III) center is entrapped by two DBCOT\(^{2-}\) anions to form a double-decker anionic sandwich \([\text{Y}(\text{DBCOT})_2^-]\) which is paired with a cationic moiety, \([\text{Y}(\text{DBCOT})(\text{THF})_4^+]\).

**Figure 4.** Crystal structure of 1-Y, ball-and-stick (left) and space-filling (right) models.
The anionic sandwich has an Y1(III) ion coordinated to the central eight-membered rings of two DBCOT$^{2-}$ anions in a $\eta^8$-mode. The Y1–DBCOT(1)$_{\text{centroid}}$ and Y1–DBCOT(2)$_{\text{centroid}}$ distances are 1.877(3) Å and 1.889(3) Å, respectively. The average Y1–C bond distances in the sandwich are 2.641(3) Å for DBCOT(1) and 2.645(3) Å for DBCOT(2) (Table 1). The two DBCOT units are rotated in respect to each other at the 31.54 ° angle (Figure 5). The planes of the central COT rings are also slightly (2.04 °) bent. As a result, the two DBCOT decks are not parallel.

**Figure 5.** The ball-and-stick model of the anionic sandwich in 1-Y.

**Table 1.** The Y1–C bond distances (Å) of the anionic sandwich with a labeled figure, ball-and-stick model (H-atoms are omitted for clarity).
The cationic moiety, \([Y(DBCOT)(THF)_4]^+\), has a \(Y(\text{III})\) center coordinated to one DBCOT\(^{2-}\) anion and four THF molecules on the opposite side of the \(\eta^8\)-bound DBCOT\(^{2-}\) deck. The \(Y2–DBCOT(3)\) centroid distance at 1.928(3) Å and the average of \(Y–C\) bond distances (2.676(3) Å) are slightly longer than the corresponding distances in the anionic sandwich. However in comparison to the only crystallographically characterized \(Y(\text{III})\)-DBCOT\(^{2-}\) complex, all \(Y–C_{\text{Centroid}}\) distances are shorter than the literature values: 1.898(3) Å (average in 1-Y) vs 1.936(3) Å.\(^{49}\) The coordination environment of \(Y(\text{III})\) center is completed by four terminally bound THF molecules with the \(Y–O_{\text{THF}}\) bond distances ranging over 2.377(18)–2.421(18) Å and with the average value of 2.401(18) Å (Table 2). The average \(Y–O_{\text{THF}}\) distances in 1-Y are slightly shorter than the literature values.\(^{52,53,54,24,55,9}\)

**Table 2.** The \(Y–C_{\text{DBCOT(3)}}\) (averaged) and \(Y–O_{\text{THF}}\) bond distances (Å) of the cationic moiety with a labeled figure, ball-and-stick model (H-atoms are omitted for clarity).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2–C(_a)</td>
<td>2.565(3)</td>
</tr>
<tr>
<td>Y2–C(_b)</td>
<td>2.622(3)</td>
</tr>
<tr>
<td>Y2–C(_c)</td>
<td>2.730(3)</td>
</tr>
<tr>
<td>Y2–C(_d)</td>
<td>2.786(3)</td>
</tr>
<tr>
<td>Y2–O(_1)</td>
<td>2.4215(18)</td>
</tr>
<tr>
<td>Y2–O(_2)</td>
<td>2.3770(18)</td>
</tr>
<tr>
<td>Y2–O(_3)</td>
<td>2.4035(18)</td>
</tr>
<tr>
<td>Y2–O(_4)</td>
<td>2.4041(18)</td>
</tr>
</tbody>
</table>
All doubly-reduced DBCOT$^{2-}$ decks in 1-Y exhibit a deviation from planarity upon complexation. The average dihedral angles of the six-membered rings of DBCOT(1), DBCOT(2), and DBCOT(3) are 7.61 °, 6.30 °, and 9.52 °, respectively. The average torsion angles (illustrating twist along the length of the core) of DBCOT(1), DBCOT(2), and DBCOT(3) are 1.94 °, 4.05 °, and 7.95 °, respectively.

In the solid-state structure of 1-Y, multiple C–H···π interactions (averaged at 2.630 Å) are observed between the adjacent cationic and anionic moieties to form a 2D extended network. Specifically, cationic moieties exhibit C–H···π interactions through the coordinated THF molecules to the adjacent negatively-charged π-decks (Figure 6).
Figure 6. Solid-state packing of 1-Y illustrating C–H···π interactions, ball-and-stick (top) and space-filling (bottom) models.

In the crystal structure of the isostructural complex, 3-Gd, one Gd(III) center is sandwiched by two DBCOT$^{2-}$ anions to form a double-decker sandwich $[\text{Gd(DBCOT)}_{2}^-]$ which is paired with the corresponding cationic moiety, $[\text{Gd(DBCOT)(THF)}_{4}^+]$ (Figure 7).

Figure 7. Crystal structure of 3-Gd, ball-and-stick (left) and space-filling (right) models.
The anionic sandwich has a Gd1(III) ion symmetrically coordinated to the central eight-membered rings of two DBCOT\(^{2−}\) anions in a \(\eta^8\)-mode. The Gd1–DBCOT(1)\(_{\text{centroid}}\) and Gd1–DBCOT(2)\(_{\text{centroid}}\) bond distances of 1.932(4) Å and 1.920(4) Å, respectively, are notably longer compared with those in 1-Y. The average Gd1–C bond distances of 2.676(4) Å and 2.683(4) Å in the sandwich are close for the DBCOT(1) and DBCOT(2) decks (Table 3). Similar to 1-Y, the two DBCOT units are rotated in respect to each other at a 31.62 ° angle.

**Table 3.** The Gd1–C bond distances (Å) of the anionic sandwich with a labeled figure, ball-and-stick model (H-atoms are omitted for clarity).

<table>
<thead>
<tr>
<th></th>
<th>Gd1–C21</th>
<th>Gd1–C22</th>
<th>Gd1–C23</th>
<th>Gd1–C24</th>
<th>Gd1–C29</th>
<th>Gd1–C30</th>
<th>Gd1–C31</th>
<th>Gd1–C32</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DBCOT(1)</strong></td>
<td>2.741(4)</td>
<td>2.641(4)</td>
<td>2.622(4)</td>
<td>2.690(4)</td>
<td>2.686(4)</td>
<td>2.629(4)</td>
<td>2.644(4)</td>
<td>2.753(4)</td>
</tr>
<tr>
<td><strong>DBCOT(2)</strong></td>
<td>2.724(4)</td>
<td>2.646(4)</td>
<td>2.648(4)</td>
<td>2.755(4)</td>
<td>2.744(4)</td>
<td>2.631(4)</td>
<td>2.611(4)</td>
<td>2.707(3)</td>
</tr>
</tbody>
</table>

In 3-Gd, the cationic moiety has Gd2(III) \(\eta^8\)-coordinated to one DBCOT\(^{2−}\) anion with the Gd2–DBCOT(3)\(_{\text{centroid}}\) distance at 1.950(4) Å and average of Gd–C bond distances of 2.693(4) Å being slightly longer than the corresponding distances in the anionic sandwich. The coordination environment of Gd(III) is completed by four terminally bound THF molecules with the Gd–O\(_{\text{THF}}\) bond distances ranging over 2.422(2)– 2.461(2) Å and the average value of 2.443(2) Å (Table 4).
Table 4. The Gd−C_{DBCOT(3)} (averaged) and Gd−O_{THF} bond distances (Å) of the cationic moiety with a labeled figure, ball-and-stick model (H-atoms are omitted for clarity).

<table>
<thead>
<tr>
<th>Gd–C</th>
<th>Gd–O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd–C$_{a}$</td>
<td>2.636(4)</td>
</tr>
<tr>
<td>Gd–C$_{b}$</td>
<td>2.594(4)</td>
</tr>
<tr>
<td>Gd–C$_{c}$</td>
<td>2.747(4)</td>
</tr>
<tr>
<td>Gd–C$_{d}$</td>
<td>2.797(4)</td>
</tr>
</tbody>
</table>

Similar to 1-Y, the doubly-reduced DBCOT$^{2-}$ decks in 3-Gd exhibit a deviation from planarity upon complexation. The average dihedral angles of the peripheral six-membered rings of DBCOT(1), DBCOT(2), and DBCOT(3) are 7.97 °, 6.79 °, and 8.24 °, respectively. The average torsion angles (illustrating twist along the length of the core) of DBCOT(1), DBCOT(2), and DBCOT(3) are 3.10 °, 1.19 °, and 6.89 °, respectively.

In the solid-state structure of 3-Gd, multiple C–H···π interactions are observed between the adjacent cationic and anionic moieties (averaged at 2.627 Å) to form a 2D extended network (Figure 8).
Figure 8. Solid-state packing of 3-Gd illustrating C–H···π interactions, ball-and-stick (top) and space-filling (bottom) models.

While both complexes are isostructural, 1-Y and 3-Gd do differ significantly in bonding characteristics consistent with the difference in the metal ionic sizes. Specifically, Y(III) has an ionic radius of 1.019 Å, while Gd(III) has an ionic radius of 1.053 Å (for coordination number 8). For the two sandwich units, the 1-Y complex exhibits shorter average M–C bond distances of 2.643 Å compared to 2.680 Å in the 3-Gd complex. The distances from the metal centers to the centroids of eight-membered rings for both decks follow a similar trend. The 1-Y complex has an
average M–DBCOT\textsubscript{centroid} distance of 1.883 Å compared to the average value of 1.926 Å in the 3-Gd complex. The separation between two DBCOT decks in the homoleptic sandwich units is also notably different and depends on the ionic radius of metal centers (Figure 9). When comparing the cationic moieties, similar trends in bond distances can be noted. The average M–C bond distance in 1-Y of 2.676(3) Å is notably shorter than 2.693(4) Å in 3-Gd. These differences are also observed in THF coordination: the average values of M–O\textsubscript{THF} are 2.401(18) Å in 1-Y vs. 2.443(2) Å in 3-Gd.

In summary, all the observed differences in main geometric parameters between 1-Y and 3-Gd correlate well with the ionic radii of the two metal centers.

**Figure 9.** Deck-to-deck separation in 1-Y and 3-Gd, ball-and-stick model.

For the next step, the two complexes of lanthanides, 4-Tb and 5-Dy, have been analyzed and compared with the crystal structure of 3-Gd (Table 5). Similar to 1-Y and 3-Gd, the geometric parameters of 4-Tb and 5-Dy follow the observed trend in terms of distances and ionic radii correlation (Table 5). The average M–DBCOT\textsubscript{centroid} distances decrease with decreasing an ionic radii with 3-Gd having the largest average value at 1.926 Å. Complex 4-Tb with the average M–DBCOT\textsubscript{centroid} distance of 1.903 Å falls between the two analogues, and 5-Dy exhibits the shortest average distance at 1.887(7) Å.
A similar trend can be seen for the M–C bond length distances. The average value of 2.649(7) Å in 5-Dy is followed by 2.663(5) Å in 4-Tb, with the longest distance of 2.680(4) Å observed in 3-Gd. The separation between two DBCOT decks in the sandwich parts also follows this trend with the greatest value of 3.852 Å in 3-Gd and the smallest distance of 3.774 Å in 5-Dy (Figure 10).

Table 5. Average bond length distances (Å) for the series of monoanionic sandwiches, [M(DBCOT)₂⁻].

<table>
<thead>
<tr>
<th></th>
<th>1-Y</th>
<th>3-Gd</th>
<th>4-Tb</th>
<th>5-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radii</td>
<td>1.019</td>
<td>1.053</td>
<td>1.040</td>
<td>1.027</td>
</tr>
<tr>
<td>M–DBCOT(1)Centroid</td>
<td>1.877(3)</td>
<td>1.920(4)</td>
<td>1.897(5)</td>
<td>1.881(7)</td>
</tr>
<tr>
<td>M–DBCOT(2)Centroid</td>
<td>1.889(3)</td>
<td>1.932(4)</td>
<td>1.909(5)</td>
<td>1.893(7)</td>
</tr>
<tr>
<td>M–C(DBCOT(1))</td>
<td>2.641(3)</td>
<td>2.683(4)</td>
<td>2.659(5)</td>
<td>2.647(7)</td>
</tr>
<tr>
<td>M–C(DBCOT(2))</td>
<td>2.645(3)</td>
<td>2.676(4)</td>
<td>2.666(5)</td>
<td>2.651(7)</td>
</tr>
</tbody>
</table>

Figure 10. Deck-to-deck separation in 3-Gd, 4-Tb, and 5-Dy, ball-and-stick models.

In the cationic moieties, the correlation of decreasing distances corresponds to the decreasing ionic radii similar to the anionic sandwich moieties (Table 6). Both the average M–
DBCOT(3)Centroid distances and the average M–CDBCOT(3) distances follow the same trend, although the corresponding distances are longer in the cationic moieties. The average M–O\textsubscript{THF} bond distances are 2.443(2) Å, 2.432(18) Å, and 2.415(4) Å in 3-Gd, 4-Tb, and 5-Dy, respectively.

<table>
<thead>
<tr>
<th></th>
<th>1-Y</th>
<th>3-Gd</th>
<th>4-Tb</th>
<th>5-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radii\textsuperscript{51}</td>
<td>1.019</td>
<td>1.053</td>
<td>1.040</td>
<td>1.027</td>
</tr>
<tr>
<td>M–DBCOT(3)Centroid (av.)</td>
<td>1.928(3)</td>
<td>1.950(4)</td>
<td>1.934(5)</td>
<td>1.928(7)</td>
</tr>
<tr>
<td>M–C\textsubscript{DBCOT (3)} (av.)</td>
<td>2.676(3)</td>
<td>2.693(4)</td>
<td>2.680(5)</td>
<td>2.675(7)</td>
</tr>
<tr>
<td>M–O\textsubscript{THF} (av.)</td>
<td>2.01(18)</td>
<td>2.443(2)</td>
<td>2.432(18)</td>
<td>2.415(4)</td>
</tr>
</tbody>
</table>

Table 6. Average bond length distances (Å) for the series of cationic moieties.

As expected, the addition of two electrons results in planarization of the doubly-reduced DBCOT\textsuperscript{2−} core.\textsuperscript{48} However, the deformation of the DBCOT\textsuperscript{2−} decks upon metal complexation can be clearly detected for both anionic and cationic moieties in the series. For the former, the DBCOT\textsuperscript{2−} decks show slight inward bending towards the metal center of the double-decker sandwiches (Figure 11 left). The average dihedral angles of DBCOT\textsuperscript{2−} in the anionic moieties are 173.05 °, 172.71 °, 173.00 °, and 172.97 ° for 1-Y, 3-Gd, 4-Tb, and 5-Dy, respectively. For the cationic moieties, the DBCOT\textsuperscript{2−} decks tend to exhibit the lengthwise core twisting (Figure 11 right). This can be illustrated by the calculated torsion angles that vary from 7.95 °, 6.89 °, 6.96 ° to 8.32 ° for 1-Y, 3-Gd, 4-Tb, and 5-Dy, respectively. For comparison, the corresponding torsion angles in the anionic moieties are smaller: 3.00 °, 2.15 °, 2.29 °, and 2.93 ° for 1-Y, 3-Gd, 4-Tb, and 5-Dy, respectively.
Figure 11. DBCOT$^{2-}$ decks of an anionic moiety with dihedral angles drawn (left) and of a cationic moiety with torsion measurements (right). H-atoms are omitted for clarity.

Since no prior examples of $\eta^8$-coordination has been confirmed crystallographically for the lanthanide complexes with DBCOT$^{2-}$ ligands, the corresponding COT-based complexes have been used for comparison. When directly comparing the Ln(III)–DBCOT ($\eta^8$-coordination) to Ln(III)–COT complexes, the former show somewhat longer Ln–C$_{Centroid}$ bond distances.$^{20,56,57,33}$ Moreover, complexes in this study show slightly longer average Ln(III)–O$_{THF}$ bond distances compared to the literature values.$^{20,58}$

The solid-state packing trends are generally the same throughout the series. Multiple C–H⋯π interactions are observed between the adjacent cationic and anionic moieties in 4-Tb and 5-Dy, similar to 3-Gd. It can be mentioned that the average C–H⋯π contacts in 4-Tb and 5-Dy (2.606 Å and 2.607 Å, respectively) are shorter compared with 3-Gd (averaged at 2.627 Å).
Conclusions

In summary, a series of novel complexes of the \([\text{M(DBCOT)(THF)}_{4}]^{+}[\text{M(DBCOT)}_{2}]^{-}\) composition has been synthesized for M(III) = Y, La, Gd, Dy, and Tb. Synthesis of new complexes has been accomplished through the ligand metathesis reaction of M(III) triiodides with K$_2$(DBCOT) in THF at ambient conditions. Subsequent crystallization via slow solvent evaporation afforded bulk single crystals of good quality. The X-ray diffraction analyses revealed that all products consist of a \([\text{M(DBCOT)(THF)}_{4}]^{+}\) cationic moiety and a double-decker anionic sandwich, \([\text{M(DBCOT)}_{2}]^{-}\), which weakly interact in the solid state. In both parts, the DBCOT$^{2-}$ anions exhibit η⁸-coordination to a metal center with the M–C$_{\text{DBCOT}}$ bond length distances following the trend in ionic radii for rare earth metals. In addition to single-crystal X-ray diffraction, all products have been characterized by UV-Vis and IR spectroscopic methods, illustrating consistency throughout the series. Furthermore, $^1$H NMR spectroscopy has been utilized in order to confirm bulk purity and to reveal solution behavior of 1-Y and 2-La. Phase purity of crystalline 3-Gd, 4-Tb, and 5-Dy products has been confirmed via X-ray powder diffraction.

Overall, this series represents the first homoleptic Ln-DBCOT complexes that are crystallographically characterized. The new complexes are also the first to exhibit a η⁸-coordination of the lanthanide cations to the central eight-membered rings of the planarized DBCOT$^{2-}$ anions in a sandwich fashion. The comprehensive analysis of the solid-state structures revealed notable deformation of the π-decks upon complexation as well as systematic trends for the series. The synthesis and characterization of this novel family of Ln-DBCOT complexes now opens the opportunity for in-depth investigation into their properties and potential applications. Further magnetic studies are underway.
Chapter 3: Experimental Section

I. Materials and Methods

The preparation and all manipulations were carried out using break-and-seal as well as Schlenk and glove-box techniques under an atmosphere of argon. Tetrahydrofuran (THF) and hexanes (Sigma-Aldrich) were dried over Na/benzophenone and distilled prior to use. THF-$d_8$ (Sigma Aldrich) was dried over NaK$_2$ alloy and vacuum-transferred. DBCOT (97%) was purchased from Tokyo Chemical Industry and sublimed in a 10 cm glass ampule at 78 °C over 4 days. Potassium metal (98%) was purchased from Sigma Aldrich and used as received. YI$_3$ (99.9%), LaI$_3$ (99.9%), GdI$_3$ (99.99%), TbI$_3$ (99.99%), and DyI$_3$ (99.99%) were purchased from Alfa Aesar and used as received. K$_2$DBCOT was prepared according to the literature procedures and stored in the glove box. The attenuated total reflection (ATR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. The $^1$H NMR spectra were measured on a Bruker Ascend-500 spectrometer at 500 MHz. All spectra were referenced to the resonances of the corresponding solvent used. The UV−vis spectra were recorded on a Thermo Scientific Evolution 201 UV−visible spectrophotometer.

II. Synthesis and Crystallization

$[\text{Y(DBCOT)}(\text{THF})_4]^+[\text{Y(DBCOT)}_2]^- \text{(1-Y)}$

Black K$_2$DBCOT powder (12.1 mg, 0.043 mmol) and YI$_3$ (13.0 mg, 0.028 mmol) (13:20, Ln:DBCOT) powder were added to a reaction flask and dissolved in 2 mL THF under inert atmosphere. After stirring the mixture in the sealed flask under nitrogen gas at room temperature (23 °C), it turned orange and cloudy and remained the same color until the reaction was stopped.
After 2 days of stirring, the orange mixture was filtered into an L-shaped glass ampule which was sealed under reduced pressure. The L-shaped ampule was placed 8 cm over a hot sand bath (110 °C) for slow solvent evaporation. After 10 days, orange block-shaped crystals appeared in the ampule. Yield: 7.6 mg, 50%.

\[ \text{[Gd(DBCOT)(THF)]}^+ \text{[Gd(DBCOT)]}^- \text{ (3-Gd)} \]

Black K\textsubscript{2}DBCOT powder (11.9 mg, 0.042 mmol) and GdI\textsubscript{3} (15.0 mg, 0.028 mmol) (2:3, Ln:DBCOT) powder were added to a reaction flask and dissolved in 3 mL THF under inert atmosphere. After stirring the mixture in the sealed flask under nitrogen gas at room temperature (23 °C), it turned dark-orange and cloudy and remained the same color until the reaction was stopped. After 2 days of stirring, the dark-orange mixture was filtered into an L-shaped glass ampule which was sealed under reduced pressure. The L-shaped ampule was placed 1 cm over a hot oven (29 °C) for slow solvent evaporation. After 16 days, brown block-shaped crystals appeared in the ampule. Yield: 8.5 mg, 50%.

\[ \text{[Tb(DBCOT)(THF)]}^+ \text{[Tb(DBCOT)]}^- \text{ (4-Tb)} \]

Black K\textsubscript{2}DBCOT powder (12.0 mg, 0.042 mmol) and TbI\textsubscript{3} (14.9 mg, 0.027 mmol) (16:25, Ln:DBCOT) powder were added to a reaction flask and dissolved in 2 mL THF under inert atmosphere. After stirring the mixture in the sealed flask under nitrogen gas at room temperature (23 °C), it turned brown and cloudy and remained the same color until the reaction was stopped. After 2 days of stirring, the brown mixture was filtered into an L-shaped glass ampule which was sealed under reduced pressure. The ampule was placed 22 cm over a hot sand bath (120 °C). After 7 days, dark-brown, block-shaped crystals appeared on the side and bottom of the ampule. Yield: 8.4 mg, 50%.
[Dy(DBCOT)(THF)]_4^+[Dy(DBCOT)]_2^- (5-Dy)

Black K$_2$DBCOT powder (10.2 mg, 0.036 mmol) and DyI$_3$ (12.6 mg, 0.023 mmol) powder (16:25, Ln:DBCOT) powder were added to a reaction flask and dissolved in 3 mL THF under inert atmosphere. After stirring the mixture in the sealed flask under nitrogen gas at room temperature (23 °C), it turned brown and cloudy and remained the same color until the reaction was stopped. After 2 days of stirring, the brown mixture was filtered into an L-shaped glass ampule which was sealed under reduced pressure. The ampule was placed 30 cm over a hot sand bath (174 °C). After 14 days the walls and the bottom of the ampule were covered in light brown branching crystals and brown block-shaped crystals. Yield: 7.1 mg, 50%.
III. UV-Vis Spectroscopic Investigation

*Sample preparation:* THF (3 mL) was added to a glass ampule (O.D. 12 mm) containing 1-Y, 2-La, 3-Gd, 4-Tb, or 5-Dy (0.2 mg). The ampule was sealed under argon, and UV-Vis spectra were collected at 25 °C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Y</td>
<td>306 (sh), 320 (sh)</td>
</tr>
<tr>
<td>2-La</td>
<td>308, 322</td>
</tr>
<tr>
<td>3-Gd</td>
<td>308, 323</td>
</tr>
<tr>
<td>4-Tb</td>
<td>307, 322</td>
</tr>
<tr>
<td>5-Dy</td>
<td>307, 322</td>
</tr>
</tbody>
</table>

*Figure S1.* UV-Vis spectra of 1-Y, 2-La, 3-Gd, 4-Tb, and 5-Dy.
IV. NMR Spectroscopic Investigation

*Sample preparation:* THF-$d_8$ (0.6 mL) was added to an NMR tube containing 1 mg of crystalline 1-Y or 2-La. The tube was sealed under argon and $^1$H NMR spectra were collected.

*Figure S2.* $^1$H NMR spectrum of 1-Y in THF-$d_8$ at 25 °C.
Figure S3. $^1$H NMR spectrum of 2-La in THF-$d_8$ at -60 °C.
V. ATR-IR Spectroscopic Investigation

*Sample Preparation:* 0.5 mg of orange/brown crystalline products of 1-Y, 2-La, 3-Gd, 4-Tb, or 5-Dy covered in mineral oil were only scanned twice, due to the product moisture and air sensitivity.

![ATR-IR spectra](image)

**Figure S4.** ATR-IR spectra of 1-Y, 2-La, 3-Gd, 4-Tb, and 5-Dy.
VI. Powder X-ray Diffraction Results

The X-ray powder diffraction data were collected on a Bruker D8 Venture single crystal diffractometer (Cu Kα INCOATEC ImuS micro-focus source, focusing multilayer mirrors monochromator, Photon 100 detector, 100 K). The crystalline samples under investigation were ground under Ar in the glove-box and mounted on a MiTeGen 10 µm MicroMount protected by a nitrogen gas flow. Le Bail fit for powder diffraction patterns was performed using TOPAS, version 4 software package (Bruker AXS, 2006).

Figure S5. X-ray powder diffraction pattern of 3-Gd and Le Bail fit. The blue and red lines are experimental and calculated patterns respectively. The grey line is the difference curve with theoretical positions shown at the bottom in blue.
Table S1. Comparison of unit cell parameters for 3-Gd from single crystal data and the Le Bail fit.

<table>
<thead>
<tr>
<th></th>
<th>Single crystal data (100 K)</th>
<th>Le Bail fit data (100 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td></td>
<td>C2</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>30.372(2)</td>
<td>30.3686(18)</td>
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<tr>
<td>$b$ (Å)</td>
<td>8.0988(6)</td>
<td>8.0979(6)</td>
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<tr>
<td>$c$ (Å)</td>
<td>22.3088(16)</td>
<td>22.3055(16)</td>
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<td>$\alpha$ (°)</td>
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<td>90.00</td>
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<td>$\beta$ (°)</td>
<td>111.070(1)</td>
<td>111.062(3)</td>
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<tr>
<td>$\gamma$ (°)</td>
<td>90.00</td>
<td>90.00</td>
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<tr>
<td>$V$ (Å$^3$)</td>
<td>5120.5(6)</td>
<td>5118.9(6)</td>
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</tbody>
</table>

Figure S6. X-ray powder diffraction pattern of 4-Tb and Le Bail fit. The blue and red lines are experimental and calculated patterns, respectively. The grey line is the difference curve with theoretical positions shown at the bottom in blue arrows.
Table S2. Comparison of unit cell parameters for 4-Tb from single crystal data and the Le Bail fit.

<table>
<thead>
<tr>
<th></th>
<th>Single crystal data (100 K)</th>
<th>Le Bail fit data (100 K)</th>
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<tr>
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<td>(a) (Å)</td>
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<td>(b) (Å)</td>
<td>8.0750(7)</td>
<td>8.0738(9)</td>
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<tr>
<td>(c) (Å)</td>
<td>22.305(2)</td>
<td>22.320(8)</td>
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<tr>
<td>(\alpha) (°)</td>
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<td>90.00</td>
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<tr>
<td>(\beta) (°)</td>
<td>111.2380(10)</td>
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<tr>
<td>(\gamma) (°)</td>
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<td>90.00</td>
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<td>(V) (Å(^3))</td>
<td>5093.0(8)</td>
<td>5092.4(9)</td>
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</table>

Figure S7. X-ray powder diffraction pattern of 5-Dy and Le Bail fit. The blue and red lines are experimental and calculated patterns, respectively. The grey line is the difference curve with theoretical positions shown at the bottom in blue arrows.

Table S3. Comparison of unit cell parameters for 5-Dy from single crystal data and the Le Bail fit.
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<tr>
<th>Space Group</th>
<th>Single crystal data (100 K)</th>
<th>Le Bail fit data (100 K)</th>
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<tr>
<td></td>
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<tr>
<td>C2</td>
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<td>a (Å)</td>
<td>30.2643(16)</td>
<td>30.2386(18)</td>
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<td>b (Å)</td>
<td>8.0668(5)</td>
<td>8.0699(6)</td>
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<tr>
<td>c (Å)</td>
<td>22.2201(12)</td>
<td>22.2267(16)</td>
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<tr>
<td>α (°)</td>
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<tr>
<td>β (°)</td>
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<tr>
<td>V (Å³)</td>
<td>5051.6(5)</td>
<td>5049.2(6)</td>
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</table>
VII. Crystal Structure Solution and Refinement

Data collections of 3-Gd, 4-Tb, 5-Dy and 1-Y were performed on a Bruker VENTURE system equipped with a PHOTON 100 CMOS detector, a Mo-target fine-focus X-ray source ($\lambda = 0.71073 \text{ Å}$), and a graphite monochromator. Data were collected at 100(2) K crystal temperature (Oxford Cryosystems CRYOSTREAM 700), 50 kV, and 30 mA with an appropriate $0.5^\circ \omega$ scan strategy. All data reduction and integration were performed with SAINT (version 8.38A). All data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2). The structures were solved by SHELXT (version 2018/2) and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3) through the OLEX2 graphical interface. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with $U_{\text{iso}}(H) = 1.2\ U_{\text{eq}}(C)$. In 3-Gd and 4-Tb, two THF molecules were found to be disordered in each structure. All disordered THF molecules were modeled with two orientations with their relative occupancies refined. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å$^2$. They were also restrained to have the same $U_{ij}$ components, with a standard uncertainty of 0.01 Å$^2$. In 5-Dy, since DBCOT dianions are composed of rigid bonds, in order to make all carbon atoms’ anisotropic displacement parameters reasonable, the anisotropic displacement parameters of the DBCOT dianions in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å$^2$. They were also restrained to have the same $U_{ij}$ components, with a standard uncertainty of 0.01 Å$^2$. Besides, 4-Tb, 5-Dy, and 1-Y were refined as inversion twin with the BASF value refined to 0.348(10), 0.403(11), and 0.445(3). These three structures were examined by PLATON and no
additional symmetry was found. Crystallographic data and details of the data collection and structure refinement are listed in Table S4. ORTEP drawings for each individual structure are shown below (Figures S8-11), along with Figure S12 showing solid-state packing.
Table S4. Crystal data and structure refinement parameters for 3-Gd, 4-Tb, 5-Dy, and 1-Y.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3-Gd</th>
<th>4-Tb</th>
<th>5-Dy</th>
<th>1-Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{64}$H$</em>{68}$Gd$_2$O$_4$</td>
<td>C$<em>{64}$H$</em>{68}$Tb$_2$O$_4$</td>
<td>C$<em>{64}$H$</em>{68}$Dy$_2$O$_4$</td>
<td>C$<em>{64}$H$</em>{68}$Y$_2$O$_4$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1215.68</td>
<td>1219.02</td>
<td>1226.18</td>
<td>1079.00</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
<td>C2</td>
<td>C2</td>
<td>C2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>30.372(2)</td>
<td>30.337(3)</td>
<td>30.2643(16)</td>
<td>30.2969(16)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.0988(6)</td>
<td>8.0750(7)</td>
<td>8.0668(5)</td>
<td>8.0776(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>22.3088(16)</td>
<td>22.305(2)</td>
<td>22.2201(12)</td>
<td>22.2551(11)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β (°)</td>
<td>111.0700(10)</td>
<td>111.2380(10)</td>
<td>111.3740(10)</td>
<td>111.4740(10)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>5120.5(6)</td>
<td>5093.0(8)</td>
<td>5051.6(5)</td>
<td>5068.3(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g·cm$^{-3}$)</td>
<td>1.577</td>
<td>1.590</td>
<td>1.612</td>
<td>1.414</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>2.618</td>
<td>2.805</td>
<td>2.986</td>
<td>2.329</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>2448</td>
<td>2456</td>
<td>2464</td>
<td>2248</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.04×0.06×0.04</td>
<td>0.02×0.11×0.1</td>
<td>0.02×0.06×0.1</td>
<td>0.05×0.19×0.2</td>
</tr>
<tr>
<td>θ range for data collection (°)</td>
<td>2.77-30.11</td>
<td>2.77-31.06</td>
<td>2.84-26.44</td>
<td>2.77-29.21</td>
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<tr>
<td>Reflections collected</td>
<td>64187</td>
<td>67042</td>
<td>57871</td>
<td>72346</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15039</td>
<td>16283</td>
<td>10340</td>
<td>13695</td>
</tr>
<tr>
<td>Transmission factors (min/max)</td>
<td>[R$_{int} = 0.0391$]</td>
<td>[R$_{int} = 0.0462$]</td>
<td>[R$_{int} = 0.0606$]</td>
<td>[R$_{int} = 0.0438$]</td>
</tr>
<tr>
<td>Data/restraints/params.</td>
<td>15039/406/70</td>
<td>16283/404/71</td>
<td>10340/649/63</td>
<td>13695/1/633</td>
</tr>
<tr>
<td>$R1$, $wR2$ (I &gt; 2σ(I))</td>
<td>0.0250, 0.0394</td>
<td>0.0312, 0.0517</td>
<td>0.0324, 0.0454</td>
<td>0.0264, 0.0498</td>
</tr>
<tr>
<td>$R1$, $wR2$ (all data)</td>
<td>0.0307, 0.0406</td>
<td>0.0387, 0.0537</td>
<td>0.0427, 0.0477</td>
<td>0.0317, 0.0514</td>
</tr>
<tr>
<td>Quality-of-fit$^c$</td>
<td>1.059</td>
<td>1.033</td>
<td>1.027</td>
<td>1.041</td>
</tr>
</tbody>
</table>

$^a$R1 = Σ||F$_0$|-|F$_c$||/|ΣF$_0$|.

$^b$wR2 = [Σ[w(F$_0^2$-F$_c^2$)]]/Σ[w(F$_c^2$)].

$^c$Quality-of-fit = [Σ[w(F$_0^2$-F$_c^2$)]/(N$_{obs}$-N$_{params}$)]$^{1/2}$, based on all data.
**Figure S8.** ORTEP drawing of the asymmetric unit of 1-Y with thermal ellipsoids shown at the 45% probability level. The color scheme used: C grey, H white, O red, Y cyan.

**Figure S9.** ORTEP drawing of the asymmetric unit of 3-Gd with thermal ellipsoids shown at the 45% probability level. The color scheme used: C grey, H white, O red, Gd orange.
**Figure S10.** ORTEP drawing of the asymmetric unit of 4-Tb with thermal ellipsoids shown at the 45% probability level. The color scheme used: C grey, H white, O red, Tb brown.

**Figure S11.** ORTEP drawing of the asymmetric unit of 5-Dy with thermal ellipsoids shown at the 45% probability level. The color scheme used: C grey, H white, O red, Dy dark-brown.
Figure S12. Solid-state packing of 1-Y, 3-Gd, 4-Tb, and 5-Dy, ball-and-stick model (top) and space-filling model (bottom).
Table S5. Selected average bond length distances (Å) of DBCOT$^{2-}$ in 1-Y, 3-Gd, 4-Tb, and 5-Dy, along with a labeling scheme.

<table>
<thead>
<tr>
<th></th>
<th>1-Y</th>
<th>3-Gd</th>
<th>4-Tb</th>
<th>5-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.408(4)</td>
<td>1.406(5)</td>
<td>1.407(7)</td>
<td>1.407(9)</td>
</tr>
<tr>
<td>b</td>
<td>1.424(4)</td>
<td>1.426(5)</td>
<td>1.424(7)</td>
<td>1.422(9)</td>
</tr>
<tr>
<td>c</td>
<td>1.450(4)</td>
<td>1.452(5)</td>
<td>1.451(7)</td>
<td>1.447(10)</td>
</tr>
<tr>
<td>d</td>
<td>1.453(4)</td>
<td>1.452(5)</td>
<td>1.452(7)</td>
<td>1.450(9)</td>
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<tr>
<td>e</td>
<td>1.352(4)</td>
<td>1.350(5)</td>
<td>1.351(7)</td>
<td>1.346(9)</td>
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<tr>
<td>f</td>
<td>1.421(4)</td>
<td>1.423(6)</td>
<td>1.421(8)</td>
<td>1.416(10)</td>
</tr>
</tbody>
</table>

Table S6. Selected average bond length distances (Å) in 1-Y, 3-Gd, 4-Tb, and 5-Dy, along with a labeling scheme.
<table>
<thead>
<tr>
<th></th>
<th>1-Y</th>
<th>3-Gd</th>
<th>4-Tb</th>
<th>5-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–DBCOT(1)$_{Centroid}$</td>
<td>1.877(3)</td>
<td>1.920(4)</td>
<td>1.897(5)</td>
<td>1.881(7)</td>
</tr>
<tr>
<td>M–DBCOT(2)$_{Centroid}$</td>
<td>1.889(3)</td>
<td>1.932(4)</td>
<td>1.909(5)</td>
<td>1.893(7)</td>
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<tr>
<td>M–C$_{DBCOT(1)}$</td>
<td>2.641(3)</td>
<td>2.683(4)</td>
<td>2.659(5)</td>
<td>2.647(7)</td>
</tr>
<tr>
<td>M–C$_{DBCOT(2)}$</td>
<td>2.645(3)</td>
<td>2.676(4)</td>
<td>2.666(5)</td>
<td>2.651(7)</td>
</tr>
<tr>
<td>M–DBCOT(3)$_{Centroid (av.)}$</td>
<td>1.928(3)</td>
<td>1.950(4)</td>
<td>1.934(5)</td>
<td>1.928(7)</td>
</tr>
<tr>
<td>M–C$_{DBCOT (3) (av.)}$</td>
<td>2.676(3)</td>
<td>2.693(4)</td>
<td>2.680(5)</td>
<td>2.675(7)</td>
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<tr>
<td>M–OTHF (av.)</td>
<td>2.401(18)</td>
<td>2.443(2)</td>
<td>2.432(18)</td>
<td>2.415(4)</td>
</tr>
</tbody>
</table>
References


47. Sygula, A.; Fronczek, F. R.; Rabideau, P. W. The First Example of η8 Coordination of Lithium Cations with a Cyclooctatetraene Dianion: Crystal Structure of


60. SAINT; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017.

61. SADABS; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017.

