

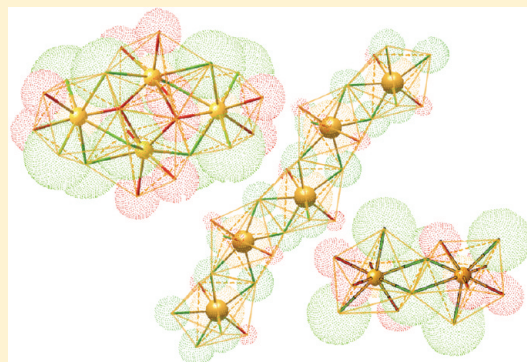
# Crystal Growth, Structural Motifs, and Optical Properties of Molecular and Polymeric Cerium Halide Materials

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**S** Supporting Information

**ABSTRACT:** A series of seven compounds,  $\text{Ce}_2\text{Br}_6(\text{CH}_3\text{OH})_8$  (**1**),  $\text{Ce}_2\text{Br}_6(\text{C}_2\text{H}_5\text{OH})_8$  (**2**),  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  (**3a**),  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  (**3b**),  $\text{CeBr}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (**4**),  $\text{Ce}_4\text{Br}_{10}((\text{CH}_3)_2\text{CHOH})_{10}(\text{H}_2\text{O})_2(\text{OH})_2$  (**5**), and  $\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (**6**) were synthesized via slow evaporation of  $\text{CeBr}_3$  or  $\text{CeCl}_3$  dissolved in an alcohol. This series structurally consists of two dimers, four polymeric chains, and one tetramer. The presence of water and/or hydroxide ions during synthesis profoundly affects the product structure by enhancing the formation of bridging halides, thus leading to polymeric rather than molecular structures. Each of the polymeric chains (**3a**, **3b**, **4**, **6**) formed in response to the presence of water, to which cerium will preferentially coordinate over an alcohol. The tetrameric compound **5** formed in response to the presence of both water and hydroxide ions. These seven compounds, six of which are new compounds, demonstrate the diversity of these seemingly simple materials, which are described herein and were analyzed for their general trends in structure preferences and bond distances. The luminescent properties of compounds **1** and **2** are discussed and contrasted with that of  $\text{CeBr}_3$ .



## INTRODUCTION

The investigation of organolanthanide chemistry has led to the preparation of a number of interesting materials<sup>1</sup> with applications that range from catalysis to scintillation.<sup>2–7</sup> In particular, the potential applications have motivated the synthesis of complexes as well as extended polymeric structures with unique motifs, created via subtle structural changes. One such group is the lanthanide halide-based complexes and polymeric structures, such as cerium(III) bromide and cerium(III) chloride based-materials, that are of interest as a new class of materials for radiation detection, as they have been shown to be efficient scintillators that maintain the ability to scintillate upon coordination to alcohols.<sup>8–12</sup> Because of the diverse potential applications of this class of coordination polymers and complexes, one goal is to develop the synthetic methodology to predict and/or control the topology of these materials, which would be invaluable for preparing new structural motifs and new compositions of materials that may have the ability to scintillate.

In order to expand upon the current library of trivalent lanthanide halide complexes, we have explored the synthetic methodologies and conditions that lead to new structural motifs.<sup>13,14</sup> Specifically, we desire to understand under which reaction conditions specific structural motifs form in solution and to use this knowledge to prepare new organolanthanide materials. This understanding may also be of value in organic catalysis, where it could provide explanations for their reactivity as demonstrated by Evans et al. in the investigations of how water affects common alkylation systems catalyzed by  $\text{CeCl}_3/\text{RLi}$ . Defining the structural

trends of organolanthanide complexes is fundamental to understanding the chemistry of these compounds.<sup>15–18</sup>

Crystal growth of these materials has been achieved through a variety of synthetic approaches, including recrystallization techniques, cooling, and slow evaporation.<sup>19</sup> The concentration of  $\text{CeX}_3$  in solution and the specific solubility in a chosen solvent appear to be a key factor in the crystal growth of complexes and polymeric materials. The ligands available during growth directly affect the crystal structure of the products, which includes molecular complexes, dimers, tetramers, and polymeric species. The presence of water has a profound effect on the dimensionality of the extended structure and, as shown herein, tends to promote the formation of bridging halides and furthermore promotes the formation of polymeric structures. In this paper, we present the synthesis and crystal structures of seven organo-cerium compounds, six of which are new compounds, to illustrate the diversity of these seemingly simple materials. An analysis of general trends in structure preferences and bond distances, as well as their optical properties, is included.

## EXPERIMENTAL SECTION

$\text{CeCl}_3$  was purchased from Alfa Aesar (99.5%) and  $\text{CeBr}_3$  was purchased from Strem Chemicals in (99.9%), both packed under argon and stored in a glovebox. Anhydrous methanol (99.8%) was purchased

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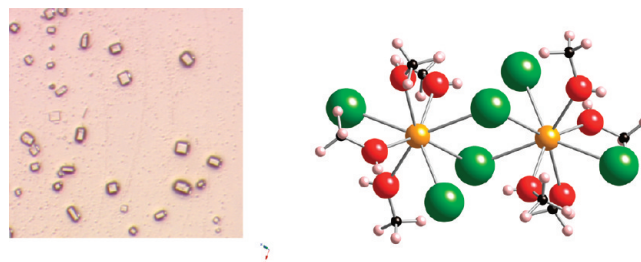
Table 1. Crystal Data and Refinement of Seven Compounds

	1	2	3a	3b	4	5	6
chemical formula	C <sub>8</sub> H <sub>32</sub> Br <sub>6</sub> Ce <sub>2</sub> O <sub>8</sub>	C <sub>16</sub> H <sub>48</sub> Br <sub>6</sub> Ce <sub>2</sub> O <sub>8</sub>	C <sub>2</sub> H <sub>10</sub> CeCl <sub>3</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>10</sub> CeCl <sub>3</sub> O <sub>3</sub>	C <sub>6</sub> H <sub>18</sub> Br <sub>3</sub> CeO <sub>3</sub>	C <sub>30</sub> H <sub>86</sub> Br <sub>10</sub> Ce <sub>4</sub> O <sub>14</sub>	C <sub>6</sub> H <sub>18</sub> CeCl <sub>3</sub> O <sub>3</sub>
<i>M</i>	1016.04	1128.24	328.57	328.57	518.05	2030.57	384.67
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	8.4166(4)	9.6245(5)	6.9877(5)	6.7897(6)	22.3210(17)	10.9064(7)	22.383(2)
<i>b</i> /Å	8.8831(4)	14.2124(7)	8.7234(6)	8.5362(7)	9.2553(7)	11.6119(8)	8.9005(8)
<i>c</i> /Å	10.5541(5)	12.7436(6)	8.7851(6)	9.1909(8)	14.2247(11)	14.1510(10)	13.7495(12)
$\alpha$ /°	112.7420(1)	90	66.0550(10)	106.2270(10)	90	108.1770(10)	90
$\beta$ /°	90.8450(1)	90.1990(10)	74.1330(10)	110.3620(10)	96.8470(10)	111.4730(10)	97.0010(10)
$\gamma$ /°	107.4010(1)	90	89.1700(10)	99.6970(10)	90	95.7490(10)	90
<i>V</i> /Å <sup>3</sup>	686.77(6)	1743.15(15)	467.93(6)	458.15(7)	2917.7(4)	1537.24(18)	2718.7(4)
<i>Z</i>	1	2	2	2	8	1	8
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
<i>F</i> (000)	470	1068	310	310	1928	960	1496
<i>D</i> <sub>calcd</sub> /Mg m <sup>−3</sup>	2.457	2.15	2.332	2.382	2.359	2.193	1.880
$\mu$ /mm <sup>−1</sup>	12.023	9.486	5.668	5.789	11.318	9.449	3.917
index ranges	−11 ≤ <i>h</i> ≤ 11 −12 ≤ <i>k</i> ≤ 12 −14 ≤ <i>l</i> ≤ 14	−12 ≤ <i>h</i> ≤ 12 −18 ≤ <i>k</i> ≤ 18 −16 ≤ <i>l</i> ≤ 16	−9 ≤ <i>h</i> ≤ 9 −11 ≤ <i>k</i> ≤ 11 −11 ≤ <i>l</i> ≤ 11	−8 ≤ <i>h</i> ≤ 8 −11 ≤ <i>k</i> ≤ 11 −11 ≤ <i>l</i> ≤ 11	−23 ≤ <i>h</i> ≤ 27 −11 ≤ <i>k</i> ≤ 10 −17 ≤ <i>l</i> ≤ 17	−14 ≤ <i>h</i> ≤ 14 −15 ≤ <i>k</i> ≤ 15 −18 ≤ <i>l</i> ≤ 18	−29 ≤ <i>h</i> ≤ 29 −11 ≤ <i>k</i> ≤ 11 −18 ≤ <i>l</i> ≤ 18
<i>R</i> <sub>int</sub>	0.0286	0.0458	0.0247	0.0202	0.0347	0.028	0.0204
data/restr/par	4043/0/129	4068/6/185	2172/6/100	2113/6/100	2981/0/138	7399/0/304	3373/3/138
GOF on <i>F</i> <sup>2</sup>	1.024	1.024	1.039	1.042	1.042	1.027	1.057
<i>R</i> <sub>1</sub> = [ <i>I</i> > 2σ( <i>I</i> )]	0.0253	0.0245	0.0198	0.0155	0.0259	0.0208	0.0183
<i>wR</i> <sub>2</sub> = [ <i>I</i> > 2σ( <i>I</i> )]	0.0586	0.055	0.0467	0.0375	0.0606	0.0451	0.0437

from EMD Chemicals, anhydrous ethanol (99.5%) was purchased from Sigma-Aldrich, and anhydrous 2-propanol (99.5%) was purchased from Acros. All anhydrous solvents were received with septa seals.

**Synthesis.** Ce<sub>2</sub>Br<sub>6</sub>(CH<sub>3</sub>OH)<sub>8</sub> (**1**) was synthesized via slow evaporation of a supersaturated solution of CeBr<sub>3</sub> and methanol. In an argon glovebox approximately 0.5 g of the salt was placed in a round-bottom flask and septa sealed. After the flask was removed from the glovebox, approximately 10 mL of anhydrous methanol was syringed into the flask to create a supersaturated solution in which some solid remained undissolved. The amount of solution varies with the relative solubility of CeX<sub>3</sub> in the desired alcohol, as more soluble salts require less solvent. The solution was syringe-filtered into a purged glass vessel and allowed to slowly evaporate in a nitrogen atmosphere. Great care must be taken to exclude water from these air-sensitive and highly hygroscopic materials. Ce<sub>2</sub>Br<sub>6</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>8</sub> (**2**) was synthesized using the same method with anhydrous ethanol. CeCl<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O) (**3a**), CeCl<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O) (**3b**), CeBr<sub>3</sub>((CH<sub>3</sub>)<sub>2</sub>CHOH)<sub>2</sub>(H<sub>2</sub>O) (**4**), Ce<sub>4</sub>Br<sub>10</sub>((CH<sub>3</sub>)<sub>2</sub>CHOH)<sub>10</sub>(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>2</sub> (**5**), and CeCl<sub>3</sub>((CH<sub>3</sub>)<sub>2</sub>CHOH)<sub>2</sub>(H<sub>2</sub>O) (**6**) were synthesized via the same method. However, in the process a small amount of water was inadvertently incorporated into the reaction vessels of **2**, **3a**, **3b**, **4**, **5**, and **6** leading to interesting structural changes. Hydroxide ions, believed to be from KOH residue from washing the glass in a standard base bath, were also incorporated into compound **5**. Stirring the saturated solvent open to the atmosphere for approximately 30–40 s can also deliberately lead to the semihydrated species.

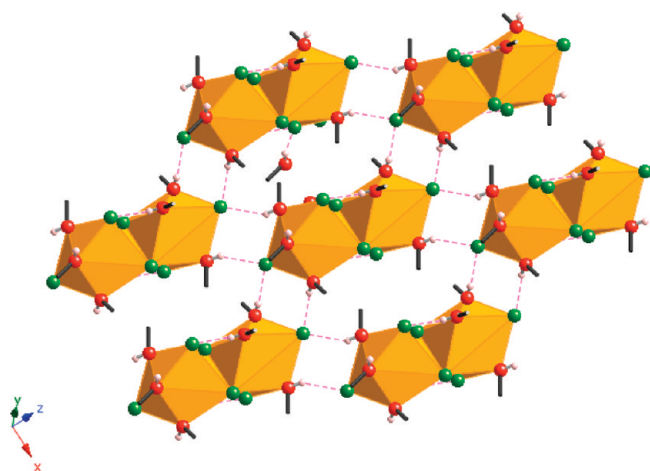
**Photoluminescence.** Polycrystalline powders, synthesized using the same method described for the crystal growth of **1** and **2**, were used to collect excitation and emission spectra using a Perkin-Elmer LS 55 Fluorescence spectrometer. All measurements were collected at room temperature. The samples were sealed between a glass slide and a quartz cover in a nitrogen atmosphere using vacuum grease, as to



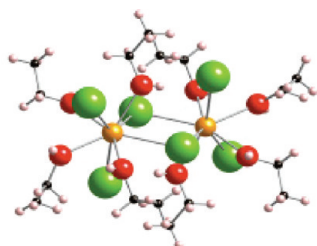
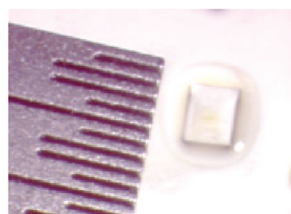
**Figure 1.** Left: optical picture of crystals of (**1**). Right: dimer of Ce<sub>2</sub>Br<sub>6</sub>(CH<sub>3</sub>OH)<sub>8</sub> (**1**), green = Br, red = O, black = C, yellow = Ce, white = H.

minimize exposure to the air and prevent moisture from reaching the sample.

**Crystal Structure Determination.** X-ray intensity data from colorless plate crystals of compounds **1**, **2**, **4**, and **6**, colorless irregular crystals of compounds **3a** and **3b**, and colorless block crystals of compound **5** were measured at 100(2) K using a Bruker SMART APEX diffractometer (Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å). The crystals are hygroscopic and liquefy within several seconds. Raw area detector data frame processing was performed with the SAINT+ and SADABS programs.<sup>20</sup> Final unit cell parameters were determined by least-squares refinement of large sets of reflections taken from each data set. Direct methods structure solution, difference Fourier calculations, and full-matrix least-squares refinement against *F*<sup>2</sup> were performed with SHELXTL.<sup>21</sup> Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. Hydrogen atoms bonded to oxygen were located in difference maps and refined isotropically. Crystal data and structure refinement results are summarized



**Figure 2.** Extended structure and packing of compound (1), yellow polyhedra represent the eight-coordinate Ce center, green = Br, red = O, black = C, white = H.



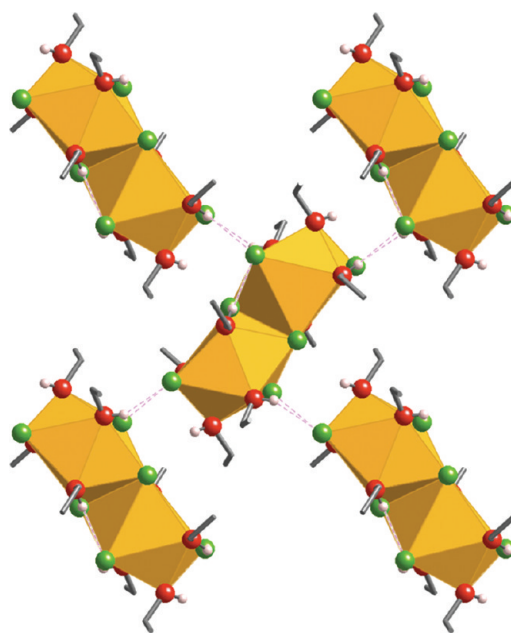
**Figure 3.** Left: Optical picture of crystal of 2. Right: dimer of  $\text{Ce}_2\text{Br}_6(\text{C}_2\text{H}_5\text{OH})_8$  (2), green = Br, red = O, black = C, yellow = Ce, white = H.

in Table 1. Hydrogen bonding tables can be found in the Supporting Information.

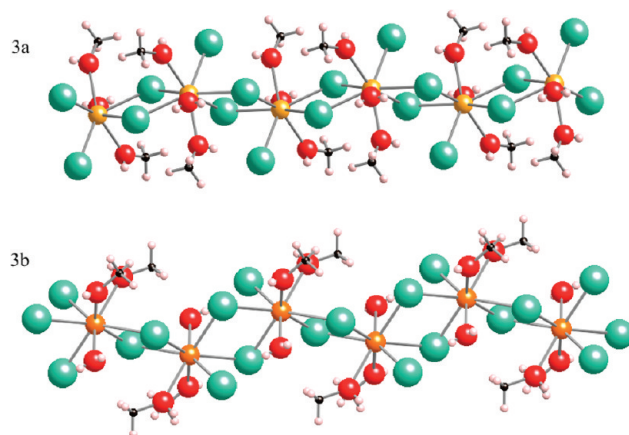
## RESULTS AND DISCUSSION

**Crystal Structure of  $\text{Ce}_2\text{Br}_6(\text{CH}_3\text{OH})_8$  (1).** Compound 1 crystallizes in the triclinic space group  $P\bar{1}$ . Each Ce(III) cation exhibits a square antiprism environment in which four of the vertices are bromine anions. Two of these bromine anions are involved in edge-sharing to a neighboring square antiprism (Figure 1). Oxygen atoms from methanol molecules occupy the remaining four vertices. The edge-shared square antiprisms are isolated adducts within the extended structure and are held together through hydrogen bonding (Figure 2). Compound 1 is isostructural with  $\text{Ce}_2\text{Cl}_6(\text{CH}_3\text{OH})_8$ , which was previously reported by Chakoumakos et al.<sup>5</sup> These two compounds differ in the identity of the halide used in the synthesis, where the main difference between the bromide and chloride derivatives is the average bond distance between Ce and the halide; the average Ce–X distance is approximately 2.861 Å for the chloride derivative and 3.046 Å for the bromide derivative, consistent with the larger size of bromine versus chlorine atoms. The average Ce–O bond distances are nearly identical for both halide derivatives at 2.505 Å and 2.449 Å, respectively. While compound 1 has been previously described, no structural description or crystallographic data have, to our knowledge, been reported.<sup>22</sup>

**Crystal Structure of  $\text{Ce}_2\text{Br}_6(\text{C}_2\text{H}_5\text{OH})_8$  (2).** Compound 2 crystallizes in the monoclinic space group  $P2_1/c$ . Like compound



**Figure 4.** Extended structure and packing of compound 2, yellow polyhedra represent the 8-coordinate Ce center, green = Br, red = O, black = C, white = H.

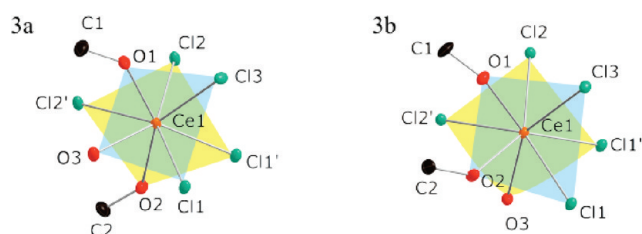


**Figure 5.** 1-D chains  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  (3a) and  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  (3b), light blue = Cl, red = O, black = C, yellow = Ce, white = H.

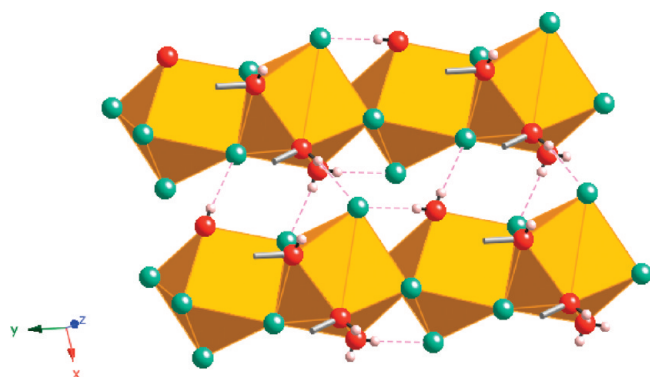
1, 2 is comprised of edge-sharing square antiprism adducts. The vertices in 2 differ from 1 in that the ligand coordinated to the Ce is an ethanol molecule rather than a methanol molecule. The average Ce–Br bond distance is 3.043 Å and the average Ce–O bond distance is 2.505 Å (Figure 3), consistent with the bond length observed for 1. In compound 2, the molecular dimers are connected into an extended network via hydrogen bonding (Figure 4).

**Crystal Structure of  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  (3a and 3b).** Compounds 3a and 3b crystallize in the triclinic space group  $P\bar{1}$  and are coordination isomers, which were isolated from the same batch and grew under identical reaction conditions. Both isomers consist of square antiprism Ce(III) centers and are coordinated to two methanol molecules, one water molecule and five bromine anions. The one-dimensional (1-D) chains of

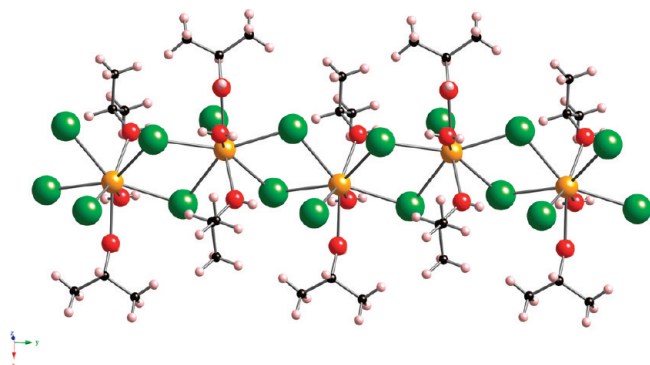




**Figure 6.** Environment around the Ce center for compounds **3a** and **3b** showing the coordination isomerism between the two compounds, light blue = Cl, red = O, black = C, yellow = Ce.



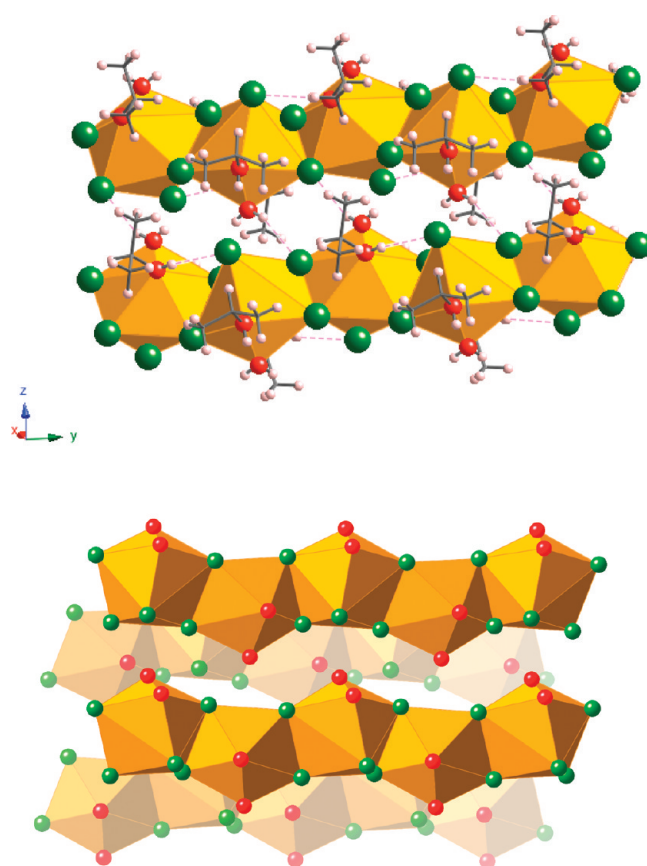
**Figure 7.** Extended structure and packing of compound **3a**, yellow polyhedra represent the 8-coordinate Ce center, light blue = Cl, red = O, black = C, white = H.



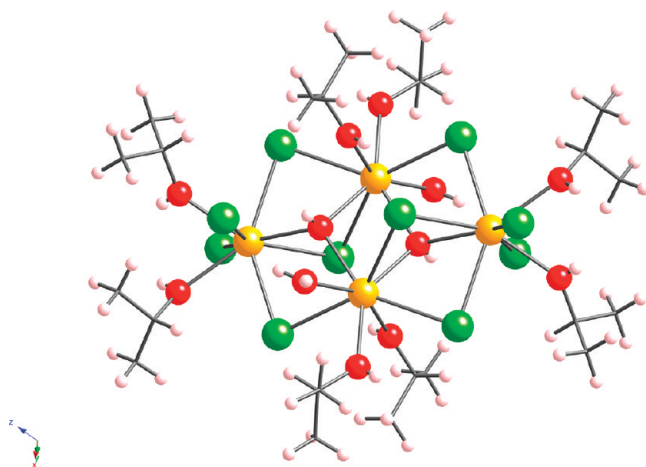
**Figure 8.** 1-D chain of  $\text{CeBr}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})(4)$ , green = Br, red = O, black = C, yellow = Ce, white = H.

the two isomers **3a** and **3b** are shown in (Figure 5), and they differ in the positions of O2 and O3, which are switched (Figure 6). This small coordination change about the Ce center changes the structure sufficiently to alter the unit cell, particularly with respect to the angles of the unit cell as can be seen in Table 1. The square antiprisms edge share on both sides to form 1-D chains, and the extended network is held together via hydrogen bonding (Figure 7). The average Ce—O bond distances are 2.483 Å in **3a** and 2.499 Å in **3b**, and the average Ce—Cl bond distances are 2.867 Å in **3a** and 2.872 Å in **3b**, all consistent with what is typically observed for Ce—O and Ce—Cl distances.

**Crystal Structure of  $\text{CeBr}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (**4**).** Compound **4** crystallizes in the monoclinic space group  $C2/c$ . The compound consists of a Ce(III) square antiprism center and is

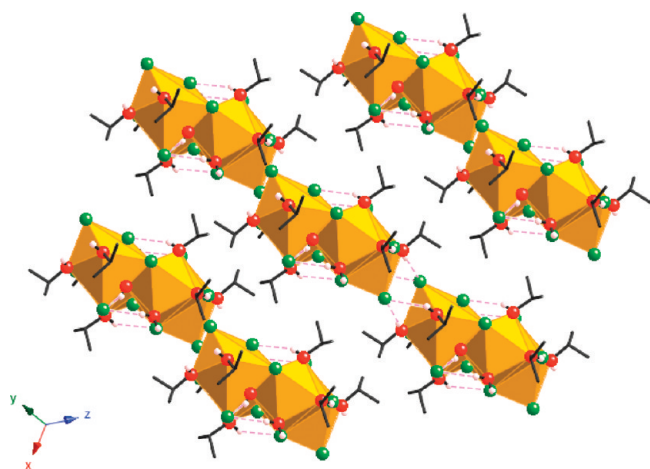


**Figure 9.** Two views of the extended structure of compound **4** showing four distinct chains within the unit cell, yellow polyhedra represent the eight-coordinate Ce center, green = Br, red = O, black = C, white = H.

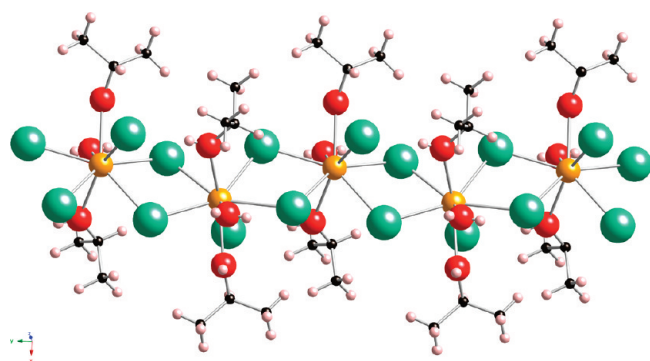


**Figure 10.** Unit cell of  $(\text{CeBr}_{2.5})_4((\text{CH}_3)_2\text{CHOH})_{10}(\text{H}_2\text{O})_2(\text{OH})_2$  (**5**), green = Br, red = O, black = C, yellow = Ce, white = H.

coordinated to one water molecule, two isopropanol molecules, and five bromine anions (Figure 8). The average Ce—O bond distance is 2.503 Å and the average Ce—Br distance is 3.020 Å. Compound **4** exhibits edge-sharing on both sides of the square antiprism and thus forms 1-D chains. There are four distinct chains in the unit cell, and the extended structure is held together through hydrogen bonding (Figure 9).



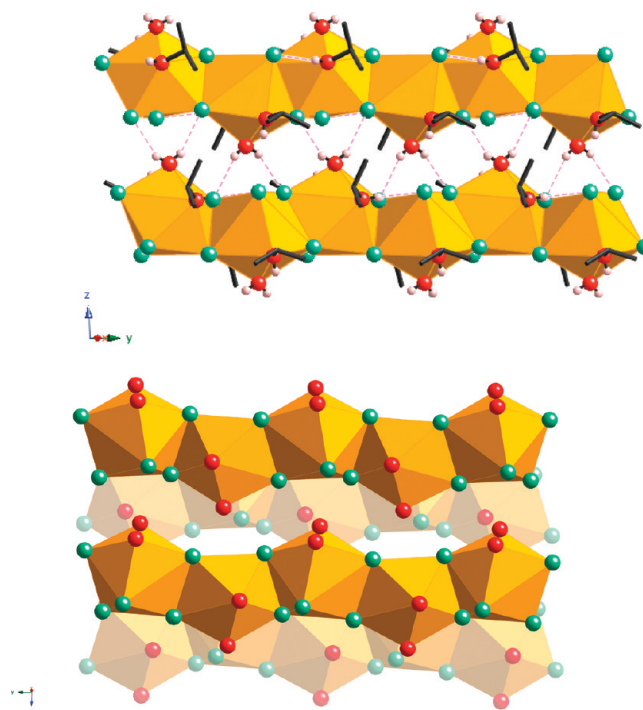
**Figure 11.** Extended structure and packing of compound **5**; yellow polyhedra represent the eight-coordinate Ce center, green = Br, red = O, black = C, white = H.



**Figure 12.** 1-D chain of  $\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (**6**), light blue = Cl, red = O, black = C, yellow = Ce, white = H.

**Crystal Structure of  $\text{Ce}_4\text{Br}_{10}((\text{CH}_3)_2\text{CHOH})_{10}(\text{H}_2\text{O})_2(\text{OH})_2$  (**5**).** Compound **5** crystallizes in the triclinic space group  $P\bar{1}$ . This compound represents a unique structure within this series of compounds. While it also is comprised of square antiprismatic Ce(III) centers, it forms as a tetrameric compound rather than as a dimer or as an extended structure. There are two distinct Ce environments as can be seen in Figure 10. Two Ce(III) cations are coordinated to five bromine anions, two isopropanol molecules, and one bridging hydroxide, while the other two Ce cations are coordinated to four bromine anions, two isopropanol molecules, one bridging hydroxide, and one water molecule. One free isopropanol molecule also resides in the molecular unit cell. Each hydroxide bridges three Ce cations that are then further bridged via the bromine anions to form the tetramer. The average Ce–O bond distance is 2.503 Å, and the average Ce–Br bond distance is 3.044 Å. The tetrameric units are discrete and are held together through intermolecular hydrogen bonding (Figure 11).

**Crystal Structure of  $\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (**6**).** Compound **6** crystallizes in the monoclinic space group  $C2/c$ . The compound consists of a Ce(III) square antiprism center and is coordinated to one water molecule, two isopropanol molecules, and five chlorine anions (Figure 12). The average Ce–O bond distance is 2.503 Å, and the average Ce–Cl distance is 2.868 Å. Compound **6** exhibits edge-sharing on both sides of the square antiprism and therefore forms 1-D chains (Figure 13).



**Figure 13.** Two views of the extended structure of compound **6** showing four distinct chains within the unit cell; yellow polyhedra represent the eight-coordinate Ce center, light blue = Cl, red = O, black = C, white = H.

Compound **6** is isostructural with **4** and differs in the identity of the halide attached to the cerium cation (chlorine vs bromine). In both structures, the extended network is held together by intermolecular hydrogen bonding.

**Structural Comparisons and Factors Influencing Topological Outcomes.** Within the series of compounds represented here, two are dimers, four have polymeric chains, and one is a tetramer. Each of the polymeric chains **3a**, **3b**, **4**, and **6** formed in response to the presence of water, which preferentially coordinates to the cerium center versus an alcohol adduct. The preference for water is due to the hygroscopic nature of  $\text{CeX}_3$  and the sterics about the metal center, where the smaller water molecule can more readily coordinate to the cation. The tetrameric compound **5** formed in response to the presence of water and hydroxide ions; the latter are believed to have been introduced to the reaction as a residue from the cleaning of the glass crystallization vessel in a standard base bath. Experiments are underway to determine the source of the hydroxide anion, as well as ascertain whether or not they can be added in the form of an alkali metal hydroxide, as this may open up a pathway to direct the formation of multicenter structures versus dimers versus polymeric chains. In our experience, these slight variations in the solvent system have led to three unique motifs — dimers in the absence of water, polymeric chains in the presence of water, and multicenter ring structures in the presence of water and hydroxides. Boyles et al. have observed similar trends within their series of methanol-substituted lanthanum halides obtaining monomeric and dimeric compounds.<sup>23</sup>

Examining the differences in the bond distances of the bridging halides reveals that, in most cases, the polymeric chain with bound water has slightly shorter bridging halide bond distances than the dimers. Even though the alcohol and water ligands are neutral donors, their coordination greatly impacts the

Table 2. Average Bond Distances and Coordination Numbers of Similar Materials

$\text{LnX}_3$	ligand	topology	$\text{Ln}-\text{O}$ bond	nonbridge $\text{Ln}-\text{X}$ bond	$\text{Ln}-\text{X}-\text{Ln}$	CN
CeCl	$\text{MeOH}^a$	dimer	2.505	2.841	2.923	8
CeCl (3a)	$\text{MeOH}/\text{H}_2\text{O}$	1-D chain	2.499	2.839	2.888	8
CeCl (3b)	$\text{MeOH}/\text{H}_2\text{O}$	1-D chain	2.483	2.854	2.876	8
CeCl (6)	$\text{iPOH}/\text{H}_2\text{O}$	1-D chain	2.502	2.787	2.889	8
CeCl	$\text{iPOH}^b$	dimer	2.478	2.763	2.918	7
CeBr (1)	$\text{MeOH}$	dimer	2.449	3.003	3.049	8
CeBr (2)	$\text{EtOH}$	dimer	2.505	2.954	3.134	8
CeBr (4)	$\text{iPOH}/\text{H}_2\text{O}$	1-D chain	2.503	2.947	3.039	8
CeBr (5)	$\text{iPOH}/\text{H}_2\text{O}/\text{OH}$	tetramer	2.503	2.979	3.056	8

<sup>a</sup> Chakomakous et al.<sup>5</sup> <sup>b</sup> Schafer et al.<sup>24</sup>

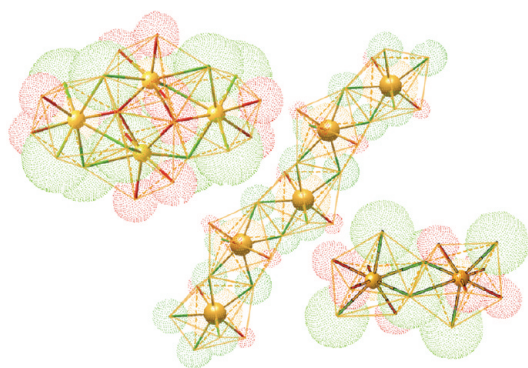


Figure 14. The coordination environment of the Ce(III) centers are shown for the dimer of compound 1, the tetramer of compound 5, and the 1-D chain of compound 4.

topological outcome of the structure. The Ce–X–Ce bridging bond distances in the structure of  $\text{CeCl}_3(\text{CH}_3\text{OH})_4$ <sup>5</sup> are 2.923 Å on average, whereas the Ce–X–Ce bridging bond distances in the polymeric structure  $\text{CeCl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})$  3a and 3b are 2.882 Å on average, the difference in the bond distances being approximately 0.041 Å. When water is coordinated to the metal center, the anion prefers to bind to another cation rather than occupy a terminal position. The water coordinating does not have an appreciable effect on the nonbridging Ce–X bond distances nor on the Ce–O bond distances.

The same observation can be made for the previously reported isopropanol containing dimer  $[\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_3]_2$ <sup>24</sup> whose average Ce–X–Ce bond distance is 2.918 Å, while  $\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_2(\text{H}_2\text{O})$  (6), has an average Ce–X–Ce bond distance of 2.889 Å. The coordination numbers of Ce in these two compounds differ: Ce in  $[\text{CeCl}_3((\text{CH}_3)_2\text{CHOH})_3]_2$  is seven-coordinate, while Ce in 6 is eight-coordinate, which affects bond distances as these increase for higher coordination numbers.<sup>25</sup>

Similar effects of the halide bond lengths occur with the larger anions such as bromine, as evidenced by compounds 1, 2, 4, and 5. Comparisons between the different alcohols suggest that the bridging halide bond length again is influenced by the presence of different alcohols. The bond lengths of the bridging halides show a difference of 0.085 Å, the longer bond belonging to compound 2 which is coordinated to ethanol as compared to compound 1 which is coordinated to methanol. Compounds 4 and 5 have similar bond distances, which would be expected as they both have coordinating waters, the main difference being the bridging hydroxide in compound 5 which tethers the cerium cations together to form the

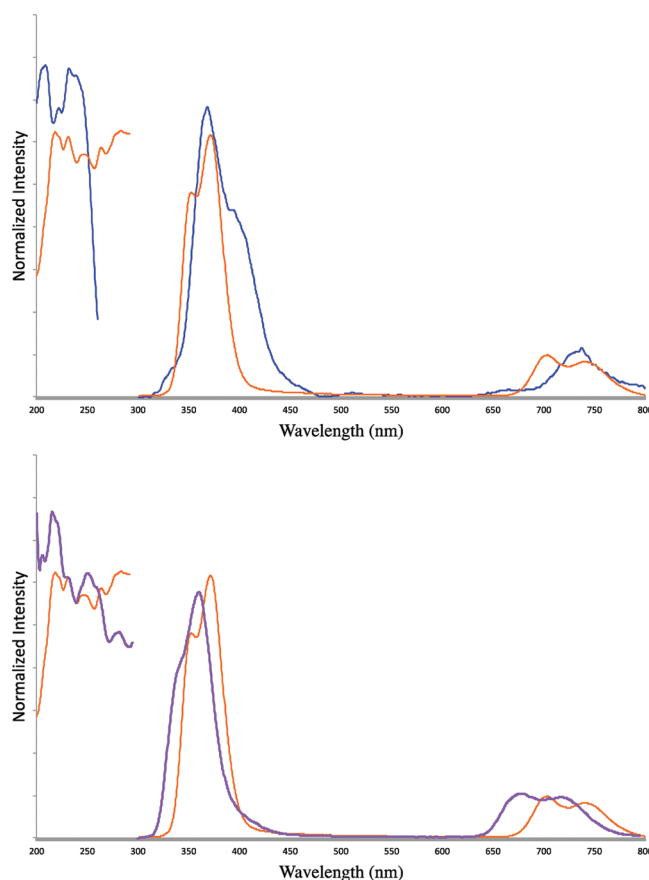


Figure 15. Emission and excitation spectra of  $\text{CeBr}_3$  are shown in orange, compound 1 is shown in blue, and compound 2 is shown in purple. Top: Compound 1 overlaid with  $\text{CeBr}_3$ . Bottom: Compound 2 overlaid with  $\text{CeBr}_3$ .

tetramer. More compounds of these types must be studied to fully evaluate the binding modes within the bromine series. A summary of bond distances and coordination numbers can be located in Table 2.

These observed differences in bond lengths within this class of materials have important implications on structure formation and suggest that they can be used in the future to direct the formation of specific structure types. Furthermore, the sterics and hydrophobicity/hydrophilicity of the ligands are expected to have an important influence on the formation of different structural motifs within this class of materials.<sup>26</sup> Rogers et al. have shown through numerous examples of  $\text{LnX}_3$  polyethylene glycol complexes that sterics play a



primary role in the formation of organolanthanide materials.<sup>27</sup> Ligands with larger hydrocarbon chains create more hydrophobic interactions that can potentially favor different structural motifs. By considering all these diverse factors, one can potentially gain some insight into the unique formation of these materials and the sensitivity to solvent coordination they exhibit (Figure 14).

**Luminescence of Compounds 1 and 2.** Compounds 1 and 2 were analyzed for their luminescence ability and compared to the luminescence characteristic of CeBr<sub>3</sub>, whose maximum emission occurs at 371 nm. Compounds 1 and 2 as well as the CeBr<sub>3</sub> were excited using a wavelength of 232 nm. As shown in Figure 15, 1 has a maximum emission at 368 nm, and 2 has a maximum emission at 360 nm, and both are thus slightly blue-shifted relative to CeBr<sub>3</sub>. The luminescence of Ce(III) is believed to result from d → f transitions, which makes the luminescence of Ce(III) very susceptible to its specific coordination environment.<sup>28,29</sup> Compound 1 was previously reported<sup>22</sup> and has been shown to scintillate. Consequently, compound 2 may be a potential scintillator, and efforts to analyze this property are underway.

## CONCLUSIONS

We have identified and analyzed six novel compounds containing CeCl<sub>3</sub> and CeBr<sub>3</sub> via single crystal X-ray diffraction. The general trends that can be observed among this series of compounds have been discussed. It is hoped that the observed trends can be applied toward the future synthesis of related materials. Specifically, it was observed that mixed ligand systems of cerium halides with alcohols, hydroxides, and water molecules tend to lead to different structural motifs, namely, dimers, polymeric chains, and tetramers, suggesting that controlling the presence of water and hydroxides in solution can affect the product morphology. Using these trends, we will attempt to influence the crystal growth of these materials with tailored solvent systems. The luminescent properties of two of the compounds were investigated.

## ASSOCIATED CONTENT

**Supporting Information.** (1) Additional crystallographic information, including displacement ellipsoid plots and tables of hydrogen bonding data. This material is available free of charge via the Internet at <http://pubs.acs.org>. (2) Crystallographic data for this paper can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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. CCDC numbers of compounds 1–6 are as follows (1) 827126, (2) 827127, (3a) 827124, (3b) 827125, (4) 827134, (5) 827133, and 836625 (6).

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