Cerium Tetrakis(tropolonate) and Cerium Tetrakis(acetylacetonate) Are Not Diamagnetic but Temperature-Independent Paramagnets
Cerium Tetrakis(tropolonate) and Cerium Tetrakis(acetylacetonate) Are Not Diamagnetic but Temperature-Independent Paramagnets

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Supporting Information

ABSTRACT: A new synthesis of cerium tetrakis(tropolonate), Ce(trop)₄, where trop is deprotonated 2-hydroxy-2,4,6-cycloheptatrienone or Ce(O₂C₇H₅)₄, is developed that results in dark-purple crystals whose X-ray crystal structure shows that the geometry of the eight-coordinate compound closely resembles a D₄d dodecahedron, based on shape parameters. The magnetic susceptibility as a function of the temperature (4–300 K) shows that it is a temperature-independent paramagnet, \( \chi = 1.2(3) \times 10^{-4} \text{ emu/mol, and the } L_{\text{III}}\text{-edge X-ray absorption near-edge structure spectrum shows that the molecule is multiconfigurational, comprised of a } t^1f^6\text{ configuration mixture in a 50:50 ratio.} \)

Ce(acac)₄ and Ce(tmtaa)₂ (where acac is acetylacetonate and tmtaaH₂ is tetramethyldibenzotetraaza[14]annulene) have similar physical properties, as does the solid-state compound CeO₂. The concept is advanced that trop⁻, acac⁻, tmtaa⁻, cot⁻⁻, and O₂⁻⁻ are redox-active ligands that function as electron donors, rendering the classi-

■ INTRODUCTION

The metal acetylacetonate and related tropolonate compounds (Scheme 1) of the f-block metals are well-known examples of high-coordination-number polyhedra that have several applications in synthesis and spectroscopy.¹ In general, the metals in the compounds are classified according to their oxidation numbers that range from IV⁺ to II⁺, with the largest population being those of III⁺. The coordination geometries of the early members of the series are usually eight or higher, depending on the steric and donor effects of the ligand. Cerium presents a broad set of compounds that are classified by their oxidation numbers of IV⁺ and III⁺. The Ce(IV,⁰) compounds are represented by Lewis structures in which the metal and ligands have closed-shell electron configurations, [Ce(IV,⁰)(L⁻)₄], and the Ce(III,⁰) compounds, [Ce(III,⁰)(L⁻)₃], have S = 1/₂ ground states. Recent experimental and computational studies of the organometallic compound cerocene, [Ce(η⁴-C₈H₈)₂], abbreviated as Ce(cot)₂, show that the ground state is multiconfigurational in which the two configurations [Ce(IV,⁰)²(cot⁻⁻)₂] and [Ce(III,⁰)²(cot⁻⁻)₂] contribute to the ground-state wave function; see below for a brief outline of these paradigm-shifting studies. The key point is that cerocene is not represented by a single Lewis structure as implied by the empirical formula. A similar difficulty is presented by the Lewis structures of the Ce(IV) compounds of the acetylacetonate and tropolonate ligands, [Ce(L₄)₂], which, by analogy, might be represented as [Ce(IV,⁰)²(L⁻)₄] and [Ce(III,⁰)²(L⁻)₃]. This manuscript describes experimental and computational studies that unravel this most interesting electronic structural ambiguity.

Background: Electronic Structure of Cerocene. The electronic ground state of the organometallic compound cerocene was initially thought to be a compound derived from Ce(IV), F₀, and two cyclooctatetraene dianions, (cot⁻⁻)₂, fragments, setting the valence of cerium as tetravalent. The traditional role of assigning integral values of oxidation...
numbers to metals is derived by assigning the valence of the ligands, assuming that they have a closed-shell configuration in the resulting Lewis structure. The application of these rules to Ce(cot)₂ and perhaps to all covalently bonded systems, is misleading because the valence of cerium is neither III⁺ nor IV⁺ but is intermediate between these two integers. Early quantum-mechanical calculations,2 followed by higher-level computational methodologies, advocated a model in which the electronic ground state is an admixture of two configurations: \[ |\text{Ce}(\text{III})\text{f}^1(\text{e}^2_u)^1|'(\text{cot})_2^1|'] (\text{ground state}), \]

and \[ |\text{Ce}(\text{IV})\text{f}^2(\text{e}^2_u)^2|'(\text{cot})_2^1|' \] (closed-shell singlet). Both configurations have the same irreducible representation of \( 1\Delta_g \) in \( D_{8h} \) symmetry, the point group of cerocene, and the ground state is an orbital singlet because \( S = 0 \). The ground-state wave function is multireference, in which the dominant one is of the form \( \Psi = C_1|\text{Ce}\text{f}^1(\text{e}^2_u)^1| + C_2|\text{Ce}\text{f}^2(\text{e}^2_u)^2| \), where the coefficients \( C_1^2 \) and \( C_2^2 \) are approximately 80:20.3,4 The conclusion of these articles, referred to as the Kerridge6,7 papers, is that the Ce(III) configuration is the leading one. Two later articles, referred to as the Dolg–Fulde papers,9 suggest that the cation state, \( \text{Cp}_3\text{Ce}^+(\text{g}) \), is multiconfigurational.14 Thus, the multireference model seems to be widely applicable to those organometallic compounds in which the electrons in filled \( \pi \)-bonding orbitals on the ligands function as electron donors to empty orbitals on the metal, as in Cp₃Yb,15 and those in which the empty \( \pi \) orbitals are acceptor orbitals, as in Cp⁺ₓYb(bipy) and related compounds.6,9-11

A question that arises naturally is, can nonorganometallic ligands used in traditional coordination compounds of formally tetravalent cerium also function as electron donors, resulting in compounds with multiconfigurational ground states? The \( \text{La}_{11} \)-edge XANES spectra of several phthanocyanine and phorphyrin compounds of formally Ce(IV) have \( \ell^2/\ell^4 \) signatures,16-22 implying that they are multiconfigurational. The variable-temperature magnetic susceptibility of tetraazamacrocycle[14]-annulene cerium, Ce(tmtaa)₂, is independent of the temperature, indicative of a nonmagnetic ground state, but the "Ce(IV)" compound was not studied in greater detail.16,23

This Article reports experimental and computational studies on Ce(tmtaa)₂, Ce(acac)₃ and Ce(trop)₄, where acac and trop are abbreviations for the deprotonated ligands of 2,4-pentanediene and 2-hydroxy-2,4,6 cycloheptatriene, respectively (Scheme 1). These studies show that the ground states are open-shell singlets that have populated open-shell triplet excited states, resulting in TIP magnetic behavior. These molecular compounds have physical properties that are related between the two results, both of them can be considered valid because, as mentioned earlier, whatever linear combination of the MOs that is used in the CASSCF calculation, only a comparison with the experiment gives insight into the valid choice. Dolg’s approach may be considered simpler because it is based on only two MOs. However, the number of possible linear combinations is infinite, and neither one of the two approaches can be viewed as the ultimate one.

The important point that emerges from the different calculations is that the ground-state wave function is multireference and multiconfigurational and cannot be described by a single Lewis structure. The magnetic susceptibility showed that Ce in cerocene is not diamagnetic because \( \chi \) demonstrates temperature-independent paramagnetism (TIP) to 300 K, resulting from thermal mixing between the ground state with the excited triplet state by the Boltzmann factor.

The computational models erase the conceptual difficulty that a strongly oxidizing metal, Ce(IV), coexists with a ligand that is strongly reducing because the net result of the intramolecular electron transfer develops a multiconfigurational ground state and the compound follows Pauling’s electroneutrality principle, and that \( \text{cot}^2 \) is a net electron donor.

Experimental studies of the magnetic properties of Ce(cot)₂ and the \( \text{La}_{11} \)-edge X-ray absorption near-edge-structure (XANES) spectroscopy as a function of the temperature showed that the magnetic susceptibility and the \( \ell^2/\ell^4 \) signatures are independent of the temperature from 30 to 300 K. The value of \( n_0 \) deduced from the XANES spectra, \( C_i^2 \), is approximately 0.88-11 in agreement with the quantum-mechanical model advocated by the Dolg–Fulde papers.9,11 Magnetic and spectroscopic studies on formally tetravalent cerium organometallic compounds bis(hexamethylpentalen)e cerium and the bis(triisopropylsilyl) analogue show that they also have multiconfigurational ground states in which cerium is intermediate valent.14,23 The photoelectron spectra of Cp₃Ce suggest that the cation state, Cp₃Ce⁺(g), is multiconfigurational.14 Thus, the multireference model seems to be widely applicable to those organometallic compounds in which the electrons in filled \( \pi \)-bonding orbitals on the ligands function as electron donors to empty orbitals on the metal, as in cerocene and Cp₃Yb,15 and those in which the empty \( \pi \) orbitals are acceptor orbitals, as in Cp⁺ₓYb(bipy) and related compounds.6,9-22

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This Article reports experimental and computational studies on Ce(tmtaa)₂, Ce(acac)₃ and Ce(trop)₄, where acac and trop are abbreviations for the deprotonated ligands of 2,4-pentanediene and 2-hydroxy-2,4,6 cycloheptatriene, respectively (Scheme 1). These studies show that the ground states are open-shell singlets that have populated open-shell triplet excited states, resulting in TIP magnetic behavior. These molecular compounds have physical properties that are related...
to those of the solid-state material CeO₂, implying that they have similar electronic structures.

### RESULTS AND DISCUSSION

**Synthesis.** The original synthesis of Ce(trop)₄ was by the addition of 2-hydroxy-2,4,6-cycloheptatrienone (tropolone) to ceric ammonium nitrate in aqueous acidic methanol, and it was described as a "black crystalline material" from dichloromethane. A new synthesis is developed by the addition of a slight excess of tropolone, pKₐ = 6.27, in water, to a toluene solution of Ce(acac)₄ (the pKₐ value of acacH is 9 in water).

\[
\text{Ce(acac)}₄ + 4\text{tropH} \rightarrow \text{Ce(trop)}₄ + 4\text{acacH}
\] (1)

The dark precipitate that forms immediately is purified by Soxhlet extraction with chloroform in air. The dark-purple crystals are insoluble in hydrocarbon solvents and sparingly soluble in chlorinated hydrocarbons. The crystals appear black to the naked eye but yellow-orange in a dilute solution of CH₂Cl₂ because of a broad absorption at approximately 450 nm (ε ≈ 2000 M⁻¹ cm⁻¹); the ultraviolet absorptions are listed in the Experimental Section. An absorption around 500 nm is assigned to ligand-to-metal charge transfer in cerium tetrakis-(pyridylnitroxide) complexes. The 1H NMR spectrum in D₂O consists of a triplet at 7.44 ppm, J = 9.6 Hz, a doublet at 7.08 ppm, J = 10.4 Hz, and a triplet at 6.90 ppm, J = 9.6 Hz, in an area ratio of 8:8:4, assigned to Hα, Hβ, and Hγ, respectively. The 1H NMR spectrum at 20 °C indicates an average stereochemistry in solution when site exchange is often rapid in eight coordination, but the spectrum is a useful indicator of purity. The 1H NMR resonances are slightly broadened, which is apparent upon a comparison of the resonances due to Hγ in the complex and free tropolone. In the free ligand, Hγ appears as a triplet of triplets centered at δHγ = 6.97 with JHγHγ = 9.0 Hz and JHγHβ = 1.2 Hz; in the complex δHγ = 6.90 ppm is a triplet with JHγHγ = 9.6 Hz and JHγHβ is not resolved within the line width. There is no exchange between these resonances on the NMR time scale when a small amount of tropolone is added.

**X-ray Crystal Structure.** The compound Ce(trop)₄(tropH) crystallizes in the monoclinic crystal system with a = 6.727 in water, to a toluene solution to slowly evaporate; small dark-purple crystals formed over a few days. The crystal data are available in the Supporting Information (SI). The compound was used by dissolving the solid, obtained from a packing diagram available in the Supporting Information (SI). The crystal used was obtained by dissolving the solid, obtained from a packing diagram available in the Supporting Information (SI). The non-H atoms are placed in ideal positions and are not refined.

![Figure 1. ORTEP of Ce(trop)₄(tropH), with 50% probability ellipsoids. The non-H atoms are refined anisotropically, and the H atoms are placed in ideal positions and are not refined. The crystallized tropH molecule is not shown; see the SI.](image)

**Table 1. Average Ce−O Distances in Ce(acac)₄ and Related Derivatives Available in the CCDC**

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Ce−O(ave)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Me</td>
<td>2.39 ± 0.02</td>
<td>a</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>2.32 ± 0.03</td>
<td>b</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>2.33 ± 0.02</td>
<td>c</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>2.33 ± 0.02</td>
<td>d</td>
</tr>
<tr>
<td>CMe₃</td>
<td>CF₃</td>
<td>2.32 ± 0.04</td>
<td>e</td>
</tr>
<tr>
<td>CH₃CHMe₂</td>
<td>PH</td>
<td>2.33 ± 0.04</td>
<td>f</td>
</tr>
<tr>
<td>Me</td>
<td>PH</td>
<td>2.34 ± 0.02</td>
<td>g</td>
</tr>
<tr>
<td>CMe₃</td>
<td>CMe₃</td>
<td>2.31 ± 0.02</td>
<td>h</td>
</tr>
<tr>
<td>CF₃</td>
<td>CF₃</td>
<td>2.24 ± 0.01</td>
<td>i</td>
</tr>
<tr>
<td>CMe₃</td>
<td>CHMe₂</td>
<td>2.31 ± 0.03</td>
<td>j</td>
</tr>
<tr>
<td>CF₃</td>
<td>PH</td>
<td>2.32 ± 0.02</td>
<td>k</td>
</tr>
<tr>
<td>CMe₃</td>
<td>C(OMe)Me₃</td>
<td>2.32 ± 0.02</td>
<td>l</td>
</tr>
</tbody>
</table>


dodecahedron, as shown by the shape parameters in Table 2 (Figure 2).

Several crystal structures of neutral and anionic eight-coordinate metal tropolonate compounds are known, and their geometries generally are closer to that of a dodecahedron (D₅d) than to that of a bicapped trigonal prism when the shape parameters are used to make this distinction. The geometries of the lanthanide anions [M(trop)₄]⁻ from Tb to Lu are close to dodecahedral, as are the neutral M(trop)₄⁺ complexes. The anion [Sc(trop)₄]⁻ and cation [Nb(trop)₄]⁺ are described as bicapped trigonal prisms distorted toward a dodecahedron.

**Variable-Temperature Magnetic Susceptibility, χ, and L₃/₉-Edge XANES Spectroscopy.** The sample used for solid-state magnetic susceptibility of Ce(trop)₄ was obtained by Soxhlet extraction in and crystallization from CHCl₃ and shown to be free from cocrystallized tropolone by ¹H NMR spectroscopy and combustion analysis. The plot for Ce(trop)₄
of $\chi$ versus $T$ is shown in Figure 3, and similar plots for Ce(acac)$_4$, Ce(tmtaa)$_2$, and the solid-state compound CeO$_2$ are shown in Figure 4. The cerium contribution to the susceptibility is isolated by subtracting the other contributions from the complex using Pascal’s constants, and each data set is subsequently fit to a conventional Curie−Weiss model with $\chi = C_J/(T - \Theta_{CW}) + \chi_0$, where $C_J$ is known as the Curie constant, $\Theta_{CW}$ is the Curie−Weiss temperature and indicates the strength of magnetic interactions, and $\chi_0$ indicates the magnitude of the temperature-independent component. The small values of $C_J$ are consistent with a paramagnetic impurity corresponding to less than 0.2% of a Ce(III) impurity in all cases. All data were collected at two applied fields to account for any ferromagnetic impurity in the container, and these correspond to less than 0.15% of Fe in all cases.

Table 2. Shape Parameters for Eight-Coordinate Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$\delta_3$</th>
<th>$\delta_4$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>ref</th>
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</thead>
<tbody>
<tr>
<td>Ce(trop)$_4$</td>
<td>31.5</td>
<td>31.8</td>
<td>33.3</td>
<td>36.1</td>
<td>0.90</td>
<td>1.77</td>
<td>this work</td>
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<tr>
<td>$\alpha$-Ce(acac)$_4$</td>
<td>9.7</td>
<td>21.1</td>
<td>44.0</td>
<td>42.9</td>
<td>12.8</td>
<td>15.3</td>
<td>b</td>
</tr>
<tr>
<td>$\beta$-Ce(acac)$_4$</td>
<td>5.3</td>
<td>5.3</td>
<td>46.7</td>
<td>46.7</td>
<td>19.7</td>
<td>19.3</td>
<td>b</td>
</tr>
<tr>
<td>Ce(tmtaa)$_2$</td>
<td>0.83</td>
<td>1.12</td>
<td>1.14</td>
<td>1.45</td>
<td>0.24</td>
<td>0.59</td>
<td>this work</td>
</tr>
<tr>
<td>Ce(nitroxide)$_4$</td>
<td>30.7</td>
<td>30.9</td>
<td>49.0</td>
<td>49.5</td>
<td>7.8</td>
<td>11.0</td>
<td>a</td>
</tr>
<tr>
<td>Zr(trop)$_4$</td>
<td>22.9</td>
<td>31.8</td>
<td>32.4</td>
<td>40.1</td>
<td>6.6</td>
<td>1.9</td>
<td>d</td>
</tr>
<tr>
<td>Hf(trop)$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>e</td>
</tr>
<tr>
<td>Sc(trop)$_4$</td>
<td>13.4</td>
<td>29.0</td>
<td>42.3</td>
<td>43.0</td>
<td>10.8</td>
<td>10.8</td>
<td>f</td>
</tr>
<tr>
<td>Nb(trop)$_4$</td>
<td>19.4</td>
<td>21.0</td>
<td>42.9</td>
<td>45.1</td>
<td>11.5</td>
<td>13.9</td>
<td>g</td>
</tr>
<tr>
<td>$D_{4h}$ dodecahedron</td>
<td>29.5</td>
<td>29.5</td>
<td>29.5</td>
<td>29.5</td>
<td>0</td>
<td>0</td>
<td></td>
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<tr>
<td>square antiprism</td>
<td>0</td>
<td>0</td>
<td>52.4</td>
<td>52.4</td>
<td>24.5</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>square prism</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>bicapped trigonal prism</td>
<td>0</td>
<td>21.8</td>
<td>48.2</td>
<td>48.2</td>
<td>14.1</td>
<td>14.1</td>
<td></td>
</tr>
</tbody>
</table>

$\chi_0 = (1.2 \pm 0.3) \times 10^{-4}$ emu/mol is corrected for residual diamagnetism using Pascal’s constants and for a small amount of magnetic impurity.

The plots of $\chi$ versus $T$ for all of these compounds show that, after the diamagnetic correction for the ligand, $\chi$ is positive and, after fitting for a small paramagnetic impurity, independent of the temperature from 5 to 300 K; none of the cerium in these “Ce(IV)” molecules and the solid-state CeO$_2$ material is diamagnetic (i.e., $\chi$ is not negative), but they are temperature-independent paramagnets, implying that the excited state (ot) is close in energy to the ground state that is an open-shell...
singlet (os). If the cerium in these compounds were diamagnetic, \( \chi < 0 \), then their electronic ground states would be closed-shell singlets, \( S = 0 \) and \( L = 0 \), and their Lewis structures would be represented as \([\text{Ce}(\text{IV}, \text{F})/(L^{-1})_{\text{ff}}]_{\text{ff}}\), in which the lower orbital population is zero and each ligand is closed-shell and a monoanion. This classical representation results when molecules are classified by the oxidation number formalism, a classification that is misleading for \( \text{Ce}(\text{III}) \) and \( \text{Ce}(\text{II}) \) compounds.54

Also be thought of as the degree of covalency in the Ce bonds (area) of peak 2 to the total weight of peak 3. This value can reduce the core effects, are obscured by the high value of \( \chi_0 \) and \( \chi_0 \). Also presented are the data for CeO2 as a canonical formally tetravalent Ce system. In this case, although it has a somewhat high value of \( n_f \), \( e_f \) is high, consistent with a strongly covalent system, and although this extended solid should not be quantitatively compared to the other molecules studied here, the high value of \( \epsilon_f \) is also consistent with the low value of \( \chi_0 \).

Calculations. The calculations are all CASSCF/CAS-SDCI methodologies. Four electrons were distributed over five orbitals (four atomic 4f orbitals and the ligand lowest lying orbital). Then, as was already done for calculations on \( \text{Ce}^2+\text{Yb}(\text{bipy}) \), the number of active electrons was reduced to two and compared to the results obtained with a larger number of active electrons. The results were found to be consistent. The choice of the starting orbitals was also carefully investigated by trying several sets of MOs. MOs arising from either the \( \pi \text{L}^2 \) or \( \pi \text{L}^8 \) SCF calculations were considered, where the term \( \pi \text{L}^7 \) or \( \pi \text{L}^8 \) refers to a generic term to describe symmetry-adapted ligand orbitals (mainly O p lone pairs). In both cases, the T1 diagnostic of the CASSCF was found to be too large, although smaller for the first choice than the second one, indicating that the MOs were not optimal to describe the states. This was due to implication of the \( \pi \) states, although to a small amount, in the wave function. Therefore, averaged orbitals arising from the two states (\( \pi \text{L}^7 \) and \( \pi \text{L}^8 \)) were considered. Although T1 was reduced, it was still too high, indicating the need to describe the \( \pi \) states. Thus, the final set of MOs used in this study were obtained by averaging the MOs of the three states, \( \pi \text{L}^6 \), \( \pi \text{L}^7 \), and \( \pi \text{L}^8 \), using different weights (5.47, 48 and 33, 33, 33). Both sets yielded the same results, described in this contribution. Finally, by the fact that T1 was still large, configuration interaction (CI) calculations were carried out on top of the CASSCF. Because single and double excitations were taken into account, the MOs were improved during the CI calculation.

Table 3. Magnetic and L\(_{\text{III}}\) Edge XANES Data and Calculated Energies between the Different States (cs, Closed-Shell Singlet; os, Open-Shell Singlet; ot, Open-Shell Triplet)

<table>
<thead>
<tr>
<th>compound</th>
<th>( \chi ) (emu/mol)</th>
<th>( n_f )</th>
<th>( \epsilon_f )</th>
<th>( \epsilon_f^e )</th>
<th>( E^{(\text{os-ot})} )</th>
<th>( E^{(\text{os-cs})} )</th>
<th>( \mu\varphi ) (( \mu_{\text{B}, 300 \text{ K}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(\text{III})</td>
<td>1.2(3)x10^{-4}</td>
<td>0.50(3)</td>
<td>5728(3)</td>
<td>5736(3)</td>
<td>0.009 (73)</td>
<td>0.059 (476)</td>
<td>0.54(7)</td>
</tr>
<tr>
<td>Ce(\text{II})</td>
<td>2.1(2)x10^{-4}</td>
<td>0.51(3)</td>
<td>5727(9)</td>
<td>5735(9)</td>
<td>0.005 (40)</td>
<td>0.065 (523)</td>
<td>0.71(4)</td>
</tr>
<tr>
<td>Ce\text{(mmtaa)}</td>
<td>2.3(3)x10^{-4}</td>
<td>0.59(3)</td>
<td>5726(8)</td>
<td>5736(6)</td>
<td>0.008 (65)</td>
<td>0.088 (710)</td>
<td>0.75(1)</td>
</tr>
<tr>
<td>CeO\text{2}</td>
<td>4.7(2)x10^{-6}</td>
<td>0.58(3)</td>
<td>5728(3)</td>
<td>5736(5)</td>
<td>0.016(2)</td>
<td>0.106(2)</td>
<td>0.58(4)</td>
</tr>
<tr>
<td>Cerocene</td>
<td>1.4(2)x10^{-4}</td>
<td>0.82(3)</td>
<td>5725(0)</td>
<td>5736(5)</td>
<td>0.016(2)</td>
<td>0.106(2)</td>
<td>0.58(4)</td>
</tr>
</tbody>
</table>

The standard deviation in the last digit is reported in parentheses for each measurement. Absolute errors are reported for \( n_f \), \( \epsilon_f \), and \( \epsilon_f^e \). The relative error is smaller, about unity in the last reported digit. The effective moment at 300 K, \( \mu\varphi \) is calculated from \( \chi_0 \) in eV (cm⁻¹).
The four possible states that define the electronic states in which two electrons, one a cerium 4f electron and the other a ligand-based electron, can be distributed as indicated in Scheme 2. The energy scale is arbitrary.

Scheme 2. General Energy Diagram of the Different Configurations Discussed in This Article

The calculations show that the ground-state configuration of the three inorganic coordination compounds is an open-shell singlet, os. In each of the compounds, the triplet state, ot, is nearly degenerate but lies slightly higher in energy than the open-shell singlet. Besides the $\ell^2$ configuration, the closed-shell singlet, $\ell^0$, configuration is highest in energy in all three compounds. The relative energies in the three compounds and configurations that contribute to the ground-state wave function are illustrated in Scheme 3.

The calculated values of $n_f$, the number of f electrons in the initial electronic ground state, which is equal to $C_{32}^2$ in the wave function $|\Psi\rangle = C_{1}[Ce(IV,4f^2)(L - L^{-1})_4] + C_{2}[Ce(III,4f^2)(L - L^{-3/4})_4]$, are in good agreement with the experimental value of $n_f$ [0.42 vs 0.50 for Ce(trop)$_4$, 0.48 vs 0.51 for Ce(acac)$_4$, 0.41 vs 0.59 for Ce(tmtaa)$_2$]. They indicate that the $\ell^2$ contribution to the wave function is about 50%, not zero for a closed-shell configuration. The value of $C_{32}^2$ in the wave function depends slightly on the ligand in the order acac > trop $\approx$ tmtaa, while the value of $n_f$ is tmtaa > acac $\approx$ trop. The role the ligand plays in determining the coefficient of the $\ell^2$ configuration more or less follows the electronegativity of the ligating atoms in the three 16-electron coordination compounds and the 20-electron organometallic compound, C $>$ N $>$ O; therefore, COT $\gg$ tmtaa $>$ acac $\approx$ trop (using the experimental values).

Accordingly, the general order of sharing of the ligand-localized electron with the appropriate empty symmetry orbitals localized on cerium is related to the relative energy separation between the ligand highest occupied molecular orbital (HOMO) and cerium lowest unoccupied molecular orbital (LUMO) energies: the closer the energies, the larger the amount of sharing of the ligand electrons with the metal orbitals.

The small-calculated separation between os and ot is responsible for the TIP behavior observed experimentally and the small net value of $\mu_{\text{eff}}$ because the os ($S = 0$) mixes with the ot in an applied magnetic field and the population depends on the Boltzmann factor.

### SUMMARY

The new synthesis of Ce(trop)$_4$ exploits the relative pK$_a$ values of tropolone and acetylacetonate and promises to be a useful and general synthetic method for the preparation of other metal tropolone compounds because the metal acetylacetonates are usually easily prepared and soluble in hydrocarbon solvents for most of the metals and nonmetals in the periodic table, provided that they are kinetically labile.

The key point that emerges from the experimental study of the four isoelectronic molecules of cerium is that cerium is not diamagnetic in any of them because $\chi > 0$ and magnetically they behave as temperature-independent paramagnets. The wave function based on computational methods provides an explanation for the TIP, i.e., the small difference in energy between the open-shell singlet ground state and the open-shell triplet first excited state ranges from 40 to 75 cm$^{-1}$, allowing for Van Vleck paramagnetism.

The energy of the open-shell singlet that corresponds to the traditional Lewis structures used to represent these molecules is 400–700 cm$^{-1}$ above the open-shell triplet. A general MO diagram for these molecules is inappropriate for these 16-electron molecules because of their different point groups, highlighting the difficulties in understanding the difference between a Lewis structure represented by a single-reference wave function and the open-shell singlet multireference wave function.

### Electronic Structure of CeO$_2$ from the Molecules

The solid-state material, CeO$_2$, plays an important role in catalysis because it can function as an O-atom donor in oxidation reactions or as a H-atom-transfer catalyst in hydrogenation reactions. CeO$_2$ is an insulator with a band gap of 6.0 eV, but its ground-state electronic structure is controversial. The measured magnetic susceptibility between 5 and 300 K of CeO$_2$ (Figure 5) features TIP behavior, and the L$_{III}$-edge XANES spectra also have signatures of both $\ell^0$ and $\ell^3$ contributions (Figure 5). From the model discussed herein
for coordination molecules, it seems that CeO$_2$ would fall in the same category. Thus, these molecules would provide a deeper level of understanding of the electronic structure and chemical and physical properties of the solid-state material CeO$_2$, a further important step.

**EPILOGUE**

The electronic structures of four molecules, Ce(cot)$_4$, Ce(acac)$_4$, Ce(trop)$_4$, and Ce(tmataa)$_2$, have similar L$_{III}$-edge XANES features attributed to both Ce(W,F)$_2$ and Ce(III,F)$_2$ and magnetic susceptibility plots showing that the molecules are temperature-independent paramagnets to 300 K. The similarity of the spectroscopic features of the molecules and CeO$_2$ shows that they have similar electronic structures. CASSCF calculations on the molecules show that the ground state is an open-shell singlet with an $n_f$ of about 0.5 and the first excited state is an open-shell triplet that is close in energy. These two states are populated, resulting in TIP behavior. The notion that Lewis structures, which are traditionally written for the set of cerium coordination and organometallic compounds, are misleading, indeed wrong, should surprise the readers of this Article. The magnetic and spectroscopic measurements coupled with multireference wave-function-based methodologies that are required to develop the new model are laborious and time-consuming but rewarding.

**EXPERIMENTAL SECTION**

**General Considerations.** All reactions were performed using standard Schlenk-line techniques or in a drybox (MBraun). All glassware was dried at 150 °C for at least 12 h prior to use. Toluene and pentane were dried over sodium and distilled, while CH$_2$Cl$_2$ and CHCl$_3$ were purified by passage through a column of activated alumina. Toluene-d$_8$ was dried over sodium, and CDCl$_3$ was used as purchased from Aldrich. All of the solvents were degassed prior to use. Tropolone was purified by sublimation in a vacuum, and Ce(acac)$_4$ was prepared by a literature method. H NMR spectra were recorded on Bruker AVB-400 MHz and Advance 300 MHz spectrometers. 1H chemical shifts are in δ ppm relative to tetramethylsilane, and coupling constants (J) are given in hertz. IR spectra were recorded as Nujol mulls between KBr plates on a Thermo Scientific Nicolet IS10 spectrometer. Samples for UV–vis–near-IR spectroscopy were obtained in a Schlenk-adapted quartz cuvette and obtained on a Varian Cary 50 scanning spectrometer.

Melting points were determined in sealed capillaries prepared under nitrogen and are uncorrected. Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley.

The samples were prepared for X-ray absorption experiments as described previously, and the same methods were used to protect the air-sensitive compounds from oxygen and water. X-ray absorption measurements were made at the Stanford Synchrotron Radiation Lightsource on beamline 11-2. The samples were prepared and loaded into a liquid-helium-flow cryostat at the beamline as described previously. Data were collected at temperatures ranging from 30 to 300 K, using a Si(220) double-crystal monochromator. A linear extrapolation of the preedge absorption was subtracted, and the data were roughly normalized to unity above the edge. Energy calibration was performed by setting the peak in the first derivative of the absorption from a CeO$_2$ sample to 5724.0 eV. Fit methods were the same as described previously, but are detailed in the SI as well. Figure S5, showing that the individual fits and any remaining fit parameters not presented here. CeO$_2$ was purchased from commercial suppliers and used without further purification.

**Magnetism.** Magnetic susceptibility measurements were made for all samples in a 7 T Quantum Design Magnetic Properties Measurement System that utilizes a superconducting quantum interference device (SQUID). Sample container and other experimental details have been described previously. Dia magnetic corrections were made using Pascal's constants.

In contrast to some of our previous work, the combination of small magnetic signals and smaller quantities of the compounds made the container correction more critical for determining the TIP contribution, $\chi_0$, for these data. Our primary method for containing samples for SQUID measurements is to sandwich them between pieces of quartz wool (as little as a few milligrams or as much as 20 mg) in a quartz tube. We consequently performed multiple measurements of quartz wool batches. It is important to note that quartz wool can have organic material on it from the manufacturing process and that we routinely bake the wool above 200 °C. However, we found that leaving the wool in an open beaker in an oven sometimes results in a higher magnetic impurity, possibly from trace amounts of iron oxide. We determined from our measurements that $\chi_0 = (3.7 \pm 0.5) \times 10^{-7}$ emu/g for quartz wool, consistent with the value obtained for covalently bonded SiO$_2$ using a Pascal constant of $-3.69 \times 10^{-7}$ emu/g. The estimated 13.5% error in the magnitude of the quartz wool correction in the data in Figures 3 and 4 gives the dominant error source in the estimate of $\chi_0$ of the reported materials.

Another important correction is to remove any ferromagnetic impurity contribution by collecting data at multiple applied magnetic fields. The magnetic susceptibility is more rigorously defined as $\chi = dM/dH$, where $M$ is the measured magnetism and $H$ is the applied field, rather than the more common use of $M/H$. Here, we define $\chi = (M_n - M_s)/(H_n - H_s)$, where the subscript indicates measurement at two fields. This definition differs from the $M/H$ estimate in the presence of a magnetic impurity, $\chi_{imp}$, and assumes a linear $M$ versus $H$ curve with a constant impurity contribution. $\chi_{imp}$ can be estimated from the $y$ intercept of $M$ versus $H$, $\chi_{imp} = M_s - \gamma H_s$. It is important when using this correction to choose fields $H_1$ and $H_2$ to be large enough to saturate $\chi_{imp}$ so that it can be treated as a constant, which is typically above 600 Oe. The data reported here were collected at 0.5 and 40 kOe. The exception is the data for CeO$_2$, which used a polycarbonate capsule container and was collected only at 1 kOe.

**Synthesis.** Ce(acac)$_4$ (1.00 g, 1.86 mmol) was added to a 250 mL round-bottomed Schlenk flask with 50 mL of toluene to yield a dark-red-brown solution. Sublimed trop (1.16 g, 8.2 mmol) was added to the flask, and this led to the immediate precipitation of a dark solid. The mixture was stirred for 1 h at room temperature and filtered to yield a dark-brown powder that was dried under reduced pressure to yield Ce(trop)$_4$ (935 mg, 80%). The dark-brown powder was recrystallized using Soxhlet extraction in CH$_3$Cl over 7 days to yield Ce(trop)$_4$·CH$_2$Cl$_2$ (7296 mg) in a quartz tube. We consequently performed multiple measurements of quartz wool batches. It is important to note that quartz wool can have organic material on it from the manufacturing process and that we routinely bake the wool above 200 °C. However, we found that leaving the wool in an open beaker in an oven sometimes results in a higher magnetic impurity, possibly from trace amounts of iron oxide. We determined from our measurements that $\gamma_0 = (3.7 \pm 0.5) \times 10^{-7}$ emu/g for quartz wool, consistent with the value obtained for covalently bonded SiO$_2$ using a Pascal constant of $-3.69 \times 10^{-7}$ emu/g. The estimated 13.5% error in the magnitude of the quartz wool correction in the data in Figures 3 and 4 gives the dominant error source in the estimate of $\gamma_0$ of the reported materials.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00928

Crystal data, tables, and ORTEP diagrams for Ce(trop)$_4$

tropH (PDF)
Article

Inorganic Chemistry

Accession Codes
CCDC 1834248 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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