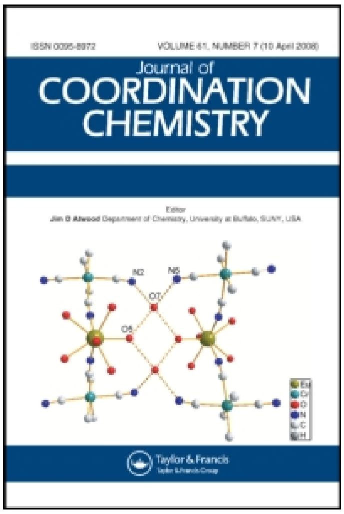

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Hydrothermal synthesis of a chiral rare earth iodate ($Gd(IO_3)_3 \cdot H_2O$) showing the rare (3, 8)-connected $(4^3)(4 \cdot 6^2)$ $(4^9 \cdot 6^{17} \cdot 8^2)$ topology

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In the presence of Cu(II) ions, a chiral rare earth iodate $Gd(IO_3)_3 \cdot H_2O$ (crystallizing in *P2₁* (no. 4) space group), was synthesized hydrothermally from Gd_2O_3 and HIO_3; the structure is the topologically (3, 8)-connected $(4^3)(4 \cdot 6^2)(4^9 \cdot 6^{17} \cdot 8^2)$ network, constructed from 3-connected trigonal nodes (I1, I3) and 8-connected tetragonal prism nodes (Gd1).

Keywords: Hydrothermal synthesis; Lanthanide iodate; Networks; (3, 8)-connected frameworks

1. Introduction

Classification and nomenclature are becoming increasingly important issues as more and more examples of 3D networks are obtained, or deliberately synthesized. Until recently, such systems mainly focused on highly symmetric building blocks with the basic/or uninodal connectivity of 3, 4, 6, or 8 and the resulting high symmetry networks such as srs, dia, pcu, or bcu [1]. By contrast, there is an increasing number of such coordination polymers based on binodal nodes [2]. However, there is only one case reported by Zhou [3], showing the binodal (3, 8)-connected topology predicted by Castro [4] and O'Keeffe [2a]. On the other hand, transition metal, lanthanide, and actinide iodates continue to attract attention due to their potential applications in nonlinear optical, piezoelectric, pyroelectric, and ferroelectric devices [5]. The water insoluble lanthanide iodates are usually obtained as powders from aqueous media, although crystal samples of several examples were obtained many years ago by crystallization from boiling concentrated mineral acids or growth in gels [6]. Recently, Hector *et al*. pioneered the study of crystal samples of lanthanide iodates through hydrothermal synthesis [7]. Within the currently reported lanthanide iodates, $G(IO_3)_3$, $G(IO_3)_3 \cdot H_2O$, and $G(IO_3)_3 \cdot 2H_2O$ belong to the centrosymmetric space group of $P2_1/c$, $C2/C$ and $P\bar{1}$, whereas $G(IO_3)_3 \cdot 1/2H_2O$ is in the noncentrosymmetric (NCS) space group of *Pn* (G = lanthanide ions). Herein, we report our synthesis of the chiral

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lanthanide iodate of $Gd(IO_3)_3 \cdot H_2O$ *via* hydrothermal synthesis in the presence of Cu(II) ions. From a topological view, this compound presents the rare (3, 8)-connected $(4^3)(4 \cdot 6^2)(4^9 \cdot 6^{17} \cdot 8^2)$ network.

2. Experimental

2.1. *Materials and methods*

All reagents were bought from commercial sources and used without further purification. Thermal gravimetric analysis was completed on a NETZSCH TG 209 instrument.

2.2. *Synthesis of $Gd(IO_3)_3 \cdot H_2O$*

An aqueous mixture (10 mL) of Gd_2O_3, $CuCl_2$, HIO_3 in the ratio of 1 : 1 : 6 was placed in a Teflon reactor (23 mL), and heated at 160°C for 3 days, and then it was cooled to room temperature at $5^\circ C\,h^{-1}$. Colorless crystals were obtained in 73% yield based on Gd. Further, $Cu(NO_3)_2$, or $Cu(SO_4)_2$, or $Cu(CH_3COO)_2$ is employed as Cu(II) ion source to generate $Gd(IO_3)_3 \cdot H_2O$, without obvious increase of yield.

2.3. *Crystallographic measurements on $Gd(IO_3)_3 \cdot H_2O$*

A colorless clear single crystal was selected for the diffraction analysis. Data collection was performed on a Rigaku *r*-axis rapid IP area detector using Mo-Kα radiation. Data were integrated and corrected for absorption using the RAXIS-RAPID Auto programs. The structure of $Gd(IO_3)_3 \cdot H_2O$ is solved by both direct and Patterson methods and refined by SHELXL-97 [8]. All non-hydrogen atoms (gadolinium, oxygen, iodine) were located first in difference Fourier maps, whereas hydrogen atom positions were found and refined with the O–H/0.85 ± 0.01, H–H/1.25 ± 0.01 restriction. Some crystallographic details are listed in table 1, and selected bond lengths and angles are listed in table 2. Further details of the crystal structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; Email: crysdata@fiz- karlsruhe.de) on quoting the depository numbers CSD 417153.

3. Results and discussion

$Gd(IO_3)_3 \cdot H_2O$ was synthesized hydrothermally by reaction of Gd_2O_3 and HIO_3 in the presence of $CuCl_2$. The compound, once formed, is air stable and insoluble in most solvents (e.g. H_2O, CH_3OH, C_2H_5OH, DMF). In addition, we initiate our further investigations by examining of whether there is the inevitable relationship between the resulted lanthanide iodate and the presence of $CuCl_2$. The research results show that $Gd(IO_3)_3$ is the only product if $CuCl_2$ is absent, which indicates that the preparation of

Table 1. Crystallographic data for **1**.

Compound	$Gd(IO_3)_3 \cdot H_2O$
Chemical formula	$GdI_3O_{10}H_2$
M	699.97
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	7.3017(15)
b (Å)	6.6502(13)
c (Å)	9.895(2)
β (°)	109.71
V (Å^3)	452.33(16)
Z	2
Density (mg m^{-3})	5.139
S	1.009
Flack factor	0.028(12)
R_1, wR_2 (all data)	0.0581, 0.0719

Table 2. The selected bond lengths (Å) and angles (°) of **1**.

Gd(1)–O(9)	2.330(5)	O(3)–I(1)–O(2)	101.1(2)
Gd(1)–O(7)	2.362(7)	O(3)–I(1)–O(1)	98.3(2)
Gd(1)–O(4)	2.384(5)	O(2)–I(1)–O(1)	96.5(2)
Gd(1)–O(8)	2.386(6)	O(5)–I(2)–O(4)	99.9(3)
Gd(1)–O(1)	2.423(4)	O(5)–I(2)–O(8)#3	97.8(2)
Gd(1)–O(6)	2.426(5)	O(4)–I(2)–O(8)#3	97.1(3)
Gd(1)–O(3)#1	2.470(5)	O(9)#4–I(3)–O(7)#5	100.2(3)
Gd(1)–O(2)#2	2.495(5)	O(9)#4–I(3)–O(6)	95.9(2)
I(1)–O(3)	1.805(6)	O(7)#5–I(3)–O(6)	99.1(3)
I(1)–O(2)	1.814(5)	I(1)–O(1)–Gd(1)	125.8(3)
I(1)–O(1)	1.815(5)	I(1)–O(2)–Gd(1)#6	141.2(3)
I(2)–O(5)	1.798(4)	I(1)–O(3)–Gd(1)#7	145.0(3)
I(2)–O(4)	1.817(6)	I(2)–O(4)–Gd(1)	135.3(3)
I(2)–O(8)#3	1.820(5)	I(3)–O(6)–Gd(1)	117.7(2)
I(3)–O(9)#4	1.792(5)	I(3)#8–O(7)–Gd(1)	141.0(3)
I(3)–O(7)#5	1.802(7)	I(2)#9–O(8)–Gd(1)	122.0(3)
I(3)–O(6)	1.832(4)	(3)#10–O(9)–Gd(1)	146.2(3)

Symmetry code: #1: $x-1, y, z$; #2: $-x+1, y-1/2, -z+1$; #3: $-x+1, y+1/2, -z+2$; #4: $x, y+1, z$; #5: $-x, y+1/2, -z+1$; #6: $-x+1, y+1/2, -z+1$; #7: $x+1, y, z$; #8: $-x, y-1/2, -z+1$; #9: $-x+1, y-1/2, -z+2$; #10: $x, y-1, z$.

$Gd(IO_3)_3 \cdot H_2O$ can be controlled by the introduction of $CuCl_2$. Interestingly, $CuCl_2$ can be replaced by other Cu(II) salts such as $Cu(NO_3)_2$, $Cu(SO_4)_2$, and $Cu(CH_3COO)_2$ to generate $Gd(IO_3)_3 \cdot H_2O$. Hence, the formation of $Gd(IO_3)_3 \cdot H_2O$ is induced by the introduction of Cu(II) ions.

3.1. *Crystal structure of* $Gd(IO_3)_3 \cdot H_2O$

Single crystal X-ray diffraction shows that $Gd(IO_3)_3 \cdot H_2O$ crystallizes in the chiral $P2_1$ space group, and features the layered 3D framework structure. Each Gd(III) ion is ligated by eight O atoms from IO_3^- to give the GdO_8 bicapped trigonal-prism geometry with chiral symmetry; the Gd–O bond lengths range from 2.330–2.495′, comparable with other Gd-containing compounds [9]. The I–O bond lengths vary from 1.792–1.832′, comparable to that observed in $Gd(IO_3)_3$ [7]. As shown in figure 1, $I(1)O_3^-$ polyhedra, as well as $I(3)O_3^-$ polyhedra, adopt the μ_3-bridging mode to link three neighboring Gd(III) ions. This connectivity pattern is repeated infinitely to give the 2D sheet structure. Furthermore, these sheets are pillared by one μ_2-linkage of $I(2)O_3^-$ to construct the elegant 3D framework architecture figure 2(a). The resulting 5.5% void volume [10] is populated by water molecules that connect to the host frameworks through O10–H10 ⋯ I2/2.675′ and O10–H11 ⋯ O9/2.971′ H-bonds.

For clarity, we will use the topological method to analyze this 3D framework structure. If eight-coordinate Gd1 and 3-coordinate I1 and I3 are considered to be the 8-, and 3-connected nodes, respectively, together with the Gd–O, I–O covalent bonds and $I(2)O_3^-$ μ_2-linkages as connectors, and then this framework can be simplified to the (3, 8)-connected network (figure 2b). Given the consideration of the coordination

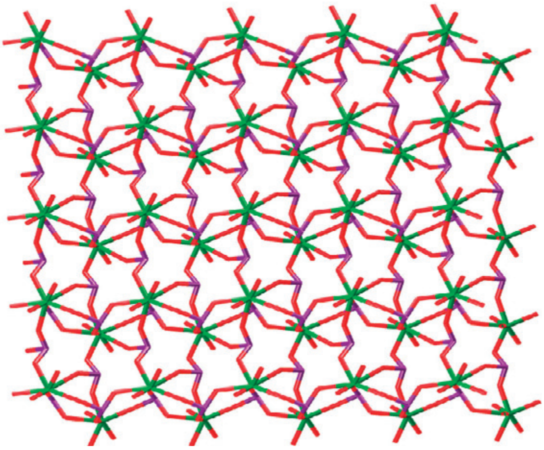

Figure 1. View of the 2D sheet structure along *a* direction.

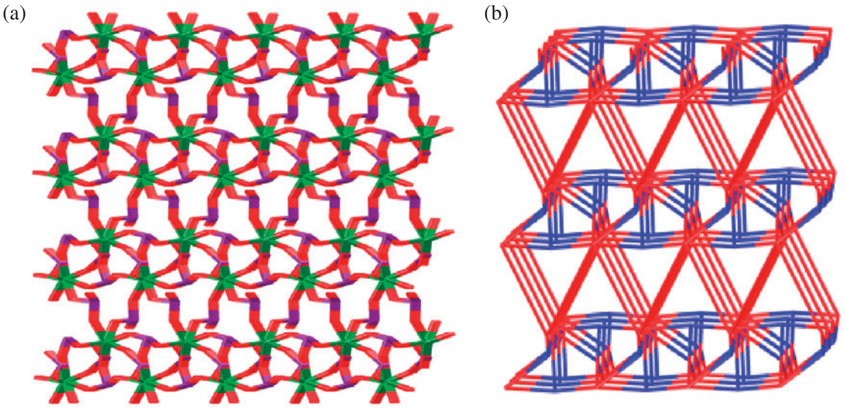

Figure 2. a) The pillared 3D frameworks of $Gd(IO_3)_3 \cdot H_2O$; b) schematic description of the $(4^3)(4 \cdot 6^2)(4^9 \cdot 6^{17} \cdot 8^2)$ network built on (3, 8)-connected nodes.

environments around each node, different long/and short Schläfli symbols are assigned to them, $4 \cdot 4_2 \cdot 4_2/4^3$ for 4-connected I3, $4_2 \cdot 6_5 \cdot 6_7/4 \cdot 6^2$ for I1, and $4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 6_3 \cdot 6 \cdot 6 \cdot 6_2 \cdot 6_2 \cdot 6 \cdot 6_2 \cdot 6 \cdot 6 \cdot 6_2 \cdot 6_2 \cdot 6_5 \cdot 6_2 \cdot 6 \cdot 6_3 \cdot 8_3/4^9 \cdot 6^{17} \cdot 8^2$ for 8-connected Gd1 [11]. Hence, according to the description about the binodal/trinodal framework [2a], such framework is defined to be the trinodal $(4^3)(4 \cdot 6^2)(4^9 \cdot 6^{17} \cdot 8^2)$ network built on triangle (I1, and I3) and tetragonal prism nodes (Gd1). Previous examples of such networks are very rare, only $H_2[Co_4O(TATB)_{8/3}]$ is known to own such (3, 8)-connected topology [3].

3.2. *TGA Studies on $Gd(IO_3)_3 \cdot H_2O$*

The thermal stability of this network and its intercalated guest molecules is primarily evaluated by using TG-DTA analysis figure 3. The first weight loss of 2.3% occurs at 160–190°C, corresponding to removal of free water molecules (Calcd 2.6%), after that, there is no weight loss until 580°C. The final product after heating to 800°C is Gd_2O_3 (Calcd: 74.1%, found: 74.3%). Remarkably, at 378°C, there may occur a phase transition, which can be corroborated by the TG-DTA plot, but the resulting phase is not clear at present.

4. Conclusion

In summary, a chiral lanthanide iodate of $Gd(IO_3)_3 \cdot H_2O$ was obtained by controlled hydrothermal synthesis. Formation of $Gd(IO_3)_3 \cdot H_2O$ requires introduction of Cu(II) ions. This compound is a layered 3D framework with 5.5% void volume occupied by water molecules. Topologically, this framework displays the first trinodal (3, 8)-connected $(4^3)(4 \cdot 6^2)(4^9 \cdot 6^{17} \cdot 8^2)$ network based on trigonal and tetragonal prism nodes.

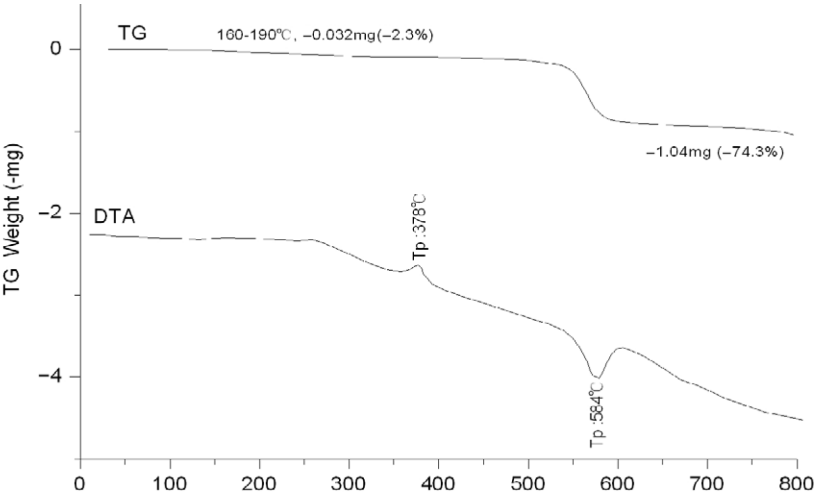

Figure 3. The TG-DAT plot of $Gd(IO_3)_3 \cdot H_2O$.

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