

## Utility of Anhydrous Neodymium Nitrate as a Precursor to Extended Organoneodymium Nitrate Networks

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Hydrated neodymium nitrates can be readily transformed to anhydrous ether solvates which react with cyclopentadienyl reagents to make organometallic nitrate complexes with variable degrees of oligomerization. Heating  $\text{Nd}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_6$  in tetrahydrofuran at reflux, removal of solvent, drying at 100 °C under high vacuum, and addition of hot THF generates  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$ , **1**. Using dimethoxyethane,  $\text{Nd}(\text{NO}_3)_3(\text{DME})_2$ , **2**, can be obtained similarly. Addition of  $\text{NaC}_5\text{Me}_5$  to **1** generates  $(\text{C}_5\text{Me}_5)\text{Nd}(\text{NO}_3)_3(\text{THF})\text{Na}(\text{THF})_x$  complexes which crystallize as  $\{[(\text{C}_5\text{Me}_5)(\text{NO}_3)_2\text{Nd}(\text{THF})(\mu\text{-NO}_3)]_2\text{Na}(\text{THF})_4\}[\text{Na}(\text{THF})_6]$ , **3**, or  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{THF})(\mu\text{-NO}_3)_3\text{Na}(\text{THF})_2]_n$ , **4**, depending on the conditions. The trimetallic  $\text{Nd}_2\text{Na}$  unit in **3** forms an extended system in **4** via bridging nitrates. Addition of  $\text{KC}_5\text{Me}_5$  and 18-crown-6 to **1** generates another extended complex  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{THF})(\text{NO}_3)(\mu\text{-NO}_3)_2\text{K}(18\text{-crown-6})]_n$ , **5**, in which an 18-crown-6 ligated potassium links neodymium centers via two bridging nitrates and an agostic interaction between a  $\text{C}_5\text{Me}_5$  methyl group and potassium.

### Introduction

The lanthanide salts that are used most commonly as precursors to organometallic lanthanide complexes are the lanthanide halides.<sup>1,2</sup> Although the halides are generally excellent precursors to organolanthanide compounds, they must be used in anhydrous form, and dehydration of the industrially produced hydrates must be done carefully. Although some water can be removed by simple heating,<sup>3</sup> complete removal of water requires temperatures high enough to generate hydroxides and oxides.<sup>4–8</sup> To avoid hydroxide and oxide formation, more elegant approaches to dehydration must be used.<sup>9</sup> For example, dehydration in the presence of  $\text{NH}_4\text{Cl}$  gives oxygen-free anhydrous  $\text{LnCl}_3$ .

In contrast to the heavy use of lanthanide halides as organometallic precursors, lanthanide nitrates are rarely

employed for this purpose. An exception is the use of the common Ce(IV) precursor, ceric ammonium nitrate,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ .<sup>10,11</sup> Nitrates are commonly used precursors for inorganic lanthanide complexes,<sup>10,11,12</sup> and Niemeyer has shown that hydrated praseodymium nitrate can be desolvated with the common dehydration agent, trimethoxymethane.<sup>12</sup> One problem in using lanthanide nitrates is that caution must be used due to the potential of explosion at high temperatures.<sup>11,13</sup>

We report here the facile conversion of hydrated neodymium nitrate to anhydrous tetrahydrofuran and dimethoxyethane adducts and subsequent reactivity with cyclopentadienyl reagents to form oligomeric organometallic species. These reactions show that nitrates can be useful precursors in organolanthanide chemistry, and the structures of the organometallic lanthanide nitrate products are good building blocks for the assembly of extended systems.

### Results

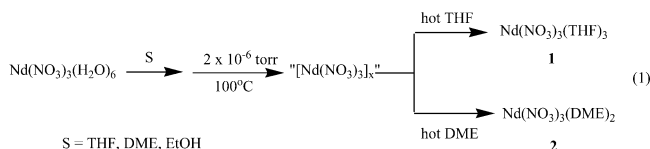
**Synthesis. Anhydrous Nitrates.** Anhydrous  $\text{Nd}(\text{NO}_3)_3 \cdot (\text{THF})_3$ , **1**, and  $\text{Nd}(\text{NO}_3)_3(\text{DME})_2$ , **2**, were readily prepared

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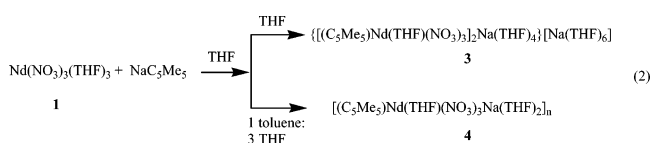
by heating  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  in THF and DME, respectively, at reflux, removal of solvent, drying at  $2 \times 10^{-6}$  Torr at  $100^\circ\text{C}$ , and recrystallizing from the appropriate solvent, eq 1. Complexes **1** and **2** can also be synthesized by heating



the hydrated nitrate salt in ethanol at reflux, removal of solvent, drying under high vacuum at  $100^\circ\text{C}$ , and recrystallizing from the appropriate solvent. The yields of **1** and **2** are nearly quantitative.

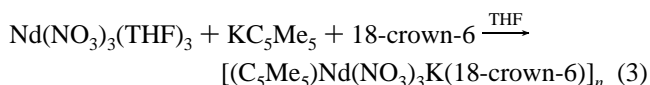
This procedure is similar to the method used to desolvate praseodymium nitrate using trimethoxymethane.<sup>12</sup> In that case, the trimethoxymethane hydrolyzes to form the methanol adduct,  $\text{Pr}(\text{NO}_3)_3(\text{MeOH})_{0.56}$ , which subsequently can be treated with THF or DME to form  $\text{Pr}(\text{NO}_3)_3(\text{THF})_4$  and  $\text{Pr}(\text{NO}_3)_3(\text{DME})_2$ . Our results show that the water in  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  can be displaced even without trimethoxymethane. Due to the potentially explosive nature of lanthanide nitrates at high temperatures, the nitrates were not heated above  $100^\circ\text{C}$  during the drying process under vacuum. Samples heated to  $120^\circ\text{C}$  were observed to decompose with formation of a brown gas, presumably nitrogen oxides.

**Organoneodymium Nitrate Complexes.** Anhydrous  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$ , **1**, reacts with the common organometallic ligand, pentamethylcyclopentadienide, to generate organometallic nitrate complexes. Reactions between **1** and one equivalent of  $\text{NaC}_5\text{Me}_5$  in THF gave two different but closely related products,  $\{[(\text{C}_5\text{Me}_5)(\text{NO}_3)_2\text{Nd}(\text{THF})(\mu\text{-NO}_3)]_2\text{Na}(\text{THF})_4\}[\text{Na}(\text{THF})_6]$ , **3**, and  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{THF})(\mu\text{-NO}_3)_3\text{Na}(\text{THF})_2]_n$ , **4**, depending upon the method of crystallization, eq 2. Both **3** and **4** have the general composition

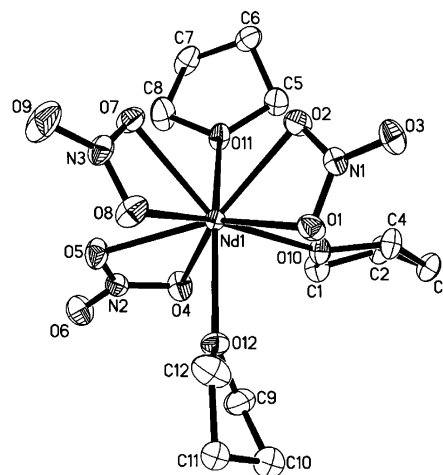


$(\text{C}_5\text{Me}_5)\text{Nd}(\text{THF})(\text{NO}_3)_3\text{Na}(\text{THF})_x$  but differ in  $x$ . Complex **3**, crystallized from THF, has five THF per Na; complex **4**, crystallized from 1:3 toluene:THF, has two THF per Na.

Preliminary studies of the reaction of **1** with  $\text{KC}_5\text{Me}_5$  did not lead to crystallographically characterizable materials as readily as the sodium reactions. However, when the reaction was done in the presence of 18-crown-6, a THF-free potassium analogue of **3** and **4** was isolated, namely  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{NO}_3)_3\text{K}(18\text{-crown-6})]_n$ , **5**, eq 3. To our knowledge, **3–5** are the first crystallographically characterized



organometallic lanthanide nitrate complexes in the literature.



**Figure 1.** Thermal ellipsoid plot of  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$ , **1**, shown at the 50% probability level.

**Structural Studies.**  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$ , **1**. Complex **1** crystallizes from THF as the tris-solvate rather than the tetrasolvate obtained for praseodymium,  $\text{Pr}(\text{NO}_3)_3(\text{THF})_4$ ,<sup>12</sup> the only other crystallographically characterized THF-solvated  $\text{Ln}(\text{NO}_3)_3(\text{THF})_x$  complex in the literature. Since Nd is smaller than Pr, it is not unreasonable that a complex of lower coordination number is isolated. The trisolvated Yb and Ho analogues of  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$  are reported on the basis of analytical data,<sup>12</sup> and it is possible that the point in which the coordination number changes in the  $\text{Ln}(\text{NO}_3)_3(\text{THF})_x$  class is between Pr and Nd.<sup>14</sup> However, two structures are not sufficient to determine this absolutely. It is also possible that crystals of both tri- and tetracoordinated complexes can be obtained.

Complex **1** is formally nine coordinate due to the three bidentate nitrate ligands and three monodentate THF solvates, Figure 1. To simplify the structural analysis, the nitrates will be considered to occupy one coordination position as is often done with this small bite chelate. This is advantageous since it avoids the high coordination number geometries which are often difficult to envision and since geometries are often very irregular due to the chelating ligands. By this convention, **1** is a six coordinate distorted octahedron with a meridional arrangement of ligands. The distortions from octahedral can be seen from the three axial angles O(11)–Nd–O(12), O(10)–Nd–N(3), and N(1)–Nd–N(2) which are  $153.23(11)^\circ$ ,  $166.17(11)^\circ$ , and  $173.66(10)^\circ$ , respectively.

The Nd–O distances in **1** vary from 2.497(3)–2.524(3) Å for the nitrate ligands and 2.445(3)–2.502(2) Å for the THF ligands. These are reasonable values compared to data in the literature which show that there is considerable variation of Ln–O( $\text{NO}_3$ ) distances depending on the coligands.<sup>10,11,13,15–17</sup> The analogous distances in  $\text{Pr}(\text{NO}_3)_3(\text{THF})_4$  are 2.537(3)–2.634(3) Å and 2.542(3)–2.577(3) Å,

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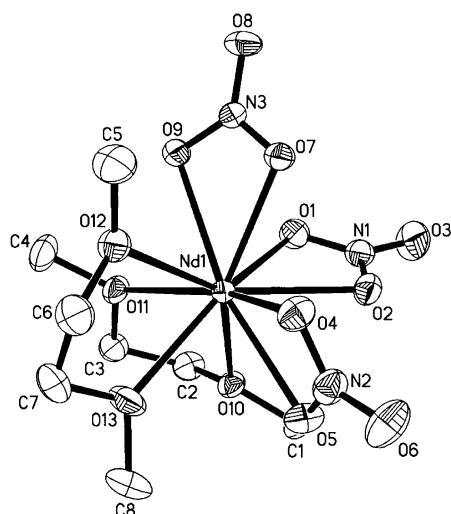
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**Table 1.** X-ray Data Collection Parameters<sup>a</sup> for Nd(NO<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>, **1**, Nd(NO<sub>3</sub>)<sub>3</sub>((dme)<sub>2</sub>), **2**, {[(C<sub>5</sub>Me<sub>5</sub>)(NO<sub>3</sub>)<sub>2</sub>Nd(THF)(μ-NO<sub>3</sub>)<sub>2</sub>Na(THF)<sub>4</sub>]}Na(THF)<sub>6</sub>, **3**, [(C<sub>5</sub>Me<sub>5</sub>)(NO<sub>3</sub>)<sub>2</sub>Nd(THF)(μ-NO<sub>3</sub>)Na(THF)<sub>2</sub>]<sub>n</sub>, **4**, and [(C<sub>5</sub>Me<sub>5</sub>)Nd(NO<sub>3</sub>)<sub>3</sub>K(18-crown-6)]<sub>n</sub>, **5**

empirical formula	C <sub>12</sub> H <sub>24</sub> N <sub>3</sub> NdO <sub>12</sub> <b>1</b>	C <sub>8</sub> H <sub>20</sub> N <sub>3</sub> NdO <sub>13</sub> <b>2</b>	C <sub>68</sub> H <sub>126</sub> N <sub>6</sub> O <sub>30</sub> Na <sub>2</sub> Nd <sub>2</sub> <b>3</b>	(C <sub>22</sub> H <sub>39</sub> N <sub>3</sub> O <sub>12</sub> NaNd) <sub>∞</sub> <b>4</b>	C <sub>26</sub> H <sub>47</sub> N <sub>3</sub> O <sub>16</sub> KNd <b>5</b>
formula weight	546.58	510.51	1842.21	704.79	841.01
temperature (K)	158(2)	173(2)	158(2)	163(2)	158(2)
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å)	7.7660(7)	10.3843(11)	9.4276(8)	9.9493(6)	10.680(3)
<i>b</i> (Å)	13.6581(12)	15.0674(12)	11.8822(10)	11.3426(7)	15.024(4)
<i>c</i> (Å)	9.4080(8)	11.3843(11)	19.6454(17)	14.0833(8)	11.683(3)
α (deg)	90	90	98.5660(10)	68.7690(10)	90
β (deg)	96.365(2)	92.467(8)	96.4690(10)	85.8170(10)	110.248(4)
γ (deg)	90	90	101.8970(10)	84.9390(10)	90
volume Å <sup>3</sup>	991.74(15)	1779.6(3)	2105.9(3)	1474.23(15)	1758.8(7)
<i>Z</i>	2	4	1	2	2
ρ <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.830	1.905	1.453	1.588	1.588
μ (mm <sup>-1</sup> )	2.683	2.986	1.310	1.837	1.667
R1 <sup>b</sup> (I > 2.0σ(I))	0.0234	0.0255	0.0336	0.0240	0.0685
wR2 <sup>c</sup> (all data)	0.0730	0.0627	0.0877	0.0607	0.1835

<sup>a</sup> Radiation: Mo-Kα (μ = 0.71073 Å). Monochromator: highly oriented graphite. <sup>b</sup> R = Σ|F<sub>o</sub> - xF<sub>d</sub>|/Σ|F<sub>o</sub>|. <sup>c</sup> wR2 = [Σ(w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)/Σ(w(F<sub>o</sub><sup>2</sup>)))]<sup>1/2</sup>.

**Figure 2.** Thermal ellipsoid plot of Nd(NO<sub>3</sub>)<sub>3</sub>(DME)<sub>2</sub>, **2**, shown at the 50% probability level.

respectively. The Pr-O distances are longer as expected for a higher coordinate complex of a larger metal.

**Nd(NO<sub>3</sub>)<sub>3</sub>(DME)<sub>2</sub>, 2.** Complex **2** crystallizes from DME as a monomeric compound with a formally 10 coordinate neodymium surrounded by three bidentate nitrate and two bidentate DME ligands, Figure 2. It is isomorphous with the cerium analogue reported earlier, Ce(NO<sub>3</sub>)<sub>3</sub>(DME)<sub>2</sub>.<sup>11</sup> Considering each of the bidentate ligands in **2** to occupy one coordination position, complex **2** is a five coordinate distorted trigonal bipyramid with N(3) at one axial position and the O(10), O(11) dimethoxyethane at the other. The Nd-O bond distances are unexceptional, Table 3.

{[(C<sub>5</sub>Me<sub>5</sub>)(NO<sub>3</sub>)<sub>2</sub>Nd(THF)(μ-NO<sub>3</sub>)<sub>2</sub>Na(THF)<sub>4</sub>]}[Na(THF)<sub>6</sub>], **3**. The (C<sub>5</sub>Me<sub>5</sub>)Nd(NO<sub>3</sub>)<sub>3</sub>Na composition isolated from the NaC<sub>5</sub>Me<sub>5</sub>/Nd(NO<sub>3</sub>)<sub>3</sub> reaction in THF crystallizes from THF as the ion pair **3** comprised of a conventional [Na(THF)<sub>6</sub>]<sup>+</sup> cation and an anion containing two [(C<sub>5</sub>Me<sub>5</sub>)-Nd(NO<sub>3</sub>)<sub>3</sub>(THF)]<sup>-</sup> units sandwiching a [Na(THF)<sub>4</sub>]<sup>+</sup> moiety via one bridging nitrate per Nd. The bridging nitrates use

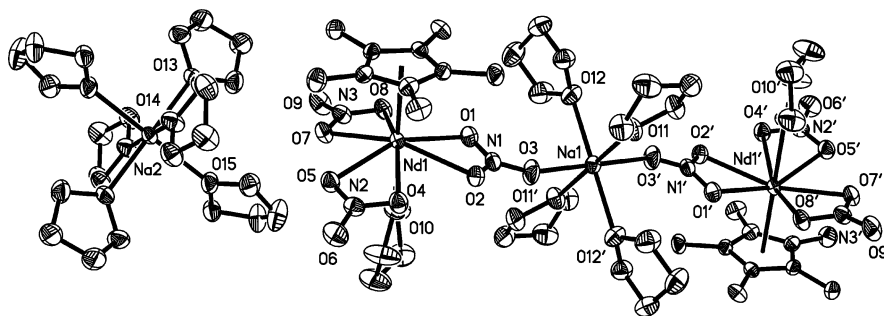
**Table 2.** Bond Distances (Å) in Nd(NO<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>, **1**, and Nd(NO<sub>3</sub>)<sub>3</sub>((dme)<sub>2</sub>), **2**

bond	<b>1</b>	<b>2</b>
Nd(1)-O(1)	2.524(3)	2.574(2)
Nd(1)-O(2)	2.509(3)	2.515(2)
Nd(1)-O(4)	2.519(3)	2.497(2)
Nd(1)-O(5)	2.506(3)	2.580(3)
Nd(1)-O(7)	2.504(3)	2.504(2)
Nd(1)-O(8)	2.497(3)	
Nd(1)-O(9)		2.563(2)
Nd(1)-O(10)	2.502(3)	2.526(2)
Nd(1)-O(11)	2.464(3)	2.538(2)
Nd(1)-O(12)	2.445(3)	2.579(2)
Nd(1)-O(13)		2.505(2)
angles	<b>1</b>	<b>2</b>
O(11)-Nd(1)-N(1)	98.71(10)	
O(12)-Nd(1)-N(1)	97.65(11)	
O(10)-Nd(1)-N(2)		97.81(8)
O(11)-Nd(1)-N(2)	84.06(10)	149.50(8)
O(12)-Nd(1)-N(2)	77.76(10)	92.85(8)
O(13)-Nd(1)-N(3)		75.50(7)
O(10)-Nd(1)-N(3)		131.76(80)
O(11)-Nd(1)-N(3)	99.59(10)	92.49(8)
O(12)-Nd(1)-N(3)	100.99(11)	75.50(7)
O(13)-Nd(1)-N(3)		137.56(8)
O(10)-Nd(1)-O(11)	76.85(10)	
O(10)-Nd(1)-O(12)	86.80(11)	
O(11)-Nd(1)-O(12)	153.23(11)	
N(3)-Nd(1)-O(10)	166.17(11)	
N(1)-Nd(1)-N(3)	91.60(11)	
N(2)-Nd(1)-N(3)	93.56(11)	
N(3)-Nd(1)-N(2)	173.66(10)	

two oxygen atoms to attach to neodymium and the third to bind sodium. The bridging nitrate from each Nd gives the sodium in the anion a six coordinate octahedral environment similar to that of the sodium in the cation.

The neodymium center with three bidentate nitrates, C<sub>5</sub>Me<sub>5</sub>, and a THF has a formal coordination number of 10 in terms of electron pairs. However, if each ligand is considered to occupy one coordination site, the complex is distorted trigonal bipyramidal.<sup>11</sup> The nitrates are roughly located in the equatorial positions: the six nitrate oxygen atoms bound to Nd define a plane to within 0.037 Å and Nd sits 0.526 Å above the plane. The N-Nd-N angles are 113.70 (7) to 116.45 (7)° rather than the 120° for a perfect trigonal bipyramid.

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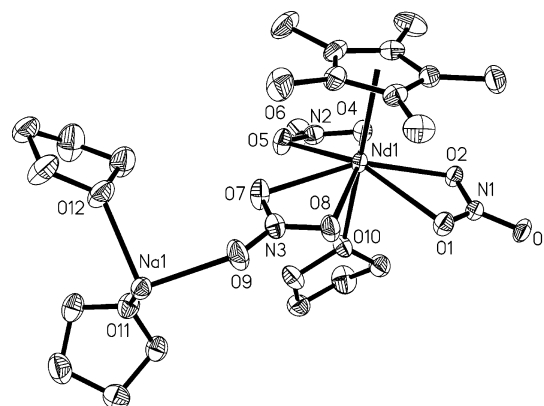
**Figure 3.** Thermal ellipsoid plot of  $[(C_5Me_5)(NO_3)_2Nd(THF)(\mu-NO_3)Na(THF)_4]_n$ , **3**, shown at the 50% probability level.

**Table 3.** Bond Distances (Å) in  $[(C_5Me_5)(NO_3)_2Nd(THF)(\mu-NO_3)_2Na(THF)_4]Na(THF)_6$ , **3**, and  $[(C_5Me_5)(NO_3)_2Nd(THF)(\mu-NO_3)Na(THF)_2]_n$ , **4**

bond	3	4	bond	3	4
Nd(1)–O(1)	2.591(2)	2.5473(16)	Nd(1)–N(1)	2.992(2)	
Nd(1)–O(2)	2.555(2)	2.5328(16)	Nd(1)–N(2)	2.968(2)	
Nd(1)–O(4)	2.546(2)	2.5664(16)	Nd(1)–N(3)	2.974(2)	
Nd(1)–O(5)	2.538(2)	2.5948(17)	Na(1)–O(3)		2.3942(19)
Nd(1)–O(7)	2.552(2)	2.5611(17)	Na(1)–O(4)		2.4603(19)
Nd(1)–O(8)	2.537(2)	2.5521(17)	Na(1)–O(6)		2.713(2)
Nd(1)–O(10)	2.530(2)	2.4859(17)	Na(1)–O(9)		2.353(2)
Na(1)–O(3)	2.433(2)		Na(1)–O(3)′	2.433(2)	2.3942(19)
Na(1)–O(3)′	2.433(2)		Na(1)–O(4)′′		2.4603(19)
Nd(1)–C(1)	2.741(3)	2.756(2)	Na(1)–O(6)′′′		2.713(2)
Nd(1)–C(2)	2.745(3)	2.747(2)	Na(1)–O(11)	2.354(2)	2.362(2)
Nd(1)–C(3)	2.763(3)	2.730(2)	Na(1)–O(12)	2.371(2)	2.324(2)
Nd(1)–C(4)	2.756(3)	2.728(2)	Na(2)–O(13)	2.394(2)	
Nd(1)–C(5)	2.748(3)	2.739(2)	Na(2)–O(14)	2.339(2)	
Nd(1)–Cnt	2.472(3)	2.462	Na(2)–O(15)	2.401(2)	
angle	3	4	angle	3	4
O(3)′–Na(1)–O(3)	180.00(13)		O(4)–N(2)–O(5)	116.6(2)	
O(3)–N(1)–O(1)	121.8(3)		N(1)–Nd(1)–N(2)	113.70(7)	
O(3)–N(1)–O(2)	120.9(3)		N(2)–Nd(1)–N(3)	116.45(7)	
O(1)–N(1)–O(2)	117.3(2)		N(3)–Nd(1)–N(1)	115.19(7)	
O(6)–N(2)–O(4)	121.6(3)		Cnt–Nd(1)–(10)	177.1	
O(6)–N(2)–O(5)	121.9(3)				

$[(C_5Me_5)Nd(THF)(\mu-NO_3)_3Na(THF)_2]_n$ , **4**. Complex **4** differs from **3** in that all of the nitrates are involved in bridging, and only two THF groups are attached to the single sodium site in the complex. The sodium in **4** is six coordinate due to two monodentate nitrates, one bidentate nitrate, and the two THF oxygen atoms. Considering the bidentate nitrate to occupy one coordination position, the sodium has a trigonal bipyramidal geometry with the O(12) THF and the O(3) nitrate ligands in axial positions [O(12)–Na–O(3), 175.80(8)°].

The Nd center in **4** is similar to that in **3**, except that in **4** all three nitrate ligands are bridging. Two of these bridge as in **3**, i.e., they use two oxygens for Nd and the third for Na. However the nitrate containing N(2) attaches to Nd with O(4) and O(5) and to Na with O(4) and O(6). Hence O(4) bridges Nd and Na and is three coordinate. This type of bridging with a three coordinate nitrate oxygen donor atom has been observed before in bimetallic La<sub>2</sub>, Ce<sub>2</sub>, and Pr<sub>2</sub> complexes<sup>18</sup> as well as in Pb<sub>2</sub>,<sup>19,20</sup> Hg<sub>2</sub>,<sup>21</sup> and a LaCu species.<sup>22</sup>



**Figure 4.** Thermal ellipsoid plot of the repeat unit of  $[(C_5Me_5)Nd(THF)(\mu-NO_3)_3Na(THF)_2]_n$ , **4**, shown at the 50% probability level.

The overall bridging generates a ladder polymer as shown in Figure 5. The rails of the ladder are comprised of Nd–[N(2) nitrate]–Na–[N(3) nitrate] linkages and the rungs by Nd–[N(1) nitrate]–Na connections. Outside the rails are alternating C<sub>5</sub>Me<sub>5</sub> and THF ligands attached to alternatively, Nd and Na.

The Nd–(C<sub>5</sub>Me<sub>5</sub> ring centroid) distances in **3** and **4** are nearly identical at 2.472 and 2.462 Å, respectively. Likewise

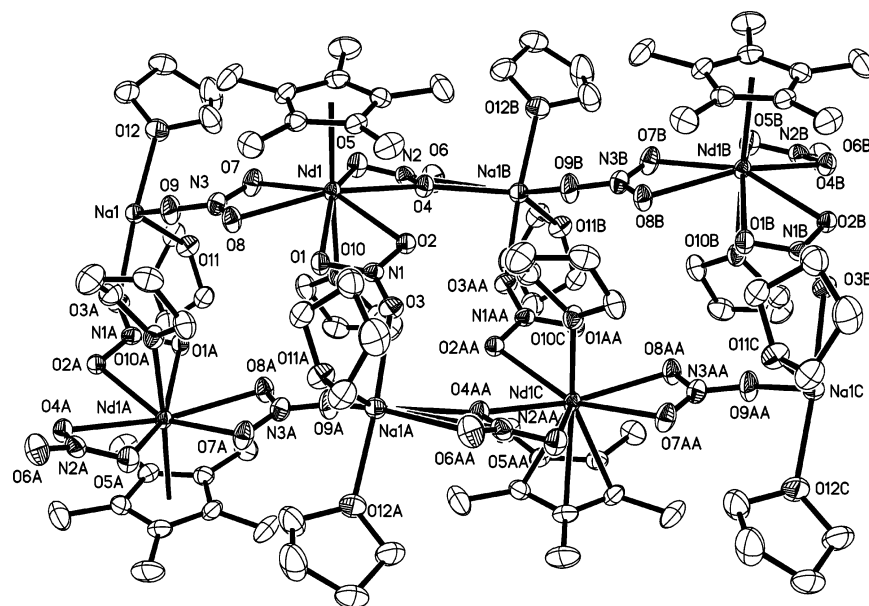
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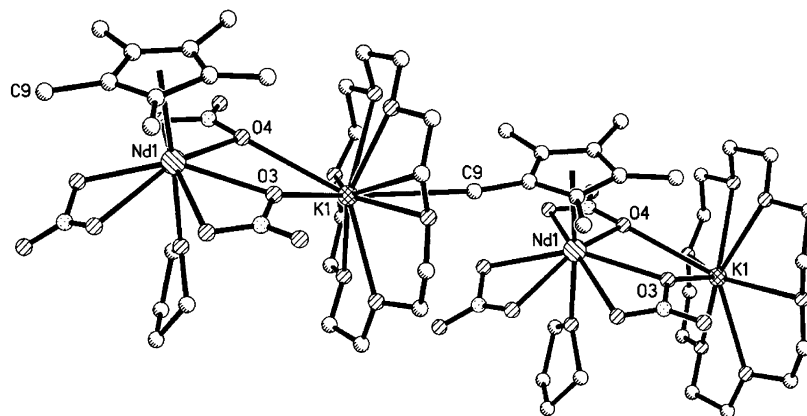
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**Figure 5.** The chain structure of  $[(C_5Me_5)Nd(THF)(\mu-NO_3)_3Na(THF)_2]_n$ , **4**.



**Figure 6.** The chain structure of  $[(C_5Me_5)Nd(THF)(NO_3)(\mu-NO_3)_2K(18-crown-6)]_n$ , **5**.

the Nd–O(nitrate) ranges are similar: 2.530(2)–2.591(2) and 2.533(2)–2.595(2) Å, respectively. Interestingly, the Nd–O(THF) distances differ, 2.530(2) Å for **3** and 2.486(2) Å for **4**, in a way that has the shorter distance with the complex with the more extensive nitrate bridging.

$[(\mu-C_5Me_5)Nd(THF)(NO_3)(\mu-NO_3)_2K(18-crown-6)]_n$ , **5**. The diffraction data on **5** were weak, and only connectivity could be determined. Complex **5** crystallizes from THF with a local Nd structure much like that in **3** and **4**, i.e., each Nd is distorted trigonal bipyramidal with  $C_5Me_5$  and THF axial. The extended structure again is formed by sandwiching the alkali metal between neodymium centers, but in this case the potassium is large enough to be ligated by 18-crown-6 as well as bridging ligands.

If one considers the potassium and the 18-crown-6 ligand to roughly occupy a plane, the bridging on each side is quite different. On one side potassium is ligated by O(3) and O(4) from two different nitrate ligands. These oxygen atoms are also bound to neodymium and are three coordinate as in O(4) in the unique nitrate in **4**. However, in **5** only one oxygen nitrate is ligated to the alkali metal. Consequently, each bridging nitrate in **5** has one oxygen bound to both K and

Nd, one oxygen bound to just Nd, and one oxygen not coordinated to any metal. The bridging on the other side of the “K 18-crown-6 plane” is even more unusual. On that side a methyl group of a  $C_5Me_5$  ring is oriented toward the potassium. This arrangement of bridging generates a chain structure for **5**, as shown in Figure 6. Since the crystal data were too weak to obtain bond distances, this apparent agostic interaction cannot be analyzed further.

## Discussion

Commercially available neodymium nitrate,  $Nd(NO_3)_3 \cdot (H_2O)_6$ , can be readily dehydrated to form the THF and DME adducts,  $Nd(NO_3)_3(THF)_3$  and  $Nd(NO_3)_3(DME)_2$  by heating in those solvents at reflux, drying the resulting solids, and adding solvent. Care must be exercised to avoid heating above 100 °C, which can lead to decomposition.

$Nd(NO_3)_3(THF)_3$  is a viable starting material for organo-metallic synthesis and has provided the first crystallographically characterized organolanthanide nitrates in the literature. Interestingly, in these preliminary reactions with  $MC_5Me_5$  salts ( $M = Na, K$ ), the neodymium nitrate retains all of the nitrate ligands and forms  $[(C_5Me_5)Nd(NO_3)_3(THF)_xM]$  “ate”

complexes by addition of  $\text{MC}_5\text{Me}_5$  rather than  $(\text{C}_5\text{Me}_5)_x\text{-Nd}(\text{NO}_3)_{3-x}$  complexes by substitution. This differentiates the nitrates from chlorides as starting materials.

The cyclopentadienyl neodymium nitrate salts that form in these reactions show a high propensity to associate in the solid state. Nitrate is an effective ligand for bridging sodium and potassium to the lanthanide. As shown with these  $[(\text{C}_5\text{Me}_5)(\text{THF})\text{Nd}(\text{NO}_3)_3\text{ML}_x]_n$  complexes, nitrate is able to form several linkage isomers. Hence, the nitrate can bridge with (a) two oxygens for Nd and the third for Na, or (b) one oxygen each for Nd and for Na and the third for both metals, or (c) or one oxygen for Nd, one for both Nd and Na, and the third unattached.

The flexibility in nitrate binding allows variability in distances and angles such that several types of oligomers can be made. In this case, ion pairs containing trimetallic subunits, chain, and ladder polymers were all isolated from the same basic  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{NO}_3)_3(\text{THF})_x\text{M}]$  building block. Since complexes **3** and **4** differ only in the amount of THF present, it seems that the bridging interactions are comparable in strength to metal THF bonds.

The  $\text{C}_5\text{Me}_5$  methyl to potassium linkage in **5** is an unusual bridging assembly. Although potassium is known to form long-range interactions with many organic moieties,<sup>23–26</sup> this is the first example to our knowledge involving chain formation via a  $\text{C}_5\text{Me}_5$  ring.

## Conclusion

Neodymium nitrate can be readily dehydrated to make ether solvates compatible with organometallic ligands. Alkali metal  $\text{C}_5\text{Me}_5$  reagents add to  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$  to form organometallic nitrate salts. The pentamethylcyclopentadienyl/nitrate ligand set readily forms extended structures and has the potential to be a useful building block in the assembly of extended oligomeric heteropolymetallic organo-lanthanide structures.

## Experimental Section

Solvents, benzene- $d_6$ , and THF- $d_8$  were distilled over NaK alloy and benzophenone.  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  was purchased from Strem and used without further purification. KH, NaH, 18-crown-6, THF, ethanol, and dimethoxyethane were purchased from Aldrich and used without any further purification.  $\text{C}_5\text{Me}_5\text{H}$  was purchased from Strem and dried over molecular sieves before used.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using an Omega 500 MHz and a GN 500 MHz NMR spectrometers. IR spectra were obtained as thin films using an ASI ReactIR 1000 spectrometer. Complexometric analyses were performed as previously described.<sup>27</sup>

**Nd(NO<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>, 1.**  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  (3.2 g, 5.3 mmol) was placed in a 500 mL Schlenk flask, and 80 mL of THF was added. The flask was mounted in a well shielded hood and heated at reflux for 24 h under nitrogen. The solvent was then removed under

vacuum, and the purple solids were placed in a new 100 mL round-bottom flask in air. The solids were dried under high vacuum ( $2 \times 10^{-6}$  Torr) at 100 °C overnight using an oil bath. The solids were dissolved in hot THF in a nitrogen-containing glovebox. Purple crystals of **1** (3.13 g, 96%) were isolated at –35 °C. The  $^1\text{H}$  NMR spectrum of this paramagnetic Nd(III) complex (typical  $\mu_{\text{eff}} = 3.6^{28}$ ) was not informative, and the complex was definitively identified by X-ray crystallography. IR (thin film) 2976 m, 2876 m, 1505 w, 1274 w, 1177 w, 1069 s, 1023 s, 911 m, 864 s, 787 m, 733 m, 667 m. Anal. Calcd. for  $\text{C}_{12}\text{H}_{24}\text{N}_3\text{O}_{12}\text{Nd}$ : Nd, 26.4; C, 26.4; H, 4.4; N, 7.7 Found: Nd, 27.1; C, 26.7; H, 4.8; N, 7.9. Complex **1** can also be made by refluxing in ethanol, removal of solvent as described above, drying under high vacuum ( $2 \times 10^{-6}$  Torr) at 100 °C overnight, and addition of hot THF.

**Nd(NO<sub>3</sub>)<sub>3</sub>(DME)<sub>2</sub>, 2.** Following the same procedures described above for **1**, complex **2** (0.96 g, 95%) can be prepared from  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  (1.2 g, 2.0 mmol) and 100 mL of dimethoxyethane (DME). Complex **2** was also definitively identified by X-ray crystallography. IR (thin film) 2961 m, 2926 m, 2856 m, 1502 s, 1270 s, 1019 s, 856 s, 810 s, 737 m, 671 m. Anal. Calcd. for  $\text{NdC}_8\text{H}_{20}\text{N}_3\text{O}_{13}$ : Nd, 28.3; C, 18.8; H, 4.0; N, 8.2. Found: Nd, 29.1; C, 18.9; H, 4.4; N, 7.9. Complex **2** can also be made by refluxing in ethanol, removal of solvent as described above, drying under high vacuum ( $2 \times 10^{-6}$  Torr) at 100 °C overnight using an oil bath, and addition of hot DME.

**{[(C<sub>5</sub>Me<sub>5</sub>)(NO<sub>3</sub>)<sub>2</sub>Nd(THF)(μ-NO<sub>3</sub>)]<sub>2</sub>Na(THF)<sub>4</sub>}<sub>n</sub>Na(THF)<sub>6</sub>, 3, and [(C<sub>5</sub>Me<sub>5</sub>)Nd(THF)(μ-NO<sub>3</sub>)<sub>3</sub>Na(THF)<sub>2</sub>]<sub>n</sub>, 4.** In a nitrogen-containing glovebox, addition of  $\text{NaC}_5\text{Me}_5$  (0.036 g, 0.20 mmol) to **2** (0.126 g, 0.20 mmol) in 10 mL of THF produced a blue solution. The solution was stirred overnight, and the THF solution was concentrated to 2 mL. Blue crystals of **3** (0.39 g, 92%) grew from the concentrated solution at –35 °C. Calcd. for  $\text{Nd}_2\text{Na}_2\text{C}_{68}\text{H}_{126}\text{N}_6\text{O}_{30}$ : Nd, 15.7; Found: Nd, 16.2. Due to the high degree of solvation in this complex, complete elemental analytical data were not obtained. However, the C:H:N ratio of 4:6.5:1 found for complex **3** matched that expected for the complex with a single THF, 4:6.3:1.  $^1\text{H}$  NMR ( $d_8$ -THF, 25 °C)  $\delta$  7.50 (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}$  NMR ( $d_8$ -THF, 25 °C)  $\delta$  129.1 ( $\text{C}_5\text{Me}_5$ ), –20.6 ( $\text{C}_5\text{Me}_5$ ). IR (thin film) 2964 w, 2941 w, 2903 m, 2860 m, 2729 w, 2513 w, 2239 m, 2127 w, 2092 m, 1772 w, 1660 w, 1586 w, 1502 s, 1451 s, 1320 s, 1289 s, 1170 m, 1100 m, 1031 s, 1000 m, 838 m, 753 w, 706 w, 603 w  $\text{cm}^{-1}$ .

Following the same procedures described above for **3** with **2** (0.151 g, 0.28 mmol) and  $\text{NaC}_5\text{Me}_5$  (0.044 g, 0.28 mmol) in 50 mL of THF, purple solids were obtained and dissolved in a mixture of hot 1:3 toluene:THF. Recrystallization at –35 °C produced a variant of **3**,  $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{THF})(\mu\text{-NO}_3)_3\text{Na}(\text{THF})_2]_n$ , **4** (0.15 g, 77%) which was identified by X-ray crystallography. Attempts to repeat this crystallization procedure yielded good crystals of **3**.

**[(C<sub>5</sub>Me<sub>5</sub>)Nd(THF)(NO<sub>3</sub>)(μ-NO<sub>3</sub>)<sub>2</sub>K(18-crown-6)]<sub>n</sub>, 5.** Following the same procedures as described above for **3**, **5** (0.17 g, 89%) was synthesized by the addition of  $\text{KC}_5\text{Me}_5$  (0.053 g, 0.30 mmol), to a solution of THF containing **2** (0.166 g, 0.30 mmol) and 18-crown-6 (0.080 g, 0.30 mmol).  $^1\text{H}$  NMR ( $d_8$ -THF, 25 °C)  $\delta$  7.04 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 3.28 (s, 24H,  $\text{CH}_2\text{CH}_2$ ), 3.54 (s, THF), 1.70 (s, THF).  $^{13}\text{C}$  NMR ( $d_8$ -THF, 25 °C)  $\delta$  142.4 ( $\text{C}_5\text{Me}_5$ ), 71.1 ( $\text{CH}_2\text{CH}_2$ ), –21.3 ( $\text{C}_5\text{Me}_5$ ). IR (thin film) 2907 m, 2860 m, 2497 w, 2239 m, 2127 w, 2088 m, 1768 w, 1729 w, 1660 w, 1598 w, 1463 s, 1355 m, 1297 s, 1251 m, 1108 s, 1031 m, 1004 w, 961 w, 838 m, 753 w, 703 w, 610 w, 525 w  $\text{cm}^{-1}$ . Due to the high degree of solvation

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in this complex, complete elemental analytical data were not obtained. However, the C:H:N ratio of 7.4:13.1:1 found for complex **5** matched that expected for the complex with no THF, 7.3:13.0:1

**X-ray Data Collection, Structure Determination, and Refinement for 1–5.**  $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$ , **1**. A blue crystal of approximate dimensions  $0.26 \times 0.26 \times 0.30$  mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART<sup>29</sup> program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT<sup>30</sup> and SADABS<sup>31</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>32</sup> program. The diffraction symmetry was  $2/m$ , and the systematic absences were consistent with the monoclinic space groups  $P2_1$  and  $P2_1/m$ . It was later determined that the noncentrosymmetric space group  $P2_1$  was correct. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>33</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Carbon atoms C(10) and C(11) were disordered and included using multiple components with partial site-occupancy-factors. At convergence,  $wR2 = 0.0730$  and  $GOF = 1.108$  for 251 variables refined against 4013 data. As a comparison for refinement on F,  $R1 = 0.0234$  for those 3914 data with  $I > 2.0\sigma(I)$ . The absolute structure was assigned by refinement of the Flack parameter.<sup>34</sup>

$\text{Nd}(\text{NO}_3)_3(\text{DME})_2$ , **2**. A blue crystal of approximate dimensions  $0.15 \times 0.27 \times 0.33$  mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The XSCANS<sup>35</sup> program package was used to determine the Laue symmetry, crystal class, unit-cell parameters, and for data collection. Intensity data were collected at 173 K using a  $2\theta/\omega$  scan technique with  $\text{MoK}\alpha$  radiation. The raw data were processed with a local version of CARESS<sup>36</sup> which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviations from the measured 96-step profiles. Subsequent calculations were carried out using the SHELXTL<sup>37</sup> program. All data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The Laue symmetry was  $2/m$ , and the systematic absences were consistent with the centrosymmetric monoclinic space group  $P2_1/n$  which was assigned and later determined to be correct. The structure was solved by direct methods

and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>38</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence,  $wR2 = 0.0627$  and  $GOF = 1.081$  for 226 variables refined against 4094 data. As a comparison for refinement on F,  $R1 = 0.0255$  for those 3585 data with  $I > 2.0\sigma(I)$ .

$\{[(\text{C}_5\text{Me}_5)(\text{NO}_3)_2\text{Nd}(\text{THF})(\mu\text{-NO}_3)]_2\text{Na}(\text{THF})_4\}\text{Na}(\text{THF})_6$ , **3**. A pale blue crystal of approximate dimensions  $0.21 \times 0.36 \times 0.42$  mm was handled as described for **1** except that 20 s/frame scan time was used. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $\bar{P}1$  was assigned and later determined to be correct. Atoms Na(1) and Na(2) were located on inversion centers. At convergence,  $wR2 = 0.0877$  and  $GOF = 1.069$  for 490 variables refined against 9858 data. As a comparison for refinement on F,  $R1 = 0.0336$  for those 8815 data with  $I > 2.0\sigma(I)$ .

$[(\text{C}_5\text{Me}_5)\text{Nd}(\text{NO}_3)_3(\text{THF})\text{Na}(\text{THF})_2]_n$ , **4**. A light purple crystal of approximate dimensions  $0.10 \times 0.13 \times 0.28$  mm was handled as described for **1**. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $\bar{P}1$  was assigned and later determined to be correct. At convergence,  $wR2 = 0.0607$  and  $GOF = 1.073$  for 364 variables refined against 6942 unique data (As a comparison for refinement on F,  $R1 = 0.0240$  for those 6502 data with  $I > 2.0\sigma(I)$ ).

$[(\text{C}_5\text{Me}_5)\text{Nd}(\text{NO}_3)_3\text{K}(\text{18-crown-6})]_n$ , **5**. A purple crystal of approximate dimensions  $0.17 \times 0.40 \times 0.52$  mm was handled as described for **1**. The diffraction symmetry was  $2/m$ , and the systematic absences were consistent with the monoclinic space groups  $P2_1$  and  $P2_1/m$ . It was later determined that the noncentrosymmetric space group  $P2_1$  was correct. Carbon atom C(13) was disordered and included using multiple components with partial site-occupancy-factors. The final least-squares refinement yielded  $wR2 = 0.1835$  and  $GOF = 1.090$  for 204 variables refined against 7164 data ( $0.80 \text{ \AA}$ ). As a comparison for refinement on F,  $R1 = 0.0685$  for those 6821 data with  $I > 2.0\sigma(I)$ . The absolute structure assignment was attempted; however, neither refinement of the Flack parameter<sup>6</sup> nor refinement using the TWIN command yielded a definitive assignment. (Several atoms were nonpositive-definite. Only Nd and K refined anisotropically.)

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**Supporting Information Available:** Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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