



Crystal growth and structural motifs of luminescent $\text{PrCl}_3 \cdot \text{ROH}$ complexes: Molecular adducts and 1-D chains of tetradecanuclear rings

Shae Anne Vaughn, Rachel C. Severance, Mark D. Smith, Hans-Conrad zur Loye*

University of South Carolina, Department of Chemistry and Biochemistry, 631 Sumter Street, Columbia, SC 29208, USA

ARTICLE INFO

Article history:

Received 8 March 2012

Received in revised form

29 May 2012

Accepted 30 May 2012

Available online 19 June 2012

Keywords:

Praseodymium chloride

Lanthanide–organic hybrid material

Tetradecanuclear ring

Molecular adducts

Optical properties

Luminescence

ABSTRACT

$\text{Pr}_2\text{Cl}_6(\text{CH}_3\text{OH})_8$ (**1**), $\text{Pr}_2\text{Cl}_6((\text{CH}_3)_2\text{CHOH})_8$ (**2**) and $(\text{PrCl}_3)_7(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_{18} \cdot (\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})$ (**3**) were synthesized via slow evaporation of a supersaturated solution of PrCl_3 in methanol, isopropanol and *n*-propanol respectively. The crystal structures were determined, revealing two very different topological arrangements. The evaporation in the presence of methanol and isopropanol lead to dimeric molecular adducts, while *n*-propanol leads to the formation of 1-D chains of tetradecanuclear rings. The molecular adducts are held together via edge sharing polyhedra while the rings are held together via edge- and face-sharing polyhedra. The absorbance and luminescence of these compounds was also investigated.

© 2012 Elsevier Masson SAS. All rights reserved.

1. Introduction

Complexes of the lanthanide elements have been studied extensively for a variety of applications, including luminescence, magnetism, and catalysis [1–4]. The high coordination numbers and the non-directional nature of bonding within the lanthanides [5] have led to a variety of lanthanide–organic hybrid materials [6–8], and both molecular and polymeric structures have been obtained through a variety of synthetic techniques. Several different types of networks of praseodymium containing complexes can be obtained in the presence of different organic ligands, including carbohydrates and amino acids [9–12]. Furthermore, it has been shown that simple dimeric adducts of lanthanide halides can be achieved through the coordination of small ligands such as methanol, THF, and isopropanol [13–18]. These materials can easily form chains when water is incorporated into the structure [19,20]. The ability to predict and/or control the topology of these materials could be invaluable for preparing new motifs and compositions of materials whose properties could then be investigated. While cerium halide based complexes and extended structures have been investigated by several groups [15–20], significantly less is known about the neighboring lanthanides, such as the adjacent praseodymium, which is the focus of this

publication. We have previously studied CeCl_3 and CeBr_3 based lanthanide–organic hybrid materials, where we have obtained a series of new structural topologies when *n*-propanol or *n*-butanol are used as the coordinating crystallization solvents [21]. The work presented within, the solid state investigation into the topological variations that PrCl_3 exhibits when coupled with differing alcohols, represents an extension of this cerium halide work to the adjacent praseodymium cation, and has resulted in the formation of a series of related materials.

The crystal growth of these types of materials via coordinating crystallization solvents may provide an insight into some of the potential species being formed in solution, in alcoholic solutions in particular, as the alcohol method of synthesis is used in the development of glasses via the sol–gel process, where PrCl_3 is a common additive to optical glasses. Spectroscopic studies have been carried out in order to explain the optical properties of the rare earth metal ions and the effect that the solvent has on the metal centers in these systems [22]. Observable shifts in the absorbance and emission spectra indicate that other species are forming in solution, particularly at higher concentrations [23]. Glinski et al. have suggested that perhaps these observations are due to coordination of chloride anions [24,25].

Herein we report three novel compounds that exhibit two very different topological motifs that were created by the use of methanol, isopropanol, and 1-propanol as coordinating crystallization solvents. This discovery may offer insight into some of the species

* Corresponding author. Tel.: +1 803 777 6916; fax: +1 803 777 8508.

E-mail address: zurloye@mailbox.sc.edu (H.-C. zur Loye).

that may form in solution at differing concentrations. It was observed that the use of methanol or isopropanol resulted in the formation of molecular dimers that are isostructural to previously reported lanthanide derivatives. However, an intriguing new structural motif was obtained when *n*-propanol was used as the coordinating crystallization solvent. Rather than the formation of dimeric species, the self assembly of a 1-D chain of catenated tetradecanuclear rings, containing fourteen Pr(III) cations, occurred. Thus the choice of crystallization solvent dramatically affected the topological outcome of the crystal structure.

2. Materials and methods

PrCl₃, packed under argon, was purchased from Alfa Aesar (99.5%) and stored in a glovebox. Anhydrous methanol (99.8%) was purchased from EMD Chemicals, anhydrous isopropanol (99.5%) was purchased from Acros, and anhydrous 1-propanol (99.7%) was purchased from Sigma Aldrich. All anhydrous solvents were received with septa seals.

3. Experimental

Pr₂Cl₆(CH₃OH)₈ (**1**), Pr₂Cl₆((CH₃)₂CHOH)₈ (**2**) and (PrCl₃)₇(CH₃CH₂CH₂OH)₁₈·(CH₃CH₂CH₂OH) (**3**) were synthesized via slow evaporation of a supersaturated solution of PrCl₃ in methanol, isopropanol and 1-propanol respectively. In an argon glovebox, approximately 0.5 g of the salt was placed in a round bottom flask and sealed with a septum. Upon removal from the glovebox, approximately 10 mL of anhydrous methanol was transferred via nitrogen-purged syringe into the flask to create a saturated solution. The amount of solution varies with the relative solubility of the PrCl₃ salt in the desired alcohol. The saturated solution was syringe-filtered into a nitrogen-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 extremely hygroscopic materials. Polycrystalline powders were obtained of compounds **1–3** using the same method as previously described; these powders were carefully sealed between quartz plates with grease in a nitrogen atmosphere in order to obtain the

optical measurements. All fluorescence measurements were made at room temperature using a Perkin Elmer LS 55 spectrofluorometer. All absorbance measurements were made at room temperature using a Perkin Elmer Lambda 35 UV/vis spectrometer outfitted with a reflectance spectroscopy accessory. Attempts to collect PXRD patterns were unsuccessful due to the hygroscopic nature of these materials.

3.1. Crystal structure determination

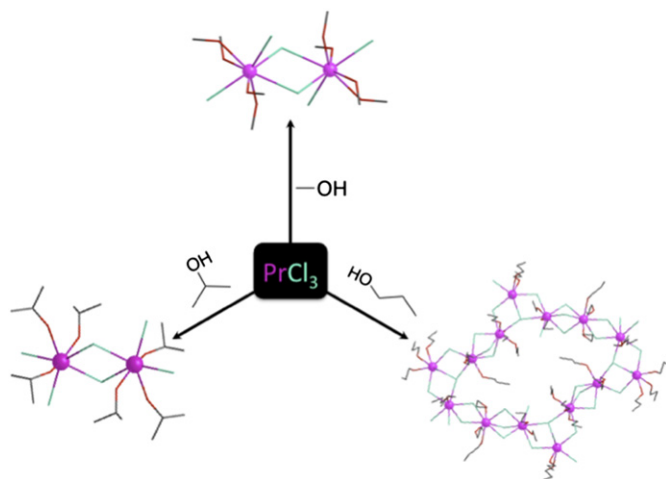
X-ray intensity data from colorless irregular crystals of compounds **1** and **3** and colorless needle crystals of compound **2** were measured at 100(2)K using a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). The crystals are hygroscopic and liquefy within several seconds. Raw area detector data frame processing was performed with the SAINT+ and SADABS programs [26]. 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^2 were performed with SHELXTL [27]. Crystal data and structure refinement results are summarized in Table 1. The refinement of compound **3** included disorder modeling of four of the nineteen 1-propanol ligands. Further refinement details of all the compounds and hydrogen bonding tables for compounds **1** and **2** can be found in the Supporting information.

4. Results and discussion

Compounds **1** and **2** form dimeric molecular adducts which are isostructural to cerium and lanthanum halide compounds found in the literature, while compound **3** forms a 1-D chain comprised of tetradecanuclear rings as seen in Scheme 1. Steric effects have been shown to play a major role in the topology of these structures. Rogers et al. have shown through numerous examples of LnX₃ polyethylene glycol complexes that steric effects are a major contributing factor to the structural outcome [28]. The hydrophobicity/hydrophilicity of the ligands is also expected to influence the formation of different structural motifs within this class of

Table 1
Crystal data and refinement of 3 compounds.

	1	2	3
Chemical formula	Pr ₂ Cl ₆ (CH ₃ OH) ₈	Pr ₂ Cl ₆ ((CH ₃) ₂ CHOH) ₈	(PrCl ₃) ₇ (CH ₃ CH ₂ CH ₂ OH) ₁₈ ·(CH ₃ CH ₂ CH ₂ OH)
<i>M</i>	750.86	855.08	2853.45
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /c	P-1	P-1
<i>a</i> /Å	8.6811(5)	5.9261(5)	14.0420(12)
<i>b</i> /Å	18.4369(10)	11.1699(9)	20.1617(16)
<i>c</i> /Å	8.1967(5)	13.2231(10)	21.2359(17)
α /°	90	68.8610(10)	104.041(2)
β /°	109.000(1)	78.0530(10)	105.910(2)
γ /°	90	86.1900(10)	98.646(2)
<i>V</i> /Å ³	1240.43(12)	798.67(11)	5455.5(8)
<i>Z</i>	2	1	2
<i>T</i> /K	100(2)	100(2)	100(2)
<i>F</i> (000)	728	424	2794
<i>D</i> _{calcd} (Mg m ⁻³)	2.01	1.778	1.737
μ /mm ⁻¹	4.553	3.543	3.626
Index ranges	−10 ≤ <i>h</i> ≤ 10 −23 ≤ <i>k</i> ≤ 23 −10 ≤ <i>l</i> ≤ 10	−7 ≤ <i>h</i> ≤ 7 −14 ≤ <i>k</i> ≤ 14 −17 ≤ <i>l</i> ≤ 17	−17 ≤ <i>h</i> ≤ 17 −25 ≤ <i>k</i> ≤ 25 −26 ≤ <i>l</i> ≤ 26
<i>R</i> _{int}	0.0591	0.0261	0.0583
Data/restr/parm	2546/4/129	3751/21/193	22410/20/914
GOF on <i>F</i> ²	1.038	1.183	0.987
<i>R</i> ₁ = [<i>I</i> > 2 σ (<i>I</i>)]	0.028	0.0203	0.0423
<i>wR</i> ₂ = [<i>I</i> > 2 σ (<i>I</i>)]	0.0603	0.0486	0.1045



Scheme 1. Diagram of the coordinating crystallization solvents that resulted in either, dimeric or polymeric lanthanide organic hybrid materials, hydrogen atoms and disordered ligands omitted for clarity. (Pr = purple, Cl = aquamarine, O = red, C = gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

materials, where ligands with longer hydrocarbon chains create more hydrophobic interactions that can potentially favor the formation of layered structures, as observed for **3**.

4.1. Crystallographic studies of compounds **1–3**

4.1.1. Crystal structure of $\text{Pr}_2\text{Cl}_6(\text{CH}_3\text{OH})_8$ (**1**)

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ as irregular colorless crystals. The structure of **1** is comprised of edge-sharing square antiprisms, where the alcohol ligands are present as metal adducts. The coordination sphere around the 8-coordinate Pr(III) cation consists of four chlorine anions, two of which are bridging halides and four methanol ligands (Fig. 1). The average Pr–Cl bond distance is 2.85 Å and the average Pr–O distance is 2.48 Å. The dimers are held together through a network of hydrogen bonding.

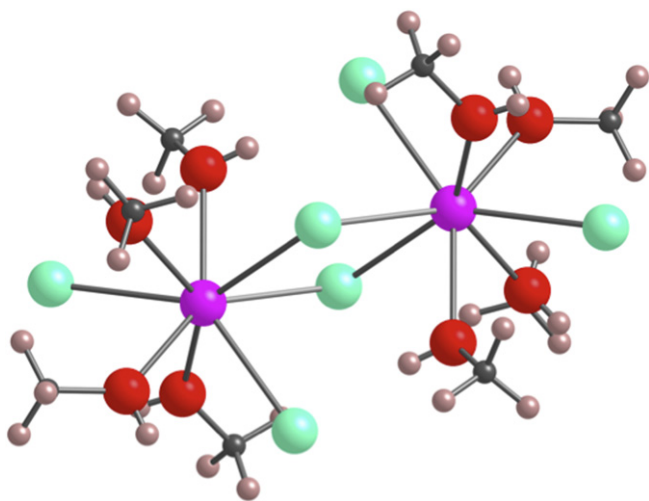


Fig. 1. Dimeric adduct of compound (**1**), Pr = pink, Cl = aquamarine, O = red, C = gray, H = pink. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

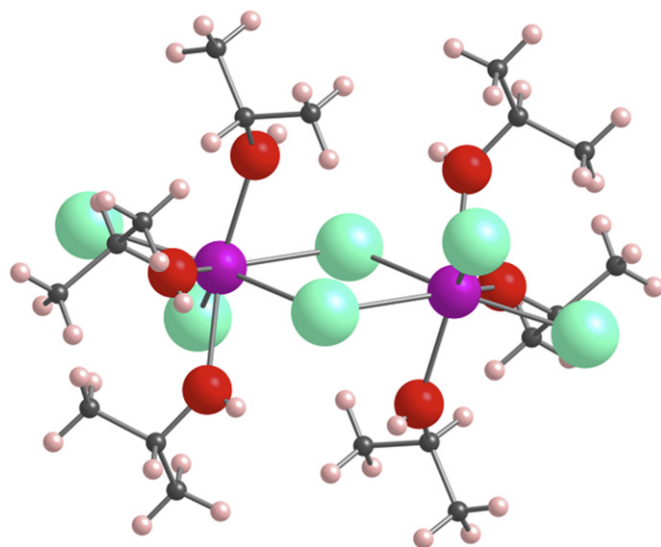


Fig. 2. Dimeric adduct of compound (**2**), Pr = purple, Cl = aquamarine, O = red, C = gray, H = pink. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.1.2. Crystal structure of $\text{Pr}_2\text{Cl}_6((\text{CH}_3)_2\text{CHOH})_8$ (**2**)

Compound **2** crystallizes in the triclinic space group $P-1$ as colorless needle crystals. The structure of **2** is comprised of edge-sharing distorted, capped octahedra, where the alcohol ligands are present as metal adducts. Major differences between compounds **1** and **2** can be found in the coordination spheres around the Pr (III) cation; while compound **1** is 8-coordinate, compound **2** is 7-coordinate. The Pr coordination environment in **2** consists of four chlorine anions, two of which are bridging halides, and three isopropanol ligands (Fig. 2). The average Pr–Cl bond distance is 2.82 Å and the average Pr–O distance is 2.46 Å. The dimers are held together through a network of hydrogen bonding.

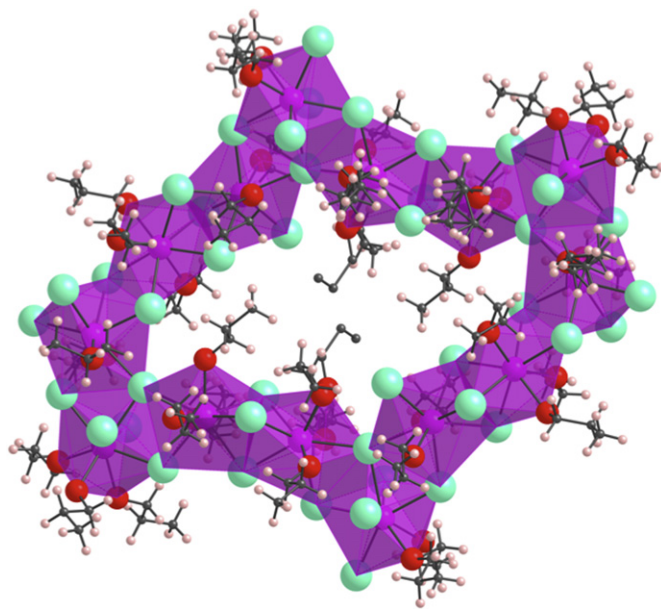


Fig. 3. One tetradecanuclear ring of **3**, Pr (III) polyhedra shown in purple to highlight the inorganic backbone of the structure. (Pr = purple, Cl = aquamarine, O = red, C = gray, H = pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Coordination spheres of Pr(III) cations in compound **3**.

Pr (III) cations	Terminal chlorides	Bridging chlorides	Propanol ligands
Pr 1	1	4	3
Pr 2	0	6	2
Pr 3	2	3	3
Pr 4	0	5	3
Pr 5	0	5	3
Pr 6	3	3	2
Pr 7	1	5	2

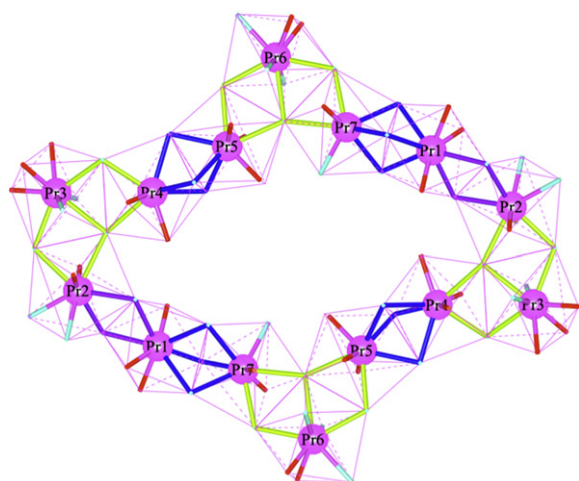


Fig. 4. Connectivity of compound **3**, edge-sharing μ_3 -bridged polyhedra shown in green, bonds involved in edge-sharing shown in purple, bonds involved in face-sharing shown in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.1.3. Crystal structure of

$(\text{PrCl}_3)_7(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_{18} \cdot (\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})$ (**3**)

Compound **3** crystallizes in the triclinic space group *P*-1 as pale yellow plates. The asymmetric unit of **3** consists of seven praseodymium cations, twenty-one chlorine anions, eighteen coordinated propanol ligands, and one uncoordinated propanol molecule that resides in the middle of the tetradecanuclear ring (Fig. 3). The coordination spheres around each 8-coordinate Pr(III) cation as well as the individual bridging motifs vary; specifically there are six distinct coordination environments among the seven Pr (III) cations, which are detailed in Table 2.

The inorganic backbone forms 1-D chains of tetradecanuclear rings linked via an intricate array of bridging chloride anions. Pr1

edge-shares with Pr2, which edge-shares with Pr3. Pr3, one of four keystones within the structure, edge-shares with both Pr2 and Pr4 through a μ_3 -bridging bromide ligand; the ring propagates from Pr4 to Pr5 via face-sharing polyhedra. Pr5 edge-shares with Pr6, the second keystone within the ring. Pr6 has the same connectivity as Pr3, but a different coordination sphere due to the presence of two *n*-propanol ligands and three terminal chlorides as compared to three *n*-propanol ligands and two terminal chlorides. Pr6 edge-shares to Pr7, which in turn face-shares to a symmetrically equivalent Pr1. The ring continues clock-wise with the same connectivity through symmetrically equivalent cations (Fig. 4). Pr2 edge-shares with a symmetrically equivalent Pr2 thereby propagating the 1-D chain of rings.

The chains of rings self assemble into a layered structure in which the hydrophobic tails of the propanol ligands reside between the layers (Fig. 5). The dimensions of the ring structure is $17.8 \times 12.1 \text{ \AA}^2$, as demarcated by the inorganic backbone, were defined as the distance between symmetrically equivalent chloride anions. The average bond distance for the bridging halides is $\sim 2.88 \text{ \AA}$, while the average bond distance for the terminal halides is $\sim 2.80 \text{ \AA}$. The average bond length for the Pr–O bond is 2.47 \AA , which is consistent within the series. The interlayer spacing of 12.3 \AA is defined as the average distance from the Pr(III) cations in one chain to a lattice plane that passes through the Pr(III) cations in an adjacent chain. Viewing the structure down the *x*-axis reveals crystallographically observable channels (Fig. 6).

4.2. Investigation of optical properties

Polycrystalline powders of compounds **1–3** were used to collect absorbance and emission spectra. The absorbance bands observed are typical of the well-studied PrCl_3 [29,30]. Absorbance spectra of the starting material and hydrated PrCl_3 , were obtained as a reference. The observed energy bands are attributed to the electronic transitions from the ground state $^3\text{H}_4$ to the excited $^3\text{P}_2$, $^1\text{I}_6$, $^3\text{P}_0$ multiplets and $^1\text{D}_2$ singlet (Fig. 7). The absorbance spectra for the solid-state materials, corresponds well with previously reported solution studies where, for example $^3\text{P}_2$ occurs at 446.6 nm , 445.9 nm , and 446.25 nm for compounds **1–3** respectively. While solution studies show $^3\text{P}_2$ at 445.9 nm in methanol, and 444.1 nm in isopropanol [21]. The compounds reported might offer insight into the species that are forming in solution and subsequently the types of species that may be incorporated into complex matrices such as gels and glasses. Absorption spectra ranging from 200 nm to 900 nm are provided in the Supporting information.

While most pure praseodymium salts do not exhibit fluorescence, PrCl_3 has been well studied and has been shown to fluoresce

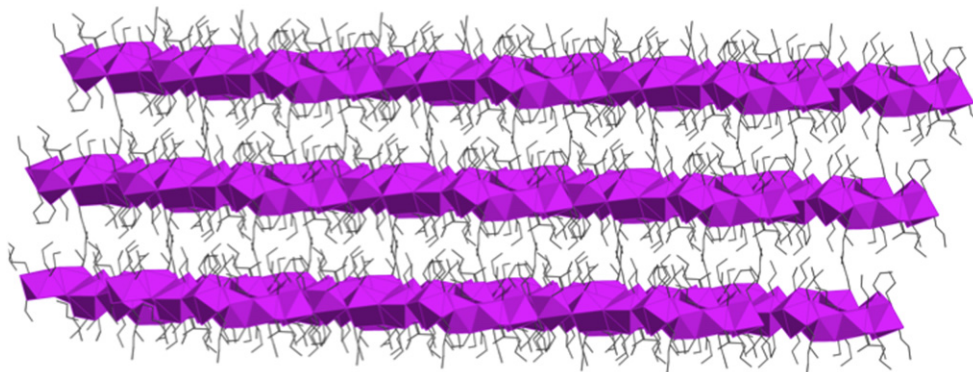


Fig. 5. Layered sheet structure of **3** when viewed down the *z*-axis of the unit cell. (Pr = purple, Cl = aquamarine, O = red, C = gray, H = pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

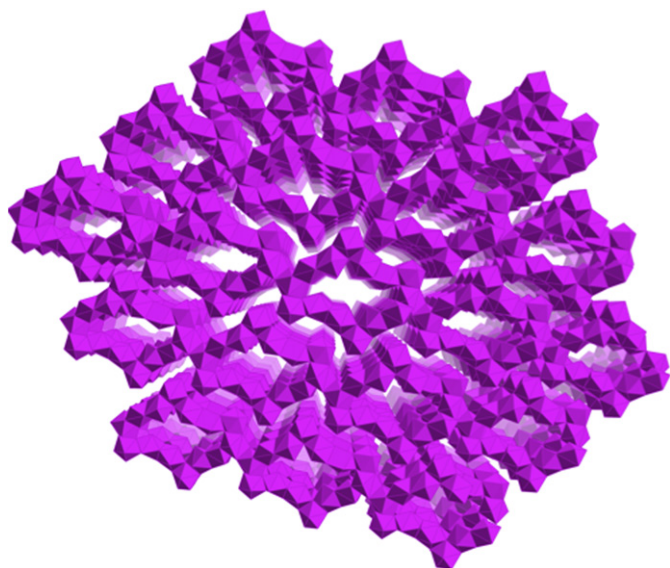


Fig. 6. Inorganic backbone of **3** when viewed down the x -axis of the unit cell, to highlight the nature of the supramolecular structure. Praseodymium polyhedra shown in purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[29]. Therefore the emission spectra of compounds **1–3** were also investigated. All compounds and reference materials were excited at 230 nm with a 290 nm emission filter at room temperature. The most noticeable trend in the emission spectra is observable at higher wavelengths, in the 550–700 nm range. The polycrystalline powders emit at 610.3 nm, 584.2 nm, and 617.2 nm for compounds **1–3** respectively. Compound **3** has a second emission in this region at 686.3 nm. The emission spectra are all shifted to higher wavelengths in comparison to the PrCl_3 starting material, which emits at 558.40 nm in this region. Both dimeric compounds with coordinated methanol (**1**) and isopropanol (**2**) ligands are shifted by 51.9 nm and 25.8 nm respectively, while the n -propanol containing compound **3** is shifted by 56.9 nm for the first peak and 127.9 nm for the second peak in this region as compared to the starting material. Interestingly when PrCl_3 is exposed to the atmosphere and becomes partially hydrated due to its hygroscopic nature a much more intense fluorescence than that of the salt can be observed, and emits at 560.3 nm (Fig. 8). Compounds **1–3** as well as

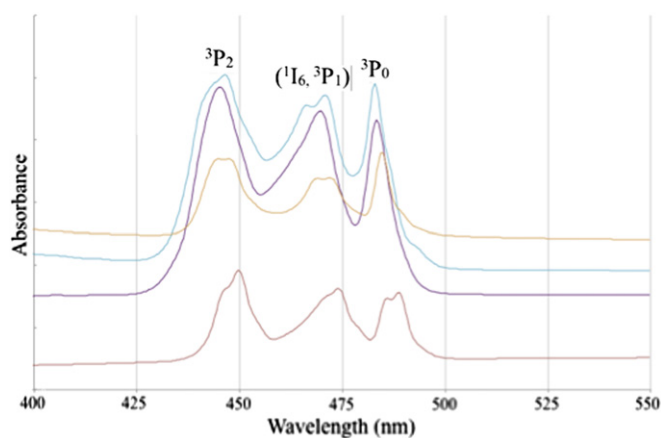


Fig. 7. Normalized absorbance spectra, PrCl_3 (red), compound **1** (purple), compound **2** (blue), compound **3** (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

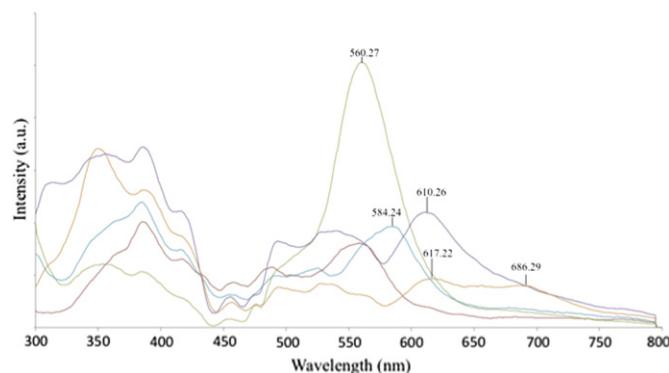


Fig. 8. Emission spectra upon excitation at 230 nm, PrCl_3 (red), PrCl_3 Hydrate (green) compound **1** (purple), compound **2** (blue), compound **3** (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the PrCl_3 powder exposed to the atmosphere exhibit light-green luminescence that is observable in a standard black-box outfitted with a UV source. As the transitions observed in the lanthanides are sensitive to their surrounding environment [31], the differences observed between the spectra may be attributable to the level of halide bridging as well as the coordination number. Luminescence spectra including excitation spectra of each compound can be found in the Supporting information.

5. Conclusions

Three new praseodymium containing organic–inorganic hybrid materials were synthesized and structurally characterized. The structures revealed a unique topological shift upon the coordination of a longer alkyl chain alcohol. Upon coordination to methanol and isopropanol, two dimeric species were formed. However, the coordination of an n -propanol ligand dramatically shifted the topology to a motif in which tetradecanuclear rings form polymeric 1-D chains via two bridging halides. This is one example of a series of large lanthanide ring polymers and is analogous to the related CeBr_3 - and CeCl_3 -containing crystal structures. Furthermore, the optical properties of polycrystalline powders of these materials were investigated and showed absorbance bands similar to what was reported in previous solution studies. This suggests that compounds **1–3** may be potential species that form in solution at higher concentrations. Potentially, this synthetic approach can be used to grow crystals of a number of large lanthanide ring containing complexes, and it will be interesting to explore complexes containing other lanthanide cations and to discover the affect of the lanthanide contraction on the resultant structural motifs.

Acknowledgments

Funding for this research was provided by CHE-0714439. Special thanks to Dr. Lynn Boatner and Dr. Bryan Chakoumakos from Oak Ridge National Laboratory for helpful discussions and suggestions.

Appendix A. Supporting information

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.solidstatesciences.2012.05.032>.

References

- [1] S. Mishra, Coord. Chem. Rev. 252 (2008) 1996–2025.
- [2] T. Gunnlaugsson, F. Stomeo, Org. Biomol. Chem. 5 (2007) 1999–2009.

- [3] M. Albrecht, Z. Anorg. Allg. Chem. 636 (2010) 2198–2204.
- [4] C. Piguet, J.-C.G. Buenzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, J. Alloys Compd. 225 (1995) 324–330.
- [5] S. Cotton, Lanthanide and Actinide Chemistry, John Wiley & Sons, Ltd, Chichester, UK, 2006.
- [6] J. Lhoste, A. Perez-Campos, N. Henry, T. Loiseau, P. Rabu, F. Abraham, Dalton Trans. 40 (2011) 9136–9144.
- [7] J. Lhoste, N. Henry, T. Loiseau, F. Abraham, Inorg. Chem. Commun. 14 (2011) 1525–1527.
- [8] Z. Zheng, Chem. Commun. (2001) 2521–2529.
- [9] Y. Limin, Z. Ying, X. Yizhuang, J. Xianglin, W. Shifu, T. Wen, W. Jinguang, X. Guangxian, Carbohydr. Res. 334 (2001) 91–95.
- [10] W. Xiaoping, X. Yuyuan, S. Jie, Polyhedron 15 (1996) 3569–3574.
- [11] R. Srinivasan, J. Glaser, S. Tragl, H.-J. Meyer, Z. Anorg. Allg. Chem. 631 (2005) 479–483.
- [12] G.R. Willey, P.R. Meehan, P.A. Salter, M.G.B. Drew, Polyhedron 15 (1996) 4227–4232.
- [13] G.R. Willey, T.J. Woodman, M.G.B. Drew, Polyhedron 16 (1997) 3385–3393.
- [14] T.J. Boyle, L.A.M. Ottley, T.M. Alam, M.A. Rodriguez, P. Yang, S.K. McIntyre, Polyhedron 29 (2010) 1784–1795.
- [15] B.C. Chakoumakos, R. Custelcean, J.O. Ramey, J.A. Kolopus, R. Jin, J.S. Neal, D.J. Wisniewski, L.A. Boatner, Cryst. Growth Des. 8 (2008) 2070–2072.
- [16] E.V. van Loef, J. Glodo, W.M. Higgins, K.S. Shah, IEEE Nucl. Sci. Symp. Conf. Rec. (2009) 1415–1416.
- [17] D.M. Barnhart, T.M. Frankcom, P.L. Gordon, N.N. Sauer, J.A. Thompson, J.G. Watkin, Inorg. Chem. 34 (1995) 4862–4867.
- [18] M. Schafer, R. Herbst-Irmer, Acta Cryst. C50 (1994) 1256–1258.
- [19] W.J. Evans, J.D. Feldman, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 4581–4584.
- [20] S.A. Vaughn, R.C. Severance, M.D. Smith, Hans-Conrad L. zur, Crystal Growth Des. 11 (2011) 5072–5078.
- [21] S.A. Vaughn, R. Custelcean, J.O. Ramey, M.D. Smith, L.A. Boatner, H.-C. zur Loye, Inorg. Chem., Submitted for publication.
- [22] S. Jana, S. Mitra, Spectrochim. Acta A Mol. Biomol. Spectrosc. 83 (2011) 52–55.
- [23] B. Keller, J. Legendziewicz, J. Przybylski, M. Guzik, J. Glinski, J. Alloys Compd. 341 (2002) 197–202.
- [24] J. Glinski, B. Keller, J. Legendziewicz, S. Samela, J. Mol. Struct. 559 (2001) 59–66.
- [25] J. Glinski, B. Keller, J. Legendziewicz, New J. Chem. 23 (1999) 47–52.
- [26] SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
- [27] G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
- [28] R.D. Rogers, J. Zhang, C.B. Bauer, J. Alloys Compd. 249 (1997) 41–48.
- [29] G.H. Dieke, R. Sarup, J. Chem. Phys. 29 (1958) 741–745.
- [30] K.R. German, A. Kiel, H. Guggenheim, Appl. Phys. Lett. 22 (1973) 87–89.
- [31] D.E. Henrie, R.L. Fellows, G.R. Choppin, Coord. Chem. Rev. 18 (1976) 199–224.