

# [Na<sub>5</sub>(THF)<sub>10</sub>Ce(mnt)<sub>4</sub>]<sub>∞</sub>: A Honeycomb Network Polymer That Yields Homoleptic Cerium(III) Tetrakis(Dithiolene) Complexes in Donor Solvents

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The first example of a lanthanide tetrakis(dithiolene) complex, [Na<sub>5</sub>(THF)<sub>10</sub>Ce(mnt)<sub>4</sub>] (**1**) (mnt = 1,2-maleonitrile-1,2-dithiolate), has been synthesized and characterized by X-ray crystallography and spectroscopic methods. In the solid state, **1** exists as a 2-D corrugated honeycomb network polymer in which the monomeric units comprising the trigonal nodes are knitted together by interlocking dative Na–N bonds extended from nitrile groups of bifunctional mnt ligands coordinated through the sulfur atoms to adjacent cerium centers. Individual honeycomb sheets are separated by 14.8 Å. Compound **1** dissolves in donor solvents such as THF and acetonitrile to give soluble [Ce(mnt)<sub>4</sub>]<sup>5-</sup> units that exhibit spectroscopic features (i.e., NMR, luminescence, UV–vis) that are consistent with the 4f<sup>1</sup> Ce(III) ion. In the first examination of the redox chemistry of a lanthanide dithiolene complex, cyclic voltammetry measurements conducted on **1** reveal a single irreversible oxidation wave that is likely attributable to ligand-centered oxidation.

## Introduction

Dithiolenes are an important class of redox-active ligands that are able to tune the redox behavior of the metals to which they are coordinated,<sup>1,2</sup> in some instances generating *non-innocent* complexes through extensive electron delocalization in which oxidation state assignments of both the metal and the ligand(s) become ambiguous.<sup>3</sup> This subtle interplay between metal and ligand redox properties has produced interesting optical and magnetic behavior, as well as anomalous phenomena, such as thermochroism<sup>4</sup> and superconductivity,<sup>5</sup> and is prominent in dithiolene-containing molybdopterin enzymes that catalyze a number of redox reactions.<sup>6</sup>

In contrast to the extensive use of these ligands with transition metals, literature reports of lanthanide complexes containing dithiolene ligands remain sparse,<sup>7,8</sup> and the only structurally characterized derivatives have just recently been

described from Ephritikhine's group.<sup>9,10</sup> Further, despite the well-established redox properties of these ligands, electrochemical studies have not been conducted on lanthanide dithiolene complexes. Large lanthanide ions can accommodate a diverse coordination sphere and possess open shell f<sup>n</sup> electronic structures that exhibit redox, optical, and magnetic properties that differ from the transition metals, thus offering an interesting contrast to study the coordination chemistry and redox behavior of lanthanide dithiolene complexes, particularly for Ce, which has access to a tetravalent oxidation state. Accordingly, we report herein the solid-state structure and solution spectroscopic properties of the first example of a lanthanide tetrakis(dithiolene) complex, along with the first examination of the redox chemistry between coordinated dithiolenes and a lanthanide ion.

## Experimental Section

**General Considerations.** Unless otherwise stated, all manipulations were conducted under an inert atmosphere of dry oxygen-free dinitrogen in a MBraun Labmaster 130 glovebox equipped with a MB 20G purification system or in standard Schlenk-type glassware on a dual vacuum/dinitrogen line. Toluene, diethyl ether, and hexanes (Fisher) were dried by passage through an MBraun

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solvent purification system (MB-SPS) consisting of one column of activated alumina and one column of activated copper catalyst (toluene, hexanes) or two columns of alumina (diethyl ether). Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. <sup>1</sup>H NMR spectra (referenced to the nondeuterated impurity in the solvent) were recorded on a Bruker AMX-250 or -300 spectrometer. <sup>13</sup>C NMR spectra (referenced to the sample's solvent peak) were run at 121.42 MHz on the AMX-300 instrument. Chemical shifts are reported in parts per million, and all coupling constants are reported in hertz unless otherwise noted. Infrared spectra were obtained as a mull in a mixture of type NVH and type B immersion oil pressed between KBr plates on a Thermo Nicolet Nexus 670 FT-IR spectrometer. UV-vis spectra were obtained as THF and acetonitrile solutions on a Hewlett-Packard 8452A diode-array spectrophotometer. Cyclic voltammetric studies were performed with a Bioanalytic Systems EpsilonEC-2000-Xp C3 model potentiostat/galvanostat under computer control using BAS software. Samples were run in a 0.1 M NBu<sub>4</sub>PF<sub>6</sub> solution in THF at a platinum working electrode with a silver wire quasi-reference electrode in the glovebox. Measured potentials were calibrated using the ferrocene/ferrocenium couple ( $E_{1/2} \approx 0.55$  V vs SCE). Elemental analyses were performed by Desert Analytics (combustion analyses; C, H, N) and the Missouri University Research Reactor (neutron activation analysis; Ce, Na, I). Cerium chips 99.9% (Aldrich), sodium cyanide (Acros Organics), and carbon disulfide (Alfa-Aesar) were used as received. Iodoethane (Aldrich) was degassed with dry nitrogen prior to use. Disodium maleonitriledithiolene<sup>11</sup> (Na<sub>2</sub>mnt) and CeI<sub>3</sub>(THF)<sub>4</sub><sup>12</sup> were synthesized according to literature procedures.

**Synthesis of [Na<sub>5</sub>(THF)<sub>10</sub>Ce(mnt)<sub>4</sub>]<sub>∞</sub> (1).** An olive yellow suspension of Na<sub>2</sub>mnt (0.41 g, 2.20 mmol) was combined with a pale yellow solution of CeI<sub>3</sub>(THF)<sub>4</sub> (0.45 g, 0.56 mmol) in 50 mL of THF at 23 °C. The mixture was allowed to stir for 12 h, and the dark brown solution was then filtered. Vapor diffusion of hexanes into a THF solution generated red crystals of **1** as a minor product along with a much larger quantity of tan colored solid. <sup>1</sup>H NMR for **1** (25 °C, CD<sub>3</sub>CN): δ 1.77 (br m, 40H, O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 3.62 (br m, 40H, O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>). <sup>13</sup>C NMR (25 °C, CD<sub>3</sub>CN): δ 26.0 (s), 68.1 (s), 129.0 (s), 129.7 (s). IR: ν(CN) 2187, 2220 cm<sup>-1</sup>. Anal. Calcd for Na<sub>5</sub>Ce(mnt)<sub>4</sub>·4NaI·(THF), C<sub>20</sub>H<sub>8</sub>CeI<sub>4</sub>N<sub>8</sub>Na<sub>9</sub>OS<sub>8</sub>: C, 16.14; H, 0.54; N, 7.53; Ce, 9.42; I, 34.12; Na, 13.91. Found: C, 15.26; H, 0.63; N, 7.19; Ce, 9.25; I, 27.5; Na, 13.57.

**X-ray Crystallographic Data.** A single crystal of **1** of suitable quality for X-ray analysis, obtained by layering a THF solution with toluene, was mounted on a glass fiber. Intensity data were obtained at -100 °C on a Bruker SMART CCD area-detector system using the ω-scan technique with Mo Kα radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multiscan method. Space group, lattice parameters, and other relevant information are given in Table 1. The structures were solved by direct methods with full-matrix least-squares refinement, using the SHELX package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the refinement using a riding model, with fixed isotropic *U*. The final difference map contained no features of chemical significance.

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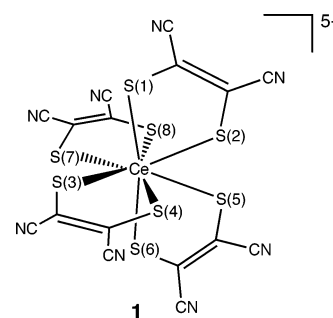
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**Table 1.** Summary of X-ray Crystallographic Data for [Na<sub>5</sub>(THF)<sub>10</sub>Ce(mnt)<sub>4</sub>]<sub>∞</sub> (**1**)

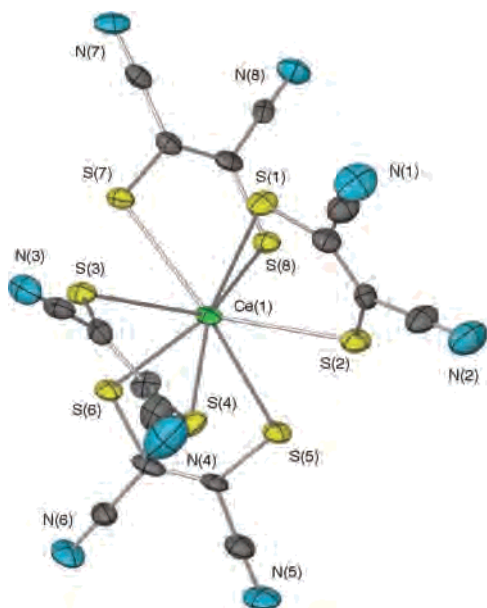
empirical formula	CeNa <sub>5</sub> C <sub>56</sub> H <sub>80</sub> N <sub>8</sub> O <sub>10</sub> S <sub>8</sub>
fw	1536.83
space group	<i>P</i> 1
<i>a</i> (Å)	14.805(5)
<i>b</i> (Å)	14.895(5)
<i>c</i> (Å)	18.492(6)
α (deg)	74.914(5)
β (deg)	73.190(6)
γ (deg)	71.560(5)
<i>V</i> (Å <sup>3</sup> )	3639(2)
<i>Z</i>	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.403
<i>T</i> (K)	173(2)
μ (mm <sup>-1</sup> )	0.941
θ range (deg)	1.47–27.18
total reflns	25 182
unique reflns	15 343
params	793
R1	0.0871
wR2	0.2017
max, min peaks (e Å <sup>-3</sup> )	3.459, -2.990
GOF	1.001

## Results and Discussion

**Synthesis and Structural Characterization.** The addition of 4 equiv of Na<sub>2</sub>mnt (mnt = 1,2-maleonitrile-1,2-dithiolate) to a THF solution of CeI<sub>3</sub>(THF)<sub>4</sub> generates [Na<sub>5</sub>(THF)<sub>10</sub>Ce(mnt)<sub>4</sub>]<sub>∞</sub> (**1**) as air-sensitive red-brown crystals after slow vapor diffusion of hexanes into a THF solution, along with an amorphous air-sensitive tan precipitate. The relative proportions of these materials vary slightly in repeated reactions, although in all instances, the amorphous material appears earlier from the reaction mixture and in much greater (>90%) quantity. Elemental analyses performed on this precipitate indicate a heterogeneous chemical composition related to **1** containing reduced quantities of THF and 4–5 equiv of NaI, indicating incorporation of both products of the metathesis reaction into this amorphous, presumably polymeric, material. The high iodine content (variable from sample to sample) was confirmed through neutron activation analysis. In maintaining the mass balance from this reaction, only minor quantities of NaI are filtered from the reaction mixture with the remaining mother liquor enriched in **1**. Refluxing the reaction mixture in various solvents, such as acetonitrile or THF, has proven to be ineffective in further separating these compounds, although the NMR spectroscopic data discussed below support the assertion that this amorphous material contains the same cerium chemical units as found in **1**.



Single crystals suitable for X-ray diffraction were obtained for **1**. A thermal ellipsoid drawing of the [Ce(mnt)<sub>4</sub>]<sup>5-</sup> anion



**Figure 1.** Thermal ellipsoid drawing of the  $[\text{Ce}(\text{mnt})_4]^{5-}$  anion of **1** showing the atom-labeling scheme used in the tables. Displacement ellipsoids are shown at 50% probability.

**Table 2.** Bond Lengths (Å) and Angles (deg) for **1**

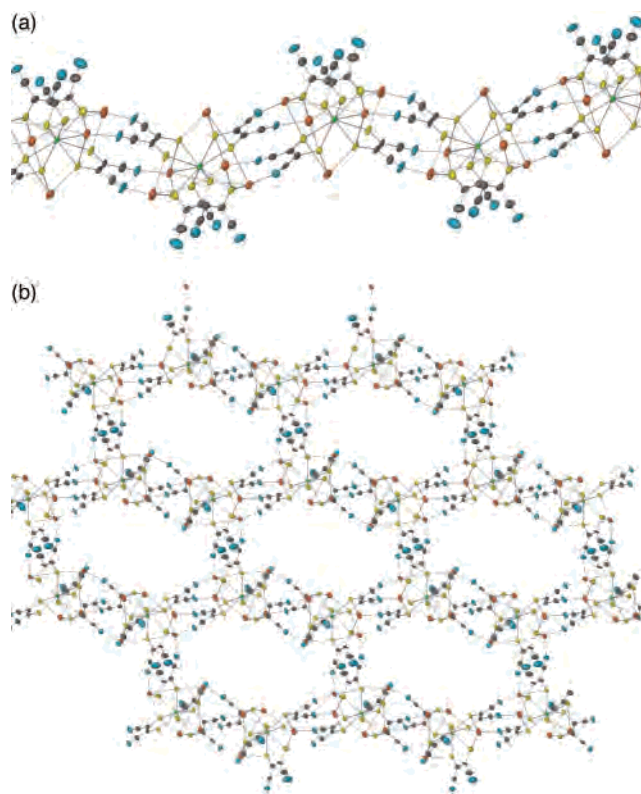
Ce(1)–S(5)	2.919(2)	S(5)–Ce(1)–S(4)	78.53(6)
Ce(1)–S(4)	2.930(2)	S(5)–Ce(1)–S(1)	131.72(7)
Ce(1)–S(1)	2.941(2)	S(4)–Ce(1)–S(1)	100.08(7)
Ce(1)–S(6)	2.948(2)	S(5)–Ce(1)–S(6)	70.44(6)
Ce(1)–S(7)	2.955(2)	S(4)–Ce(1)–S(6)	87.81(7)
Ce(1)–S(3)	2.976(2)		
Ce(1)–S(2)	2.990(3)		
Ce(1)–S(8)	2.999(2)		

of **1** is shown in Figure 1, and selected bond distances and bond angles are listed in Table 2. Each cerium center is coordinated by four chelating dithiolene ligands. The only other example of a metal tetrakis(dithiolene) complex is the uranium derivative  $[\text{Na}_4(\text{THF})_8\text{U}(\text{dddtd})_4]$  (dddtd = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) isolated as a one-dimensional network polymer.<sup>13</sup>

The eight-coordinate geometry of the S atoms around the cerium center is best described as a distorted dodecahedron,<sup>14</sup> where S(1), S(2), S(5), and S(6) comprise a coplanar trapezoid that is orthogonal to another trapezoid containing S(4), S(3), S(7), and S(8). When the conformational flexibility in the metal–ligand bonding is considered, this geometry possesses approximate  $D_{2d}$  point-group symmetry.

Five sodium atoms surround each  $[\text{Ce}(\text{mnt})_4]^{5-}$  anion in approximate trigonal bipyramidal geometry with respect to the central cerium atom. An octahedral coordination geometry is observed for each sodium atom, obtained by fac coordination of three S atoms from the inner  $[\text{Ce}(\text{mnt})_4]^{5-}$  core, with the three remaining sites combined from 3 –  $n$  THF ligands and  $n$  dative interactions from nitrile N atoms of dithiolenes that are coordinated to other cerium centers.

It is worth noting that although the mnt ligands are potentially bifunctional there is minimal electron density



**Figure 2.** (a) View of the zigzag chain in **1**. (b) View of the distorted honeycomb network in **1**. THF molecules have been omitted in both views for clarity.

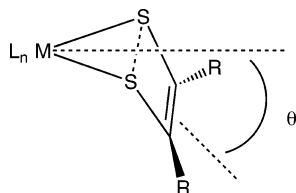
residing on the nitrile N atoms and therefore few examples in which this end of the ligand is coordinated to another metal center.<sup>15,16</sup> That this dative bonding occurs in **1** in the presence of a coordinating solvent is rather unusual, which we attribute to enhanced nucleophilicity associated with the large formal 5– charge in the monomeric units. Importantly, these bridging N–Na interactions furnish the links between the  $\text{Ce}(\text{mnt})_4$  units that generate the observed extended structure in **1**. For example, N(5) and N(6) of one dithiolene ligand are bound to Na(3) and Na(5), respectively, belonging to the coordination sphere of an adjacent  $\text{Ce}(\text{mnt})_4$  unit. This connection is reciprocated from the second cerium center to the first forming a loop structure. A zigzag-linked chain is propagated by replicating this loop structure with N(7) and N(8) from another dithiolene ligand to Na(1) and Na(4), respectively, belonging to the coordination sphere of a third Ce center (Figure 2a). Finally, separate helical chains are knitted together by additional cross-linking reciprocal bridges involving N(3) from a dithiolene ligand of one chain and Na(3) associated with an adjacent chain. The helical nature of the main chain causes alternating Ce atoms to reside above and below the  $bc$  plane, so that the cross-links along the main chain produce a honeycomb network of distorted nonplanar hexagonal units (specifically, chair-conformation parhexagons) defined by cerium atoms situated at trigonal pyramidal nodes. The overall appearance is that of a

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**Figure 3.** Schematic representation of the fold angle,  $\theta$ , in metal dithiolene complexes.

corrugated two-dimensional sheet along the *bc* plane (Figure 2b) with a spacing of 14.8 Å (equivalent to the unit cell distance *a*) between individual sheets.

The Ce–S bond distances range between 2.941(2) and 2.999(2) Å with an average value of 2.96(1) Å, consistent with values found in Ce(III) dithiolene and thiolate complexes.<sup>9,17,18</sup> The C–S (1.73–1.75 Å) and C=C (1.35–1.38 Å) bond parameters indicate that the mnt units are coordinating as dianionic dithiolene ligands (as opposed to the oxidized neutral dithioketone tautomer),<sup>1</sup> which gives the [Ce(mnt)<sub>4</sub>]<sup>5-</sup> unit the expected Ce(III) oxidation state (Ce(IV) thiolate derivatives are currently unknown).

Dithiolene ligands typically coordinate with the S–C=C–S plane tilted toward the metal center, generating a fold angle ( $\theta$ ) with the S–Ce–S plane (Figure 3). For high-valent transition metals a pronounced fold angle allows more effective overlap of filled S 3p orbitals (of  $\pi$  symmetry with respect to the S–C=C–S plane) with empty orbitals on the electrophilic metal center,<sup>19</sup> and has been similarly noted for f-element derivatives.<sup>20–22</sup> In the solid-state structure of **1**, these angles are relatively shallow, ranging between 8.3 and 29.0°, reflecting the steric constraints and electronic saturation of the cerium center provided by four dithiolene ligands. Shallow fold angles have also been observed in the analogous uranium tetrakis(dithiolene) derivative [Na<sub>4</sub>(THF)<sub>8</sub>U(ddd)<sub>4</sub>], presumably as a similar steric response.<sup>13</sup> The rare tetrakis(dithiolene) coordination geometry for the Ce(III) center in **1** results in the highest formal charge (5<sup>-</sup>) yet obtained in a homoleptic dithiolene complex. Stabilization of the [Ce(mnt)<sub>4</sub>]<sup>5-</sup> anion is likely achieved by a combination of the large electrophilic Ce(III) center, the electron-withdrawing cyano groups, the small size of the mnt ligands, and the close proximity of the Na<sup>+</sup> counterions.

**Solution Studies.** Compound **1** readily dissolves in donor solvents such as THF and acetonitrile. Because the saturated eight-coordinate cerium center is unlikely to accommodate THF coordination, it is more likely that the dative Na–N bonds holding together the extended solid-state structure are disrupted instead, generating solvated Na<sup>+</sup> ions intimately associated with soluble [Ce(mnt)<sub>4</sub>]<sup>5-</sup> units. The solution <sup>1</sup>H

NMR spectrum of paramagnetic **1** is uninformative because the mnt ligands do not contain protons, but the <sup>13</sup>C NMR spectrum in acetonitrile clearly shows two downfield resonances at 129.0 and 129.7 ppm, corresponding to the two different carbon environments of equivalent mnt ligands consistent with the averaged *D*<sub>2d</sub> symmetry of the monomeric anion. Because of the low isolated yield, we have been unable to conclusively determine whether **1** is an example of a reversible coordination polymer (i.e., polymers that reversibly break and reform, according to the addition or removal of a coordinating solvent).<sup>23</sup> Lanthanide ions present greater a likelihood of forming reversible polymers because of their combined penchant for labile coordination and large coordination numbers.

As with crystalline **1**, the amorphous tan precipitate is soluble in acetonitrile, as well as in pyridine, but has poor solubility in THF, reflecting a different polymeric network containing a much lower quantity of THF. The solution <sup>13</sup>C NMR spectrum of this material is identical to that observed for **1**, suggesting that the same [Ce(mnt)<sub>4</sub>]<sup>5-</sup> building blocks are present in solution, as opposed to a cerium species containing (for example) three dithiolene ligands. It is worth noting that the same features are observed in the solid-state <sup>13</sup>C NMR spectrum of this tan material.

The emission spectrum of **1** shows two prominent features, a peak at 330 nm and, characteristic for the 4f<sup>1</sup> Ce(III) ion, another centered near 420 nm.<sup>24</sup> There is also a broad feature at ~460 nm in the UV–vis absorption spectrum that is responsible for the red color observed for **1**. These emission and absorption features both originate from 5d–4f electronic transitions (see Figures S1 and S2, Supporting Information).<sup>25</sup>

The electronic structure of **1** provides a useful contrast with that of the cerium(IV) tetrakis(catecholate) complex Na<sub>4</sub>Ce(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub> (**2**),<sup>26</sup> which possesses similar dodecahedral coordination geometry but exists with the cerium center in the diamagnetic tetravalent oxidation state. Catechols and dithiolenes are related analogues of a rich series of 1,2-disubstituted redox-active ligands. The remarkable ability of catecholate ligands to stabilize high-valent metals is shown by the large cathodic shift (–692 mV vs SCE, –1.3 V vs Fc/Fc<sup>+</sup>) in the Ce(IV)/Ce(III) redox potential for **2**, relative to most cerium compounds. Not surprising, the softer sulfur-bearing mnt ligands in **1** are unable to sustain this high oxidation state, especially with electron-withdrawing cyano groups. However, metal dithiolene complexes have been shown to exhibit interesting redox processes involving the metal center, the dithiolene ligands, or both, and given that both metal and ligand oxidation are nominally possible for

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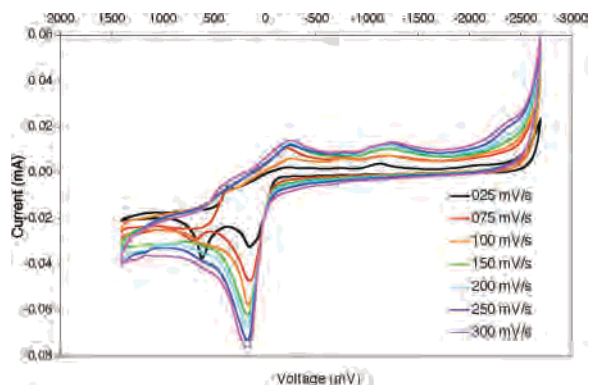
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(25) This broad absorption feature resides as a low-energy shoulder on a much stronger absorption peak associated with the mnt unit, which appears essentially unchanged compared to the spectrum obtained for the Na<sub>2</sub>mnt salt, suggesting minimal perturbation in the electronic structure of the mnt unit consistent with similar ionic bonding of this ligand with both sodium and cerium.

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**Figure 4.** Cyclic voltammograms of **1** (1.0 mM) in THF with 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as the electrolyte, versus Fc/Fc<sup>+</sup>.

**1**, we were interested in examining the electrochemistry of this species.

Cyclic voltammetry conducted on **1** shows a single irreversible oxidation wave at 180 mV with respect to the Fc/Fc<sup>+</sup> redox couple (Figure 4), although the reverse wave is partially recovered at faster scan rates. However, a second oxidation near 600 mV is introduced with scan rates slowed below 100 mV/s, indicating the onset of chemical processes following initial oxidation, which accounts for these waves not being consistently reproduced upon repeated scans. On the basis of these data, the oxidation likely represents a

ligand-centered process because metal oxidation to a Ce(IV) species would likely be reversible (i.e., with minimal structural rearrangement, similar to what has been reported for **2**) and occur at a more anodic potential.

## Conclusions

The first structurally characterized example of a homoleptic lanthanide tetrakis(dithiolene) complex is reported, which forms a 2-D honeycomb network in the solid state because of unusual dative N–Na bridging interactions from the nitrile termini of the mnt ligands. These dative bonds are readily broken in donor solvents to give soluble [Ce(mnt)<sub>4</sub>]<sup>5-</sup> units that are probably intimately associated with solvated sodium counterions. Finally, electrochemical measurements show that compound **1** exhibits an irreversible oxidation reaction that is likely ligand centered.

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**Supporting Information Available:** Figures S1 and S2 and an X-ray crystallographic file in CIF format for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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