FINAL REPORT

NEW POLYMORPHS

OF LANTHANIDE SULFATE FRAMEWORKS

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Maejo University

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ชื่อโครงการ พหุสัณฐานใหม่ของโครงข่ายแลนทาไนด์ซัลเฟต

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จากความพยายามในการสังเคราะห์ และศึกษาอัตรลักษณ์ทางโครงสร้างชนิดใหม่ของโครงข่ายแลนทาไนด์ซัลเฟต ทำให้พบพหุสัณฐานใหม่ของโครงข่าย คือ $[Ln_2(SO_4)_3(H_2O)_4]$ เมื่อ Ln = Pr และ Nd โดยทั้งสองโครงข่ายมีโครงสร้างผลึกเหมือนกัน ที่อยู่ในปริภูมิ $P2_1/m$ ลักษณะโครงสร้างผลึกเป็นโครงข่ายสามมิติ ที่เกิดจากการเชื่อมต่อระหว่างสายโซ่หนึ่งมิติของหน่วยย่อย $\{LnO_9\}$ และระนาบในสองมิติของหน่วยย่อย $\{LnO_8\}$ โดยมีกลุ่มซัลเฟตเป็นตัวเชื่อมต่อผ่านสามรูปแบบของการโคออร์ดิเนชัน คือ μ_3-η^1:η^1:η^1:η^1, μ_4-η^1:η^1:η^1:η^1 และ μ_4-η^2:η^2:η^1:η^0 โดยพบว่าในโครงสร้างผลึกชนิดใหม่นี้ปรากฏความไม่เป็นระเบียบของโครงสร้างอยู่เป็นจำนวนมาก จากการศึกษาโครงข่ายทั้งหมดของแลนทาไนด์ซัลเฟต ทำให้สรุปได้ว่าจำนวนโมเลกุลของน้ำในโครงสร้างที่ต่างกันของโครงข่าย ($[Ln^{III}_2(SO_4)_3(H_2O)_n]$ เมื่อ n = 0 - 9) ส่งผลทำให้เกิดความหลากหลายทางโครงสร้าง และความมีรูพรุน ที่เกี่ยวข้องโดยตรงกับรูปแบบการ โคออร์ดิเนชันของกลุ่มซัลเฟต และรูปทรงทางเลขาคณิตในการโคออร์ดิเนชันของแลนทาไนด์ นอกจากนี้แล้วจากความพยายามในการเตรียมสารประกอบโครงข่ายชนิดใหม่ของโครงข่ายโคออร์ดิเนชันของแลนทาไนด์ โดยเริ่มจากเกลือชนิดต่าง ๆ ของแลนทาไนด์และสารเชื่อมต่ออินทรีย์ 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA) ได้โครงข่ายใหม่ $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$ ที่เป็นโครงข่ายสามมิติที่ปราศจากรูพรุน

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ABSTRACT

Project Code TRG5780212

Project Title New Polymorphs of Lanthanide Sulfate Frameworks

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Crystal structures of two new lanthanide sulfate polymorphs, *i.e.* $[Ln_2(SO_4)_3(H_2O)_4]$ (Ln = Pr (**I**) and Nd (**II**)), have been prepared and characterized. The new polymorphs are revealed to be isostructural, crystallized in monoclinic $P2_1/m$ space group and built up from the one-dimensional chain of $\{LnO_9\}$ and the two-dimensional layer of {LnO8} connected through the SO_4^{2-} using three different coordination modes, *i.e.* μ_3-η^1:η^1:η^1:η^1, μ_4-η^1:η^1:η^1:η^1 and μ_4-η^2:η^2:η^1:η^0. Apparently, the apparent polymorphic diversity in **I** and **II** is brought about by structure disordering. Founded on the available polymorphic $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ (n = 0 - 9), different degrees of coordinating water molecules is seemingly the prime cause of structural variation, defied by framework diversity and porosity, which are closely related to coordination modes of SO_4^{2-} and coordination geometry about the Ln^{III}. In addition to the study the polymorphism of lanthanide sulfate framework, a new crystal framework of $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$ (H_6TTHA = 1,3,5-triazine-2,4,6-triamine hexaacetic acid)was also synthesized and characterized.

Keywords lanthanide sulfate; polymorph; crystal structure; UV-vis spectroscopy; thermogravimetry

PART I

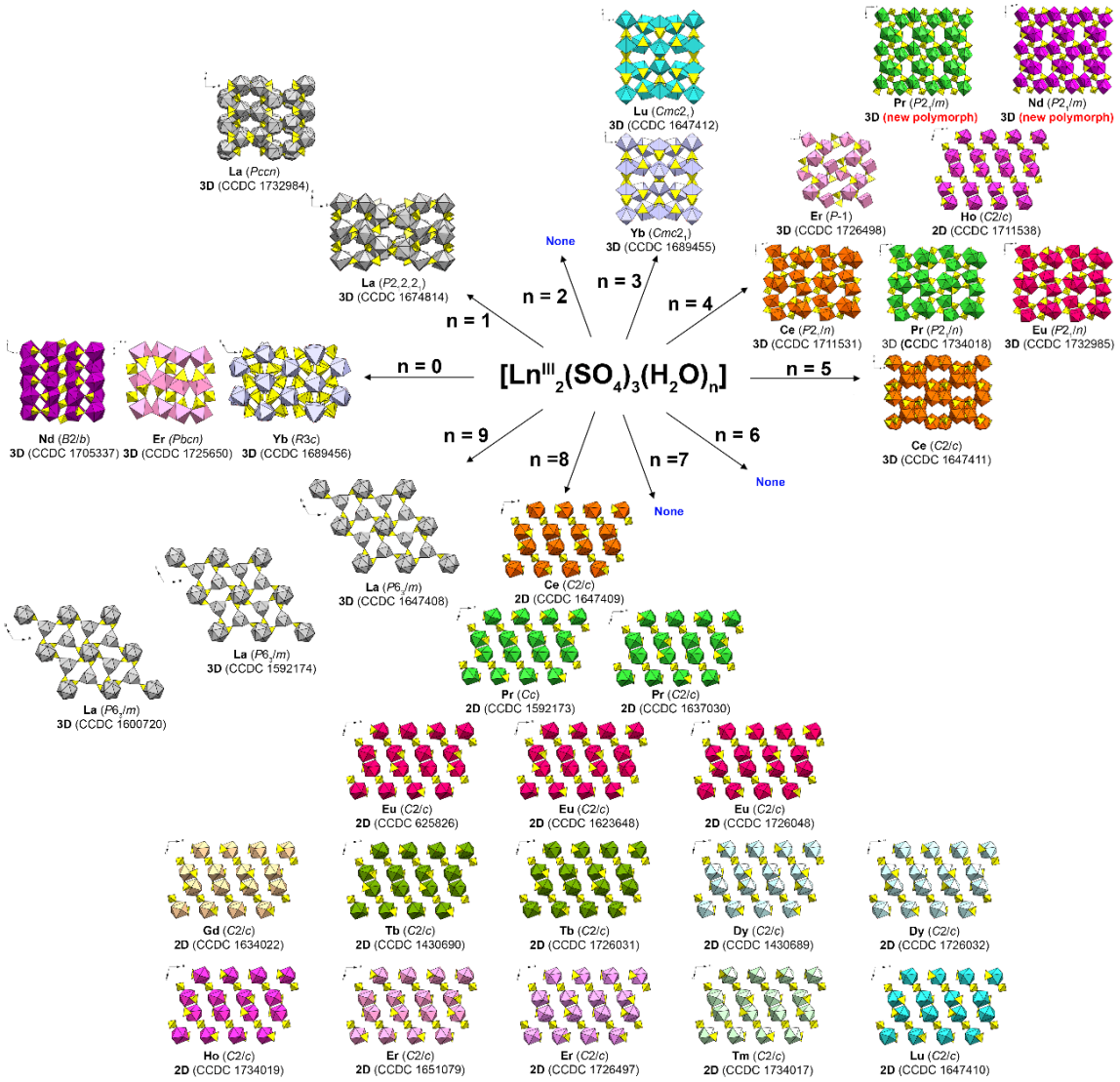
New Polymorphs of $[Ln_2(SO_4)_3(H_2O)_4]$

1. Introduction

Regarding the crystal structures of the trivalent lanthanide sulfate hydrates, different degrees of included water molecules are possible, *i.e.* $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ (n = 0-9).[1-25] There is however disparity in chemical formulas representing the structures deposited to the Cambridge Structural Database,[26] *i.e.* $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ and $[Ln^{III}_2(SO_4)_3]\cdot nH_2O$. Here, the $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ is adopted since all of the water molecules coordinate to the Ln^{III} centers (Scheme 1).

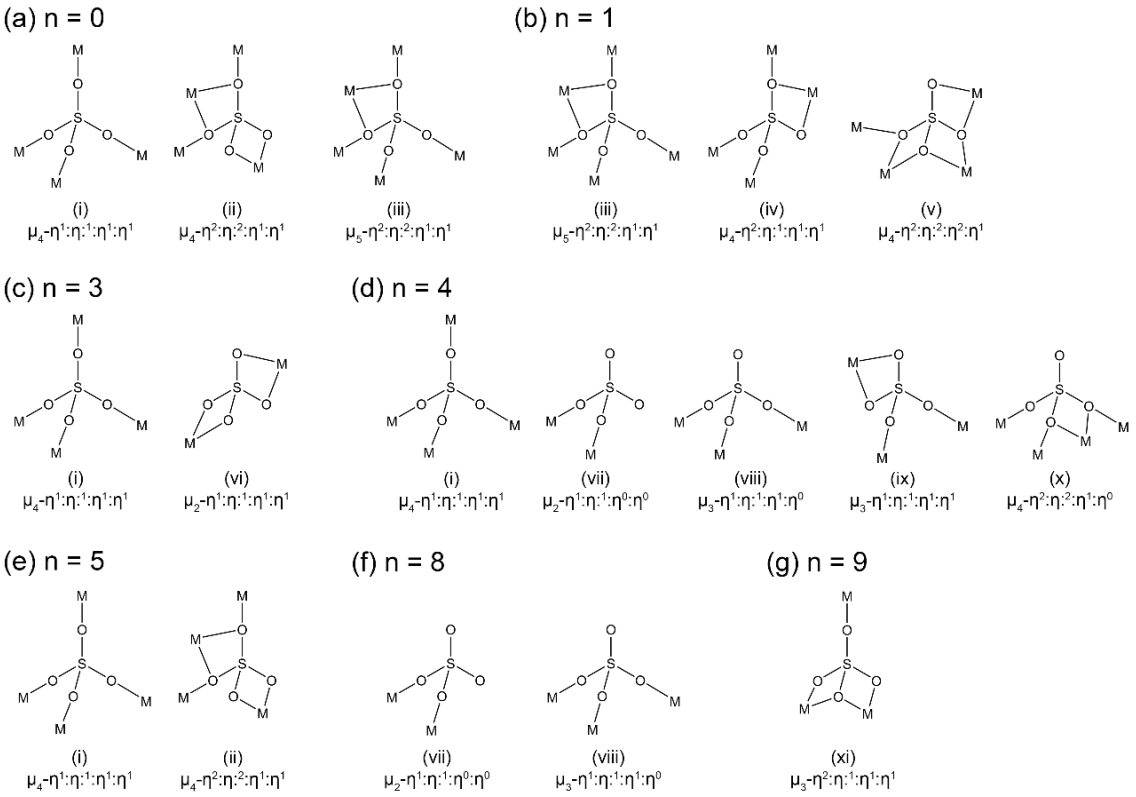
Amongst the structures deposited to the Cambridge Structural Database,[26] the most frequent structures are the octahydrates, *i.e.* $[Ln^{III}_2(SO_4)_3(H_2O)_8]$, which can be afforded for a wide range of Ln^{III}, *i.e.* Ce^{III}, Pr^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III} and Lu^{III}. The dihydrate (n = 2), the hexahydrate (n = 6) and the heptahydrate (n = 7) have, on the other hand, been unknown of. In addition, the monohydrate, the trihydrate, the pentahydrate and the nonahydrate are scarce and only observed for certain Ln^{III}, *i.e.* $[La^{III}_2(SO_4)_3(H_2O)]$,[17,21] $[Yb^{III}_2(SO_4)_3(H_2O)_3]$,[23] $[Lu^{III}_2(SO_4)_3(H_2O)_3]$,[11] $[Ce^{III}_2(SO_4)_3(H_2O)_5]$[11] and $[La^{III}_2(SO_4)_3(H_2O)_9]$.[1,3,11] There is notably not any apparent correlation between number of the water molecules n and either the lanthanide contraction or the hydration enthalpies of the Ln^{III} ions on the basis of these known structures. For instance, the monohydrate and the nonahydrate are possible for La^{III} whilst Pr^{III} can be afforded only as the tetrahydrate and the octahydrate[3,22]. Intriguingly, only the dehydrated structure has been reported for Nd^{III}.[27]

Variation in number of the water molecules in $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ evidently brings about diversity in coordination environment of the Ln^{III}, coordination mode of the SO_4^{2-} as well as architecture and dimensionality of the derived frameworks. Coordination numbers of the Ln^{III} may vary between 6 and 12, *i.e.* 6- and 9-fold in $[Ln^{III}_2(SO_4)_3]$,[10,23,27] 9- and 10-fold in $[Ln^{III}_2(SO_4)_3(H_2O)]$,[17,21] 6- and 8-fold in $[Ln^{III}_2(SO_4)_3(H_2O)_3]$,[11,23] 7- to 9-fold in $[Ln^{III}_2(SO_4)_3(H_2O)_4]$,[12,19-22] 9-fold in $[Ln^{III}_2(SO_4)_3(H_2O)_5]$,[11] 8-fold in $[Ln^{III}_2(SO_4)_3(H_2O)_8]$,[3,9,11,12,14-16,18,22,25,28] and 9- and 12-fold in $[Ln^{III}_2(SO_4)_3(H_2O)_9]$.[1,3,11]



Scheme 1. Diagrammatic summarization of $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ (n = 0-9) structures

Although being irregular, number of the coordination tends to increase with number of the water molecules. Contrary to the coordination number, number of the Ln^{III} centers fastened by the SO_4^{2-} linker seems to diversely correlate with number of the water molecules (Scheme 2). The highest variation in coordination modes of the SO_4^{2-} is observed intriguingly in the tetrahydrates, *i.e.* $[Ln^{III}_2(SO_4)_3(H_2O)_4]$ (Ln^{III} = Ce^{III}, Pr^{III}, Eu^{III}, Ho^{III} and Er^{III}),[12,19-22] which are the second most frequently reported structures following only the octahydrates.



Scheme 2. Coordination modes adopted by SO_4^{2-} in $[Ln^{III}_2(SO_4)_3(H_2O)_n]$

Although the as-described structural observations should be taken with the caution of the influences imparted from different synthesis methods, greater diversity in structures

of $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ can certainly be expected. Here, the synthesis and the crystal structures of two new $[Ln^{III}_2(SO_4)_3(H_2O)_4]$ where $Ln^{III} = Pr^{III}$ (**I**) and Nd^{III} (**II**) are reported. It must be noted that structure of **I** is a new polymorph of the previously reported $[Pr^{III}_2(SO_4)_3(H_2O)_4]$,[22] whereas there is not any prior report on $[Nd^{III}_2(SO_4)_3(H_2O)_4]$ (**II**).

2. Objective

To study polymorphism in lanthanide sulfate frameworks

3. Research methodology

3.1 Materials and methods

All chemicals were purchased and used without further purification; Pr_6O_{11} (TJTM, 99.9%), Nd_2O_3 (TJTM, 99.9%), H_2SO_4 (QRëC New Zealand, 98%) and ethanol (RCI Labscan, 99.9%). Powder X-ray diffraction (PXRD) data were collected using a Rigaku Mini Flex II X-ray diffractometer operated with Cu K_α radiation (λ = 1.5418 Å, 20 kV, 15 mA). The Infrared (IR) spectra were collected using a Perkin Elmer Spectrum RX instrument and KBr discs (BDH, 98.5%). Thermogravimetric analyses (TGA) were carried out using a Perkin Elmer Pyris Diamond TG/DTA instrument from room temperature up to 1300 °C with a heating rate of 10 °C·min^{-1} under the nitrogen gas flow. The UV-visible spectra were collected on the aqueous solution of the complexes at room temperature in the range of 200-800 nm using Hitachi UH5300 spectrophotometer.

3.2 Syntheses of I and II

Prior to the synthesis, the sulfate salts of the corresponding Ln^{III} were firstly prepared by dissolving 1.00 g of either Pr_6O_{11} or Nd_2O_3 in 250 mL of H_2SO_4 solution (0.0735 $mol \cdot L^{-1}$) from which the solid products were yielded through evaporation and dry at 100 °C followed by leave under ambient temperature.

In the synthesis of **I**, 0.0714 g of the yielded Pr^{III} powder was dissolved in 5.0 mL of deionized water into which 10.0 mL of mixed 1:1 by volume of ethanol/water solvent was successively added. The final solution was transferred into a 23 mL Teflon lined hydrothermal autoclave and the reaction was carried out under autogenous pressure generated at 180 °C for 24 h. In the synthesis of **II**, the same procedure was adopted but with Nd_2O_3. It should be noted that the green (**I**) and the violet (**II**) crystals were always yielded as the sole products of the syntheses.

3.3 Crystal structure determination

Crystallographic data sets of **I**-**II** were collected at 293(2) *K* using using a Rigaku XtaLAB SuperNova Diffractometer equipped with a single micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a Hypix Hybrid Pixel Array detector. Data collection and reduction were performed using CrysAlisPro 1.171.39.46.[29] Empirical absorption corrections were applied to all data sets using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[29] The structures were solved by intrinsic phasing methods within the SHELXT program[30] and refined on the F^2 by the full-matrix least squares technique using the SHELXL program[31] *via* the Olex[2] interface.[32] The crystallographic and refinement data for **I** and **II** are summarized in Table 1.

Table 1. Crystallographic data and refinement details for **I** and **II**.

	I	**II**	Ce[20]	Pr[22]	Eu[21]	Ho[19]	Er [12]
CCDC No.			1647411	1734018	1732985	1711538	1726498
Empirical formula	$Pr_2S_3O_{16}H_6$	$Nd_2S_3O_{16}$	$Ce_2S_3O_{10}H_8$	$Pr_2S_3O_{16}H_8$	$Eu_2S_3O_{16}H_8$	$Ho_2S_3O_{16}H_8$	$Er_2S_3O_{16}H_8$
Formula weight	641.06	640.66	640.48	642.06	664.16	762.17	-
Crystal color	Green	Violet	Colorless	Green	Colorless	Colorless	-
Temperature (*K*)	293(2)	293(2)	293	298(2)	173.0(2)	293(2)	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic,	Triclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$	P-1
a (Å)	9.1328(3)	9.1162(2)	13.1257(14)	13.051(3)	12.8680(9)	13.466(3)	6.635(2)
b (Å)	7.2250(2)	7.2057(2)	7.2520 (8)	7.2047(14)	7.1379(5)	6.6966(15)	9.055(2)
c (Å)	9.5410(2)	9.4993(2)	13.3823(14)	13.316(3)	13.1741(9)	18.183(4)	10.465(2)
α (°)	90	90	90	90	90	90	93.59(3)
β (°)	91.243(2)	91.296(2)	92.572(1)	92.55(3)	92.091(3)	101.875(3)	107.18(2)
γ (°)	90	90	90	90	90	90	99.12(3)
V (Å^3)	629.41(3)	623.84(3)	1272.5(2)	1250.9(4)	1209.24(15)	1604.6(6)	589.16
Z	4	4	4	4	4	4	2
Density (mg.m^{-3})	3.383	3.411	3.343	3.409	3.648	3.155	-
μ (mm^{-1})	8.236	8.822	7.65	8.289	10.890	10.29	14.774
F (000)	602	592	1200	1208	-	1432	-
Data/restraints/parameters	1444/6/152	1420/18/144	2201/215/16	-	-	1725/139/13	-
S	1.034	1.053	1.09	0.856	-	1.08	1.134
R_{int}	0.0631	0.0831	0.032	0.082	-	0.047	0.0124
R_1	0.0369	0.0436	0.027	0.031	0.0243	0.047	0.0248
wR_2	0.0591	0.1114	0.067	0.047	0.0599	0.130	0.0446

4. Results and Discussion

4.1 Crystal structure description of I

The two new $[Pr^{III}_2(SO_4)_3(H_2O)_4]$ (**I**) and $[Nd^{III}_2(SO_4)_3(H_2O)_4]$ (**II**) crystallize in the same monoclinic space group of $P2_1/m$ with similar unit cell parameters, but differ from the previously reported tetrahydrates (Table 1) according to the PXRD experiments. Although dissimilarity of the PXRD patterns of **I** and **II** from those of the $P\bar{1}$ (Er^{III}) and the $C2/c$ (Ho^{III}) structures is unambiguous, the patterns of the $P2_1/n$ structures (Pr^{III}, Eu^{III} and Ce^{III}) (Figure 1) are closely similar to those of **I** and **II** differing only in the presence of the tiny peak at 2θ of 14° in the patterns of **I** and **II**. The attempts to solve the structures in the space group $P2_1/n$ were noticeably not successful. In addition, there was not any alternative space group besides the $P2_1/m$ suggested though the structural validation in PLATON [33]. Two distinct crystal structures of $P2_1/n$ and $P2_1/m$ is therefore genuine and manifested clearly in the refined crystal structures from which the attribution of crystallographic disorder has been revealed. The presence of the tiny peak at 2θ of 14°, which belongs to the $P2_1/n$ structures, in the PXRD patterns of **I** and **II** may suggest therefore the co-presence of both phases in the bulk samples.

On the basis of the single crystal X-ray analyses, **I** and **II** are isostructural and the crystal structure of **I** as a representative of **I** and **II** is described here. The asymmetric unit of **I** contains twenty-one non-hydrogen atoms, including two crystallographically unique Pr^{III} ions, four coordinated water molecules and three significantly disordering SO_4^{2-} anions (Figure 2a). Whilst the $S3O_4^{2-}$ anion is fully occupied and connecting with 3 × Pr1 and 1 × Pr2 through μ_4-η^2:η^2:η^1:η^0 mode of coordination, both the $S1O_4^{2-}$ and $S2O_4^{2-}$ anions wiggle over two crystallographic settings (Figure 2b). The $S1O_4^{2-}$ anion, which anchors on

atom O4, wiggles in the way to fasten two different sets of three atoms, *i.e.* 1 × Pr1 and 2 × Pr2, using the chelating μ_3-η^1:η^1:η^1:η^1 mode of coordination. Similarly, the $S2O_4^{2-}$ anion anchoring on atom O6 rocks between two sets of four atoms, which are made up of 2 × Pr1 and 2 × Pr2, using the μ_4-η^1:η^1:η^1:η^1 mode of coordination. It may be notable, nonetheless, that the coordinating O atoms of the fully occupied $S3O_4^{2-}$ anion also exhibit severe disorder over three crystallographic sites, *i.e.* O9A and 2 × O9B. In addition to the as-described disorder, the coordinating water O13 coordinating to Pr1 shows disorder over two crystallographic sites.

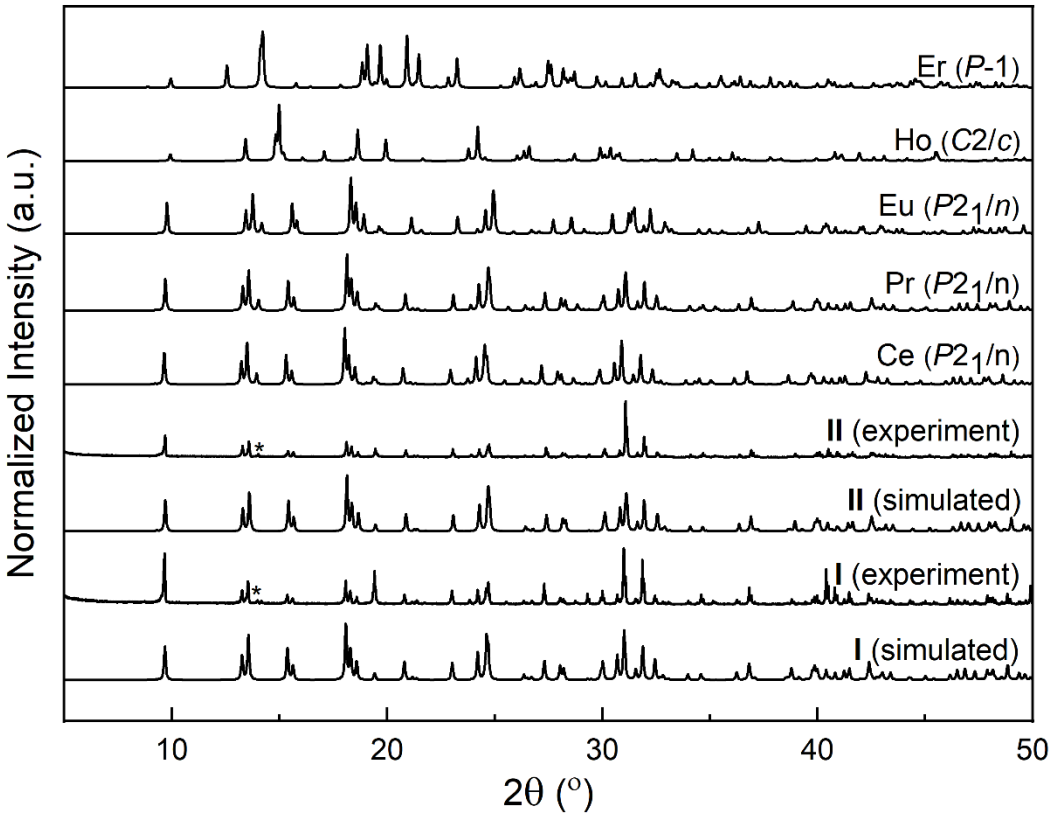


Figure 1. PXRD patterns of **I** and **II** compared with the patterns simulated from the single crystal data and the previously reported $[Ln^{III}_2(SO_4)_3(H_2O)_4]$ (∗ = diffraction of the $P2_1/n$ structures)

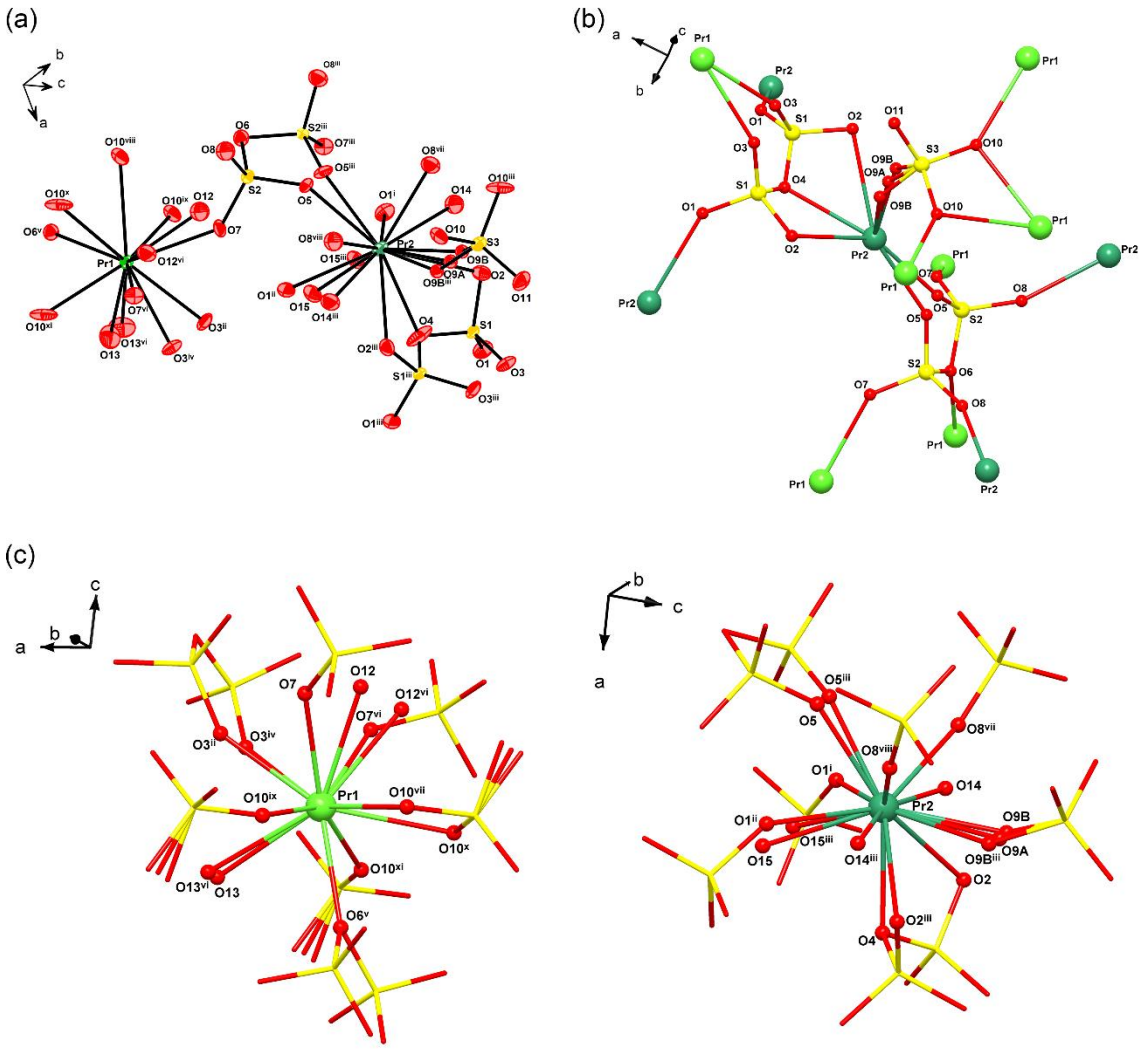


Figure 2. Depictions of (a) an extended asymmetric unit drawn with 50% probability thermal ellipsoids and labeling schemes, (b) coordination modes of SO_4^{2-} and (c) coordination environments of Pr1 and Pr2 of **I**. Symmetry codes: (i) 2-*x*, 2-*y*, 1-*z*; (ii) 2-*x*, -0.5+*y*, 1-*z*; (iii) *x*, 1.5-*y*, *z*; (iv) 2-*x*, 1-*y*, 1-*z*; (v) 1-*x*, -0.5+*y*, -*z*; (vi) *x*, 0.5-*y*, *z*; (vii) 1-*x*, 0.5+*y*, 1-*z*; (viii) 1-*x*, 1-*y*, 1-*z*; (ix) *x*, *y*, -1+*z*; (x) 1-*x*, -0.5+*y*, 1-*z*; (xi) *x*, 0.5-*y*, -1+*z*.

As the chemistry is concerned, few additional structural features need attention. Firstly, the existence of the sulfate O7 and the water O12 within the coordination sphere

of Pr1 is not viable. Secondly, the coordination sphere about Pr2 would be over crowded with the disordering sulfate O1 and O8 as well as the water O14 and O15 and therefore some of these atoms cannot co-exist. Thirdly, the laborious disorder as-described for the crystal structure of **I** is identical as that found in the crystal structure of **II** (Figure 3). The as-described arduous disorder is therefore inherent and undisputed, which attributes to the distinction of **I** and **II** from the previously reported tetrahydrates. Fourthly, the disordering coordination spheres of Pr1 and Pr2 leads to the grave deviation of their local coordination environment from regular geometries although the coordination numbers of eight or nine can be assumed. It should be noted that the Pr^{III}–O and S–O distances are in the ranges of 2.394(6) - 2.600(4) and 1.331(4) - 1.544(16) Å, respectively, which are consistent with the values reported for the relevant $[Ln^{III}_2(SO_4)_3(H_2O)_n]$ frameworks.[3,22]

The one-dimensional puckered chain of Pr1 extending along the 2_1 screw axis (the *b* direction) and the two-dimensional layer of Pr2 expanding in the *ab* plane are further fastened through the SO_4^{2-} linkers to form the three-dimensional framework of **I** (Figure 4). The one-dimensional chain is notably built up of the polyhedra of Pr1, which are fastened through the O bridges of the $S2O_4^{2-}$ and the $S3O_4^{2-}$ linkers. The two-dimensional layer, on the other hand, is fabricated from the discrete polyhedra of Pr2, which are connected with the neighboring equivalents through the O bridges of the $S1O_4^{2-}$ and the $S2O_4^{2-}$linkers. The Pr1···Pr1 distance is *ca.* 4.33 Å, which is significantly longer than the Pr2···Pr2 distance of *ca.* 5.67-7.22 Å.

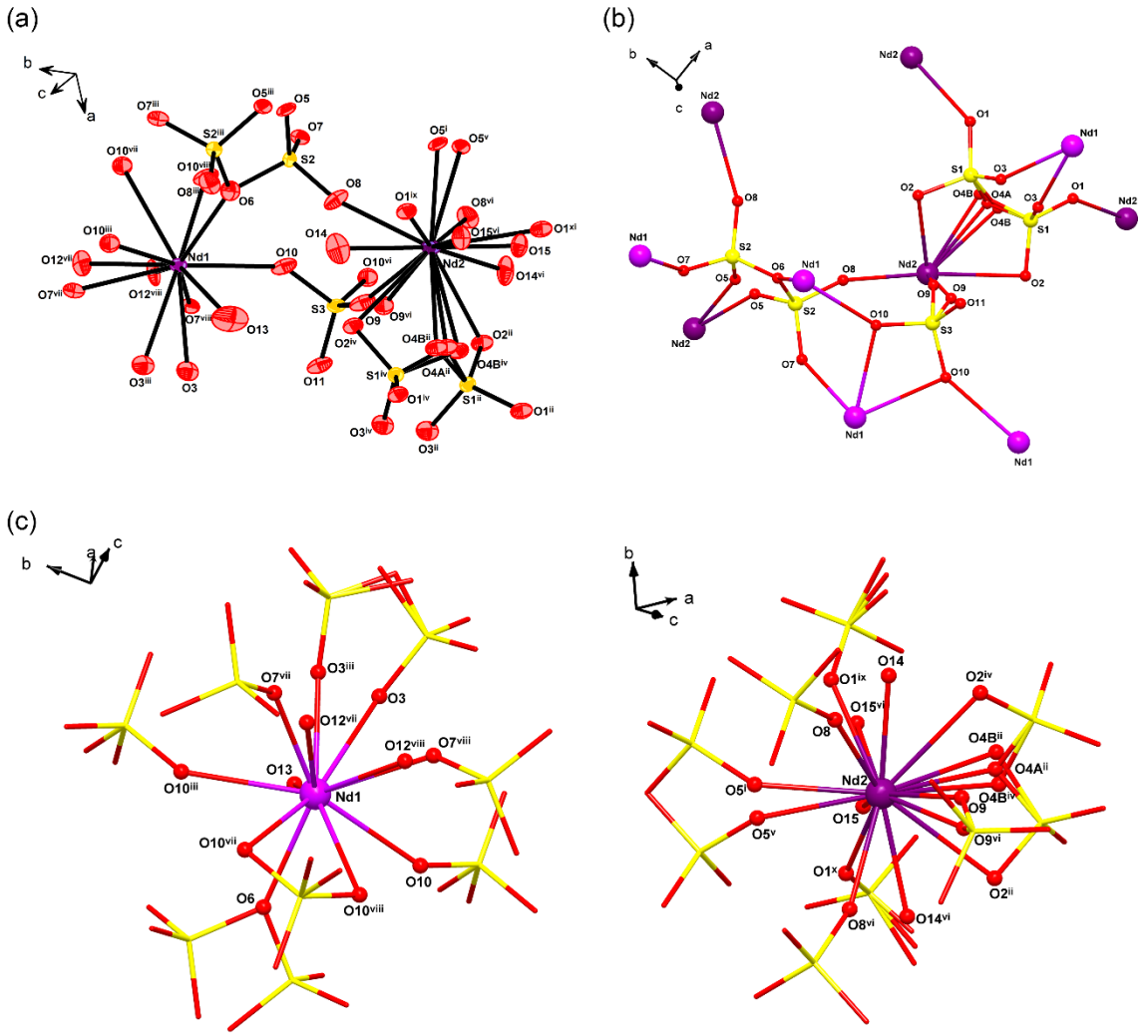


Figure 3. Depictions of (a) an extended asymmetric unit drawn with 50% probability thermal ellipsoids and labeling schemes, (b) coordination modes of SO_4^{2-} and (c) coordination environments of Nd1 and Nd2 of **II**. Symmetry codes: (i) 1-*x*, 1-*y*, -*z*; (ii) 2-*x*, -0.5+*y*, 1-*z*; (iii) *x*, 1.5-*y*, *z*; (iv) 2-*x*, 1-*y*, 1-*z*; (v) 1-*x*, -0.5+*y*, -*z*; (vi) *x*, 0.5-*y*, *z*; (vii) 1-*x*, 0.5+*y*, 1-*z*; (viii) 1-*x*, 1-*y*, 1-*z*; (ix) *x*, *y*, -1+*z*; (x) *x*, 0.5-*y*, -1+*z*.

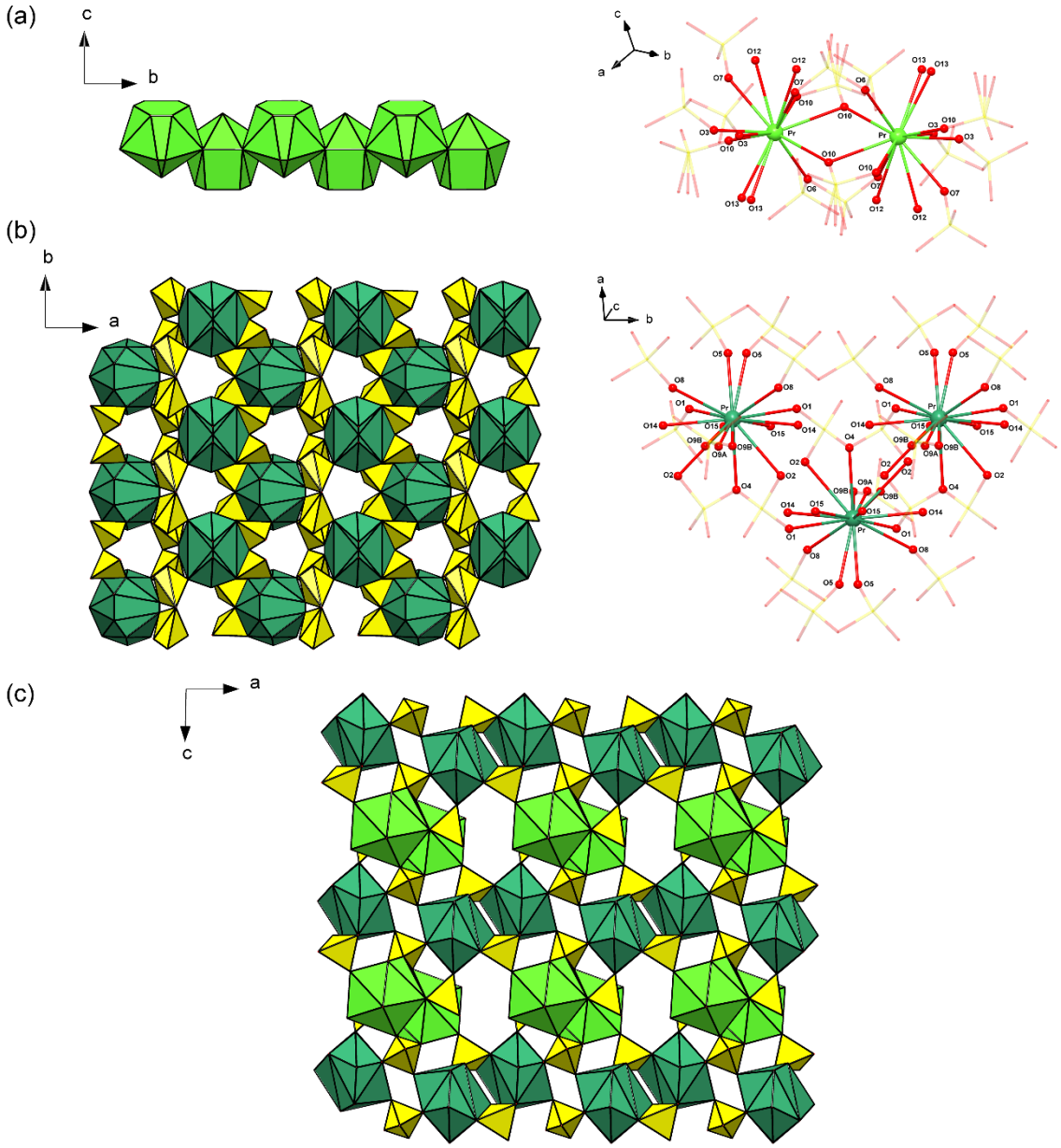


Figure 4 Views of (a) the one-dimensional infinite chain along the *b*-axis (b) the two-dimensional layer in the *ab* plane, and (c) the three-dimensional framework of **I**.

The three-dimensional framework of **I** is closely similar to the three-dimensional framework of the previously reported tetrahydrate, *i.e.* $[Pr_2(SO_4)_3(H_2O)_4]$,[22] but differs from the two-dimensional octahydrate, *i.e.* $[Pr_2(SO_4)_3(H_2O)_8]$.[3] Compared with the previously reported $P2_1/n$ structure of $[Pr_2(SO_4)_3(H_2O)_4]$,[22] a reduction in symmetry of **I** which was solved and refined in $P2_1/m$ apparently stems from the nullification of the translation because of the crystallographic disorder (Figure 5). The remained mirror plane in the crystal structure of **I** is located in the *ac* plane spanning through Pr1, Pr2, S3, O4, O6 and O9A, and perpendicular to the 2_1 screw axis lying in the *b* direction.

Regarding the crystal structure of **II**, the presence of the coordinated water molecules results in a distinct variation from the dehydrated three-dimensional framework of $[Nd_2(SO_4)_3]$ which comprises only the one-dimensional chain sub-structure.[27] Coordination modes adopted by the sulfate linkers also differ, *i.e.* μ_4-η^2:η^2:η^1:η^1 and μ_5-η^2:η^2:η^1:η^1 in $[Nd_2(SO_4)_3]$ compared with μ_3-η^2:η^1:η^1:η^0, μ_3-η^1:η^1:η^1:η^1 and μ_4-η^1:η^1:η^1:η^1 in **II**.

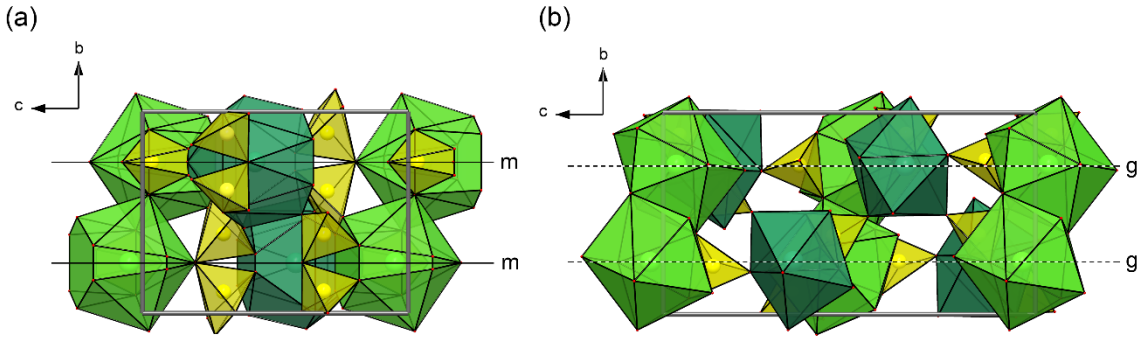


Figure 5. Views of (a) a mirror symmetry in the three dimensional framework of **I** ($P2_1/m$) and (b) a glide symmetry in the previously reported $P2_1/n$ structures.[22]

Table 2. List of potential hydrogen bonding interactions found for **I** and **II**.

	D–H···A [a]	D–H, (Å)	H···A, (Å)	D···A, (Å)	∠ D–H···A, (°)
I	O12–H12A···O5^{i}	0.8506(0)	2.3193(0)	3.0602(1)	145.762(2)
	O12–H12A···O5^{ii}	0.8506(0)	2.4535(0)	3.2664(1)	160.148(2)
	O12–H12B···O9A^{ii}	0.8505(0)	2.4422(1)	3.1542(1)	141.720(2)
	O12–H12B···O9B^{ii}	0.8505(0)	2.2430(1)	3.0222(1)	152.356(2)
	O12–H12B···O14^{ii}	0.8505(0)	2.6407(1)	3.2423(1)	128.826(2)
	O12–H12B···S3^{ii}	0.8505(0)	2.7213(1)	3.3243(1)	129.150(2)
	O13···O2^{iii}	-	-	3.0538(1)	-
	O13···O11^{iv}	-	-	2.8122(1)	-
	O14–H14A···O4^{v}	0.9114(0)	2.3926(0)	2.8832(1)	113.765(2)
	O14–H14A···O15^{v}	0.9114(0)	2.1867(0)	3.0779(1)	165.592(2)
	O14–H14A···S1	0.9114(0)	2.4955(1)	3.1700(1)	131.103(2)
	O14–H14B···O6^{v}	0.8535(0)	2.3839(1)	3.1242(1)	145.391(2)
	O14–H14B···S2^{ii}	0.8535(0)	2.3376(1)	2.7651(1)	111.352(2)
	O15–H15A···O4^{iv}	0.8500(0)	2.1060(1)	2.8924(1)	144.089(2)
	O15–H15A···O14^{iv}	0.8500(0)	2.5263(1)	3.0779(1)	123.466(2)
	O15–H15B···O2^{vi}	0.8512(0)	2.2604(1)	3.0610(1)	156.756(2)
II	O12···O1^{i}	2.9447(1)	-	-	-
	O12···O5	2.7585(1)	-	-	-
	O12···O6	2.7363(1)	-	-	-
	O12···O9	3.0538(1)	-	-	-
	O12···O14	3.2178(1)	-	-	-
	O12···S3	3.2711(1)	-	-	-
	O13···O2^{v}	2.9073(1)	-	-	-
	O13···O14	3.0602(1)	-	-	-
	O14···O4A^{vii}	2.9178(1)	-	-	-
	O14···O4B^{iii}	2.7441(1)	-	-	-
	O14···O4B^{vii}	3.0180(1)	-	-	-
	O14···O6	3.1252(1)	-	-	-
	O14···O9	2.8667(1)	-	-	-
	O14···O15^{viii}	3.0488(1)	-	-	-
	O14···O15^{ix}	3.0706(1)	-	-	-
	O14···S1	3.0922(1)	-	-	-
	O14···S2	2.7629(1)	-	-	-
	O15···O2^{vii}	3.0482(1)	-	-	-
	O15···O4A^{iv}	2.8679(1)	-	-	-
	O15···O4B^{vi}	2.8130(1)	-	-	-
	O15···O4B^{iv}	2.9870(1)	-	-	-
	O15···O5^{x}	2.9546(1)	-	-	-

[a] Symmetry codes: *(i)* 1 - *x*, 1 - *y*, 1 - *z*; *(*ii*)* 1 - *x*, -0.5 + *y*, 1 - *z*; *(*iii*)* *x*, 1.5 - *y*, -1 + *z*; *(*iv*)* 2 - *x*, -0.5 + *y*, 1 - *z*; *(*v*)* 2 - *x*, 0.5 + *y*, 1 - *z*; *(*vi*)* 2 - *x*, 1 - *y*, 1 - *z*; *(*vii*)* *x*, *y*, -1 + *z*; *(*viii*)* *x*, 0.5 - *y*, *z*; *(*ix*)* 2 - *x*, 0.5 + *y*, -*z*; *(*x*)* 1 - *x*, -0.5 + *y*, - *z*

Owing to the disorder in the crystal structures of **I** and **II**, the hydrogen bonding interactions in the two structures have been evaluated on the basis of the distances between the possible donor (D) and acceptor (A) atoms (Table 2). The D–H···A were measured if H atoms could be located. The hydrogen bonding analysis suggests the involvement of every coordinated water molecule in the hydrogen bonding interactions acting as hydrogen bonding donor. The abundance of the hydrogen bonding interactions between the water molecules and the sulfate linkers is in good accord with the apparent crystallographic disorder.

3.2 UV-vis spectroscopy and thermogravimetric properties of I and II

The characteristic absorptions attributed to the *f-f* transitions are clearly shown in the UV-vis absorption spectra of **I** and **II** from which the Tauc plots were constructed (Figure 6) and the band gap energies of 5.5 (**I**) and 6.0 (**II**) eV were estimated. All the *f-f* transitions in **I** and **II** arise from the corresponding ground levels $^{3}H_{4}$ (Pr^{III}) and $^{4}I_{9/2}$ (Nd^{III}). The UV-vis spectrum of **I** is noticeably similar to that of the previously reported $[Pr_2(SO_4)_3(H_2O)_4]$ [22] whilst there is not any previous report for the absorption spectra of $[Nd_2(SO_4)_3(H_2O)_4]$. Compare with the $Nd(CF_3COO)_3{\cdot}Bpy$ complex,[34] the absorption spectra of **II** and $Nd(CF_3COO)_3{\cdot}Bpy$ are nonetheless identical. It is therefore evident that the derived spectra are unaffected by the coordination environments of Pr^{III} and Nd^{III}.

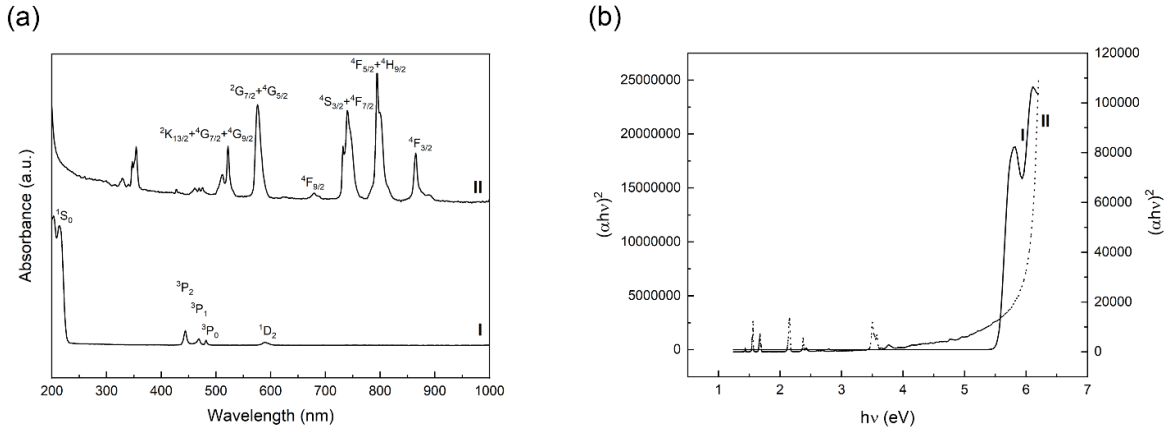


Figure 6. (a) UV-vis absorption spectra of I and II, and (b) the corresponding Tauc plots.

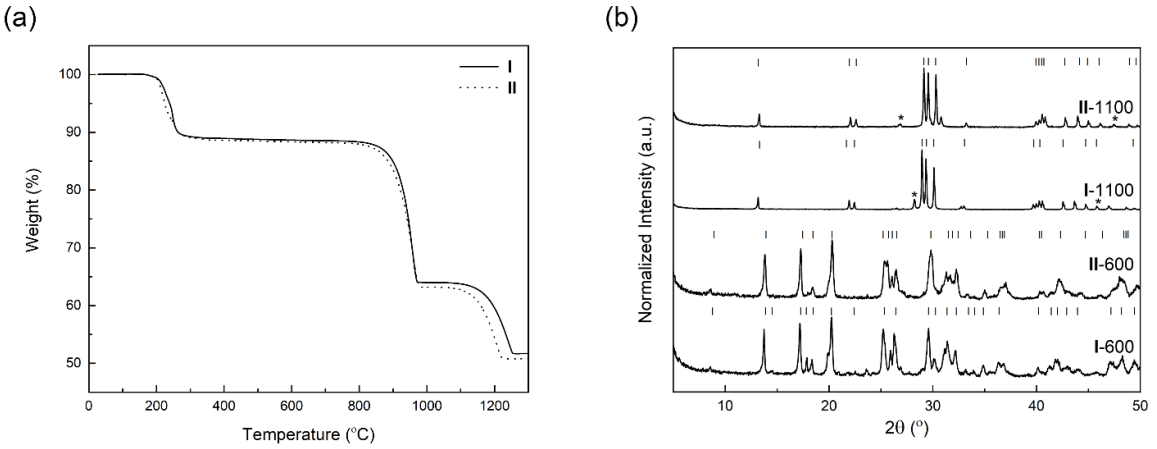


Figure 7. (a) Thermogravimetric curves of **I** (solid line) and **II** (dotted line), and (b) the PXRD patterns of **I** and **II** after the treatment at 600 °C and 1100 °C for 1 h (| = JCPDS no. 39-0302 (**I**-600), JCPDS no. 29-1073 (**I**-1100), JCPDS no. 1-083-2244 (**II**-600), JCPDS no. 48-1829 (II-1100) and *= JCPDS no. 24-0801 (**I**-1100), JCPDS no. 3-065-6729 (**II**-1100)).

Under the nitrogen gas flow, three steps of weight losses were apparent for **I** and **II** alike (Figure 7). The first step commenced at *ca.* 170 °C, affirming that these water are not the crystallizing water molecules but the coordinating ligands. The observed weight loss of 11.0% after reaching the plateau at 280 °C for both **I** and **II** corresponds well with four water molecules (11.3% and 11.2% for **I** and **II**, respectively). Accordingly, the PXRD patterns collected on **I** and **II** after the thermal treatment at 600 °C for 1 h suggested the yielded products to be the corresponding dehydrated [$Pr_2(SO_4)_3$] (JCPDS 39-0302) and [$Nd_2(SO_4)_3$] (JCPDS 1-083-2244). The second weight loss (800-1000 °C; **I**, obs. 25.0%, calc. 25.2%; **II**, obs. 25.5%, calc. 24.9%) and the third weight loss (1100-1250 °C; **I**, obs. 12.3%, calc. 12.6%; **II**, obs. 12.4%, calc. 12.5%) should attribute to the decomposition of the framework, leading to Pr_2O_3 (**I**) and Nd_2O_3 (**II**) as the final products. With reference to the PXRD patterns, the product after the treatment at 1100 °C were $Pr_2O_2SO_4$ (JCPDS 29-1073) and Pr_2O_3 (JCPDS 24-0801) for **I** and $Nd_2O_2SO_4$ (JCPDS 48-1829) and Nd_2O_3 (JCPDS 3-065-6729) for **II**. Thus, the final product after the heating at approximately 1250 °C to be Pr_2O_3 and Nd_2O_3 can be assumed. Similar decomposition pattern was reported for the [$Eu_2(SO_4)_3(H_2O)_8$] although the complete decomposition temperature of [$Eu_2(SO_4)_3(H_2O)_8$] was lower (*ca.* 1080 °C).[18]

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PART II
New Crystal Structure of $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$

1. Introduction

Coordination polymers of lanthanides (LnCPs) particularly those with multi-dimensional frameworks has captured an extensive interest owing to their fascinating framework architectures and unique properties. A wide variety of potential functions, *e.g.* gas storage, luminescent thermometer, chemosensing, biosensing, catalysis and proton conductivity, has been reported.[1,2] To fabricate new multi-dimensional LnCPs, the use of polypodal ligands is a common strategy.[3] Here, 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA) was employed due to its availability of as many as six flexible $(CH_2COOH)_2$ arms and also its capability to promote supramolecular assembly *via* hydrogen bonding and π-π stacking interactions. Based on a survey of the Cambridge Structural Database (version 5.41, Nov 2019),[4] there are 9 structures, which contain only $TTHA^{6-}$. They can be classified into 4 isostructural groups: namely, $[Ln_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Ln = Sm, Eu, Tb, Gd and Dy),[5,6] $[Yb_2(TTHA)]$,[5] $[Tb_2(TTHA)(H_2O)_2]\cdot 1.5H_2O$[7] and $[Tb_4(TTHA)_2(H_2O)_4]\cdot 7H_2O$.[8] The use of secondary ligand and heterometal added variation leading to 7 more structures of 4 isostructural groups: namely, $[Ln_4(TTHA)_2(pzac)(H_3O)_2(H_2O)]\cdot 5H_2O$ (Ln = Pr and Nd), $[Sm_8(TTHA)_4(pzac)_{0.5}(H_3O)\ (H_2O)_{7.5}]\cdot 4H_2O$) and $[Ln_4(HTTHA)_2(SO_4)(H_2O)_4]\cdot 5H_2O$ (Ln = Pr and Nd, $pzac^{2-}$ = 2,5-dioxo-piperazine-1,4-diacetate),[9] and $[M_3Tb_2(TTHA)_2(H_2O)_6]\cdot 10H_2O$ (M = Zn and Co).[10]

With the use of H_6TTHA, a new $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$ ($TTHA^{6-}$ = 1,3,5-triazine-2,4,6-triamine hexaacetate) (**I**) was synthesized. Single crystal structure,

framework architecture and topology as well as the weak interactions analysis of **I** are reported herein.

2. Objective

To synthesize a new lanthanide coordination polymer of 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA)

3. Research methodology

3.1 Synthesis of I

The H_6TTHA was synthesized following the method described in the literature.[11] The colorless block crystals of **I** were obtained as a contaminated phase of the reaction between H_6TTHA (0.142 g, 0.300 mmol) and $Eu(NO_3)_3 \cdot 5H_2O$ (0.202 g, 0.600 mmol) in 10.00 mL of deionized water under an autogenous pressure generated at 180 ^oC for 2 days. The reaction was carried out in a 23 mL Teflon-lined autoclave. The main phase of the reaction was notably the previously reported $[Eu_2(TTHA)(H_2O)_4] \cdot 9H_2O$.[5]

3.2 Crystal structure determination

Crystal data, data collection and structure refinement details are summarized in Table 1. The disorder of the two water molecules over three crystallographic sites could be clearly seen in the electron-density map and was refined using the SUMP command providing occupancies of 0.81 (O4W), 0.38 (O5W) and 0.81 (O6W).

Table 1. Crystallographic data and refinement details for **I**.

Empirical formula	$C_{15}H_{16}Eu_2N_6O_{16}\cdot H_2O$
Formula weight	858.27
Crystal color	Colorless
Temperature (*K*)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.8332 (2)
b (Å)	14.9924 (3)
c (Å)	15.6429 (4)
β (°)	89.914 (2)
V (Å^3)	2306.12 (9)
Z	4
Density (mg.m^{-3})	2.472
μ (mm^{-1})	5.49
F (000)	1649.554
Data/restraints/parameters	4578/0/380
S	1.04
R_{int}	0.046
R_1	0.034
wR_2	0.077

Computer programs: CrysAlis PRO 1.171.39.46,[12] ShelXT,[13,14] olex2.refine 1.3,[15] Olex2 1.3.[16]

4. Results and Discussion

4.1 Crystal structure description of I

Crystal structure of **I** crystallizes in the monoclinic space group $P2_1/n$. Its asymmetric unit contains forty non-hydrogen atoms, including two crystallographically unique Eu^{III} ions, one fully deprotonated $TTHA^{6-}$, four coordinated water molecules and one crystallizing water molecule (Fig. 1). The Eu1 adopts a nine-fold coordination of a distorted tricapped trigonal prismatic geometry, *i.e. TPRS*-{$Eu1O_9$}, which is delineated by seven O atoms from three $TTHA^{6-}$ (O1, O4, O5, O6, O8, O9 and O12) and two O atoms from the coordinated water molecules (O1W and O2W). Eu2 is, on the other hand, eight-fold coordinated to eight O atoms from three $TTHA^{6-}$ (O3, O5, O7, O8, O10 and O11) and two O atoms of the coordinated water molecules, *i.e.* {$Eu2O_8$}. The coordination geometry about the Eu2 is however poorly defined because of the two disordering water molecules, which are located over three crystallographic sites with approximate occupancies of 0.81

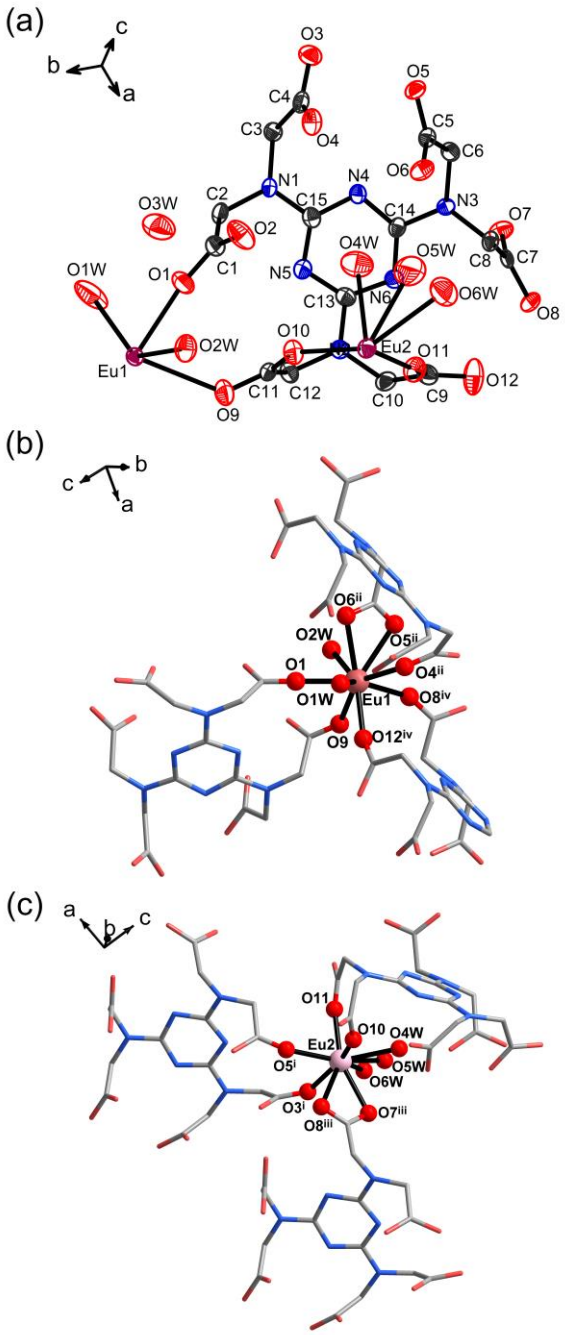

Figure 1. Views of (a) an extended asymmetric unit of **I** drawn using 50% probability ellipsoids and the coordination environments about (b) Eu1 and (c) Eu2. (Symmetry codes: (i) 0.5 + *x*, 0.5 - *y*, -0.5 + *z*; (ii) 0.5 - *x*, 0.5 + *y*, 0.5 - *z*; (iii) -0.5 + *x*, 0.5 - *y*, -0.5 + *z*; (iv) 1.5 - *x*, 0.5 + *y*, 0.5 – *z*)

(O4W), 0.38 (O5W) and 0.81 (O6W). The Eu–O and Eu–OW distances are in the ranges of 2.2567(1) - 2.6436(1) and 2.2990(0) - 2.5985(0) Å, respectively. These distances are consistent with the values reported for the other Ln^{III}-TTHA frameworks.[5-10]

The {$Eu1O_9$} and {$Eu2O_8$} units are bridged by O5 and O8 of the O5–C5–O6 and O7–C7–O8, respectively, using the μ_2-η^1:η^2 coordination mode to form an edge-sharing {Eu_2O_{15}} dimer (Fig. 2). The Eu1···Eu2 distance is 4.1129(1) Å. The three-dimensional framework of **I** can be regarded as being constructed using this {Eu_2O_{15}} dimeric building motif each of which is connected to eleven neighboring equivalents through four $TTHA^{6-}$ linkers. Four different modes of coordination are exhibited (Fig. 3), *i.e.* μ_1-η^0:η^1 (O1–C1–O2), the bridging μ_2-η^1:η^1 (*syn-syn*, O3–C4–O4 and O11–C9–O12), the bridging μ_2-η^1:η^1 (*syn-anti*, O9–C11–O10) and the chelating/bridging μ_2-η^1:η^2 (O5–C5–O6 and O7–C7–O8). The distances between centroids of the neighboring dimeric motifs are varied from 5.8959(1) to 13.0014(2) Å.

I has been yielded as a contaminated phase in the synthesis of $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$.[5] They are closely similar in view of their crystal structures both of which are constructed from the dimeric building motifs. The coordination about the Eu^{III}, modes of the coordination of $TTHA^{6-}$ as well as the crystallizing water content are however different. The dimer of **I** is made up of the {$Eu1O_9$} and {$Eu2O_8$} sub-units whereas the one of $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ is constructed from 2 × {EuO_9}. Regarding modes of coordination, there are only three modes exhibited by $TTHA^{6-}$ in $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$, *i.e.* the chelating μ_1-η^1:η^1, the bridging μ_2-η^1:η^1 (*syn-syn*) and the chelating/bridging μ_2-η^1:η^2, the latter two of which are also found in **I**. The bridging μ_2-η^1:η^1 (*syn-anti*) and the monodentate μ_1-η^0:η^1 exhibited by $TTHA^{6-}$ in **I**, however, do

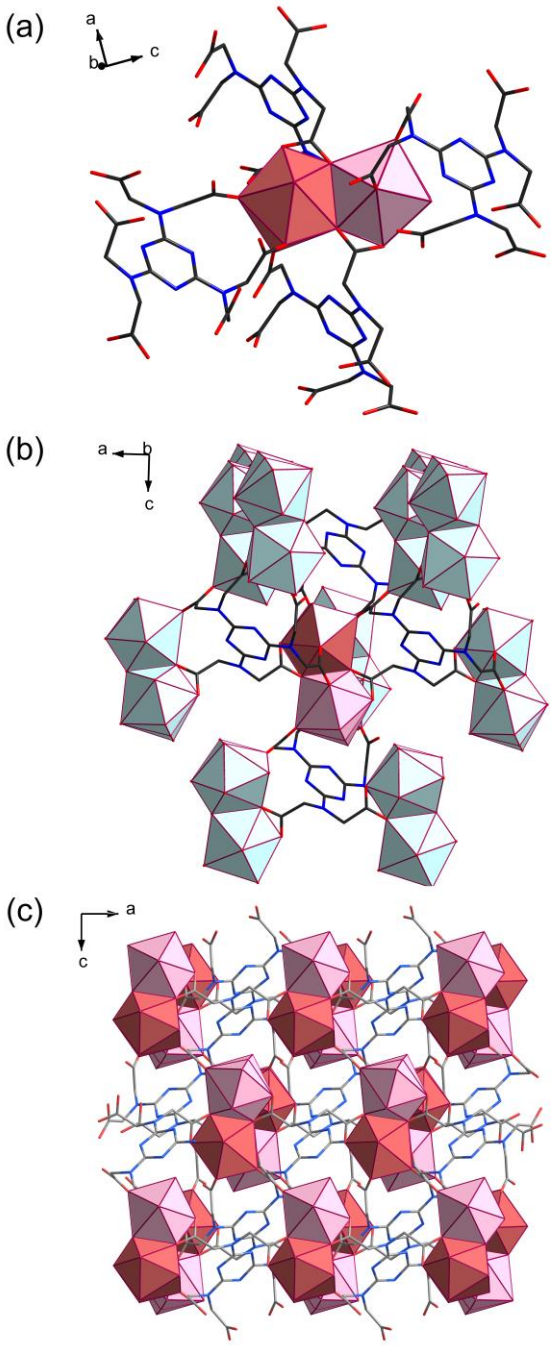

Figure 2. Views of (a) an edge-sharing of {$Eu1O_9$} and {$Eu2O_8$} units, (b) coordination environment of the dimer and (c) the three-dimensional framework of **I**

not exist in $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$. According to the as-described variances, the framework of **I** is denser in nature occupying no void space compared to $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (*ca.* 33% void), which may be accounted for the higher synthesis temperature of **I**. Similar phenomena has been reported.[17]

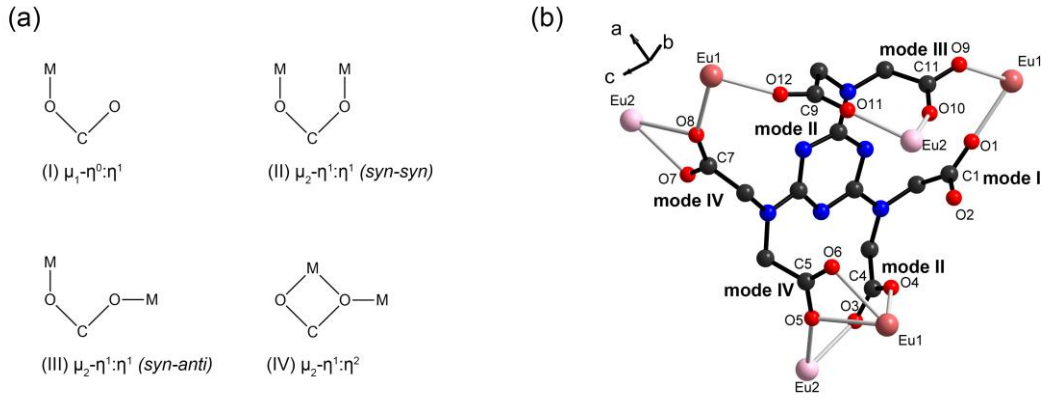

Figure 3. Views of (a) coordination modes at each -COO^- pendant, and (b) spatial arrangement of $TTHA^{6-}$ in **I**

Hydrogen bonding interactions in the structures of **I** has been analyzed using PLATON[18] and evaluated on the basis of the distances between the possible donor (D) and acceptor (A) atoms if H atoms could not be located (Table 2). The offset parallel displaced π-π interaction between the triazine rings was measured and the centroid-centroid distance and angle are 4.422 Å and 52.2°, respectively (Fig. 4).

Table 2. Hydrogen-bond geometry (Å, º)

D−H···A[a]	D−H	H···A	D···A	∠ D−H···A
O1W−H1WA···O2^{i}	0.87(3)	2.20(3)	2.804(6)	126(5)
O1W−H1WB···O7^{ii}	0.87(3)	2.38(4)	2.831(6)	113(4)
O2W−H2WB···O9^{iii}	0.80(8)	2.16(8)	2.927(6)	160(8)
O2W−H2WA···O10	0.882(6)	2.356(6)	3.184(6)	156.3(5)
O3W−H3WA···O2	0.85(5)	2.05(5)	2.820(6)	149(6)
O3W−H3WB···O6^{i}	0.85(6)	2.20(6)	2.935(6)	144(6)
O4W···O6	-	-	2.9555(1)	-
O5W···O3W^{iv}	-	-	3.1021(1)	-
O6W···O3W^{iv}	-	-	2.7786(1)	-

[a] Symmetry codes: (i) 0.5-*x*, 0.5+*y*, 0.5-*z*; (ii) 1-*x*, 1-*y*, 1-*z*; (iii) 1-*x*, 1-*y*, -*z*; (iv) 0.5-*x*, -0.5+*y*, 0.5-*z*.

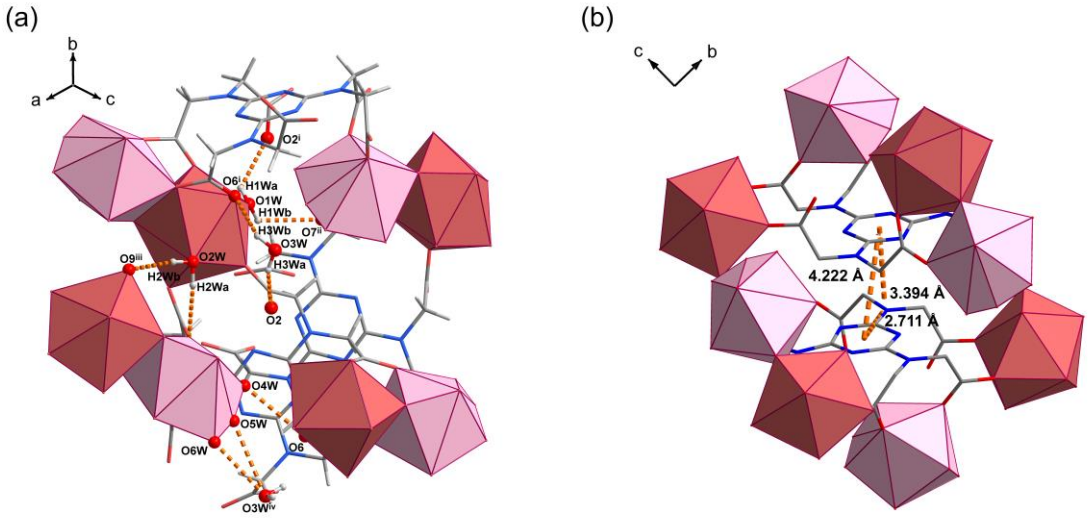

Figure 4. Views of (a) the hydrogen-bonding and (b) the π–π interactions in **I**

4.2 Topology

Topology of the three-dimensional framework of **I** was analyzed using TOPOS software.[19] If the dimeric {Eu_2O_{15}} motif and the $TTHA^{6-}$ are considered as nodes, the frameworks of **I** can be simplified to a uninodal four-connected **crb** net with a point symbol of {4.6^5} (Fig. 5),[20] which is dissimilar to the **pts** net of the porous [$Eu_2(TTHA)(H_2O)_4$]·$9H_2O$ framework.[5]

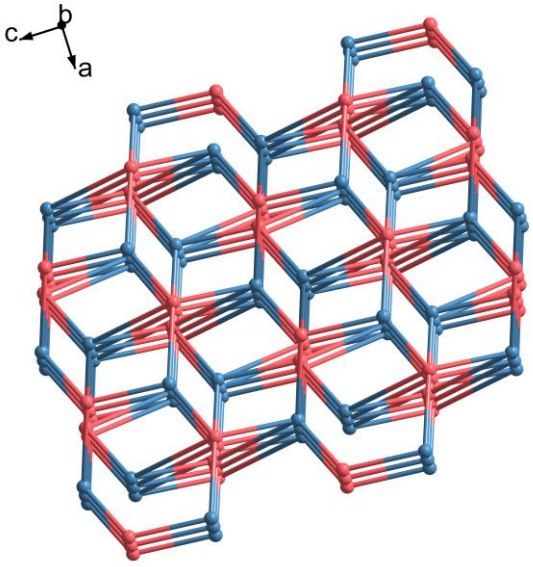

Figure 5. Topological representation of the four-connected **crb** net of **I**

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PART III
Output

Manuscript for Acta Crystallographica Section E: Crystallographic Communications

(*In preparation*)

Non-porous three-dimensional of $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$

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Abstract

A new lanthanide coordination polymer of 1,3,5-triazine-2,4,6-triamine hexaacetate ($TTHA^{6-}$), *i.e.* $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$ (**I**), were obtained as a contaminated phase of the microporous $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Zhu *et al.*, 2009). The structure of **I** crystallizes in the monoclinic $P2_1/n$ space group and exhibits a non-porous three-dimensional structure built up from the edge-sharing $\{Eu_2O_{15}\}$ dimer and $TTHA^{6-}$ linker. The framework can be simplified to a uninodal four-connected **crb** net with a point symbol of $\{4.6^5\}$.

Keywords: coordination polymer; lanthanide; triazine; TTHA, crystal structure

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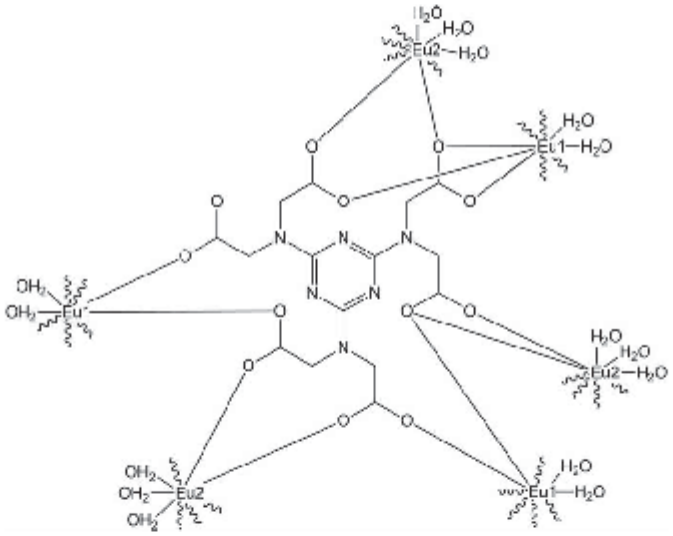

1. Chemical context

Interest in coordination polymers of lanthanides (LnCPs) particularly those with multi-dimensional frameworks has been continually growing, owing to their fascinating framework architectures and unique properties. A wide variety of potential functions, *e.g.* gas storage, sensing, catalysis and proton conductivity, has been reported (Roy *et al.*, 2014; Jiao *et al.*, 2019). To fabricate new multi-dimensional LnCPs, the use of polypodal ligands is a common strategy (Lin *et al.*, 2014). Here, 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA) was employed due to its availability of as many as six flexible $(CH_2COOH)_2$ arms and also its capability to promote supramolecular assembly *via* hydrogen bonding and π-π stacking interactions. Based on a survey of the Cambridge Structural Database (version 5.41, Nov 2019; Groom *et al.*, 2016), there are less than twenty LnCPs fabricated using H_6TTHA as a ligand (Zhu *et al.*, 2009; Surinwong *et al.*, 2013;

H3a	0.2679 (5)	0.4632 (3)	0.5467 (3)	0.0268 (13)*		
H3b	0.1562 (5)	0.5135 (3)	0.4948 (3)	0.0268 (13)*		
O3W	0.0396 (4)	0.5107 (4)	0.1402 (3)	0.0595 (13)		
H3Wa	0.107 (4)	0.480 (5)	0.158 (4)	0.089 (2)*		
H3Wb	0.073 (6)	0.545 (4)	0.102 (4)	0.089 (2)*		
C14	0.5601 (5)	0.3160 (3)	0.4619 (3)	0.0208 (11)		
C13	0.6336 (5)	0.4083 (3)	0.3597 (3)	0.0230 (11)		
C6	0.4558 (5)	0.2069 (4)	0.5539 (3)	0.0243 (11)		
H6a	0.4786 (5)	0.1513 (4)	0.5821 (3)	0.0291 (14)*		
H6b	0.4346 (5)	0.2504 (4)	0.5978 (3)	0.0291 (14)*		
C10	0.8537 (5)	0.3780 (3)	0.2965 (3)	0.0268 (12)		
H10a	0.9133 (5)	0.4034 (3)	0.2534 (3)	0.0321 (15)*		
H10b	0.8996 (5)	0.3829 (3)	0.3512 (3)	0.0321 (15)*		
O6W	0.5054 (7)	0.1195 (5)	0.2188 (4)	0.058 (3)	0.813 (18)	
C12	0.7056 (5)	0.5047 (3)	0.2422 (3)	0.0259 (12)		
H12a	0.6733 (5)	0.5550 (3)	0.2756 (3)	0.0311 (14)*		
H12b	0.7922 (5)	0.5217 (3)	0.2173 (3)	0.0311 (14)*		
O4W	0.4380 (6)	0.2923 (4)	0.2784 (3)	0.052 (2)	0.808 (12)	
O5W	0.4666 (14)	0.1886 (16)	0.2587 (11)	0.087 (10)	0.38 (2)	
H2Wb	0.369 (8)	0.511 (5)	0.001 (5)	0.09 (3)*		

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.01904 (15)	0.02013 (15)	0.02250 (16)	−0.00103 (10)	−0.00126 (11)	0.00239 (10)
Eu2	0.01851 (15)	0.02344 (16)	0.02425 (16)	0.00033 (10)	−0.00295 (11)	0.00003 (11)
O8	0.0137 (18)	0.031 (2)	0.029 (2)	0.0041 (15)	−0.0024 (14)	−0.0020 (16)
O2W	0.043 (3)	0.031 (2)	0.039 (3)	0.0042 (18)	−0.008 (2)	−0.004 (2)
O1	0.045 (2)	0.030 (2)	0.035 (2)	−0.0033 (18)	0.0055 (19)	0.0099 (18)
O6	0.024 (2)	0.036 (2)	0.026 (2)	0.0014 (16)	0.0001 (16)	−0.0091 (17)
O7	0.022 (2)	0.042 (2)	0.023 (2)	0.0017 (16)	0.0008 (16)	−0.0056 (17)
O5	0.0170 (19)	0.030 (2)	0.033 (2)	0.0022 (15)	0.0027 (15)	−0.0006 (17)
O11	0.028 (2)	0.040 (2)	0.037 (2)	0.0035 (17)	−0.0088 (19)	0.0011 (18)
O4	0.039 (2)	0.020 (2)	0.032 (2)	0.0009 (16)	−0.0099 (18)	−0.0064 (17)
O3	0.039 (2)	0.026 (2)	0.039 (2)	−0.0049 (17)	0.0118 (18)	0.0013 (18)
O10	0.032 (2)	0.026 (2)	0.036 (2)	−0.0004 (16)	−0.0075 (17)	0.0036 (18)
N1	0.024 (2)	0.020 (2)	0.025 (2)	0.0070 (18)	0.0023 (18)	0.0051 (18)
O9	0.036 (2)	0.030 (2)	0.041 (2)	0.0021 (17)	−0.0080 (18)	0.0104 (19)
O2	0.071 (3)	0.032 (2)	0.037 (2)	−0.017 (2)	−0.005 (2)	0.0023 (19)
N3	0.010 (2)	0.024 (2)	0.029 (2)	−0.0024 (17)	−0.0006 (17)	0.0053 (19)
N6	0.020 (2)	0.028 (2)	0.030 (3)	0.0008 (18)	0.0015 (19)	0.0065 (19)
N4	0.021 (2)	0.022 (2)	0.021 (2)	0.0023 (18)	−0.0030 (17)	0.0020 (19)
O12	0.053 (3)	0.037 (3)	0.061 (3)	0.012 (2)	−0.032 (2)	−0.001 (2)
N2	0.020 (2)	0.028 (2)	0.027 (2)	0.0016 (18)	0.0004 (18)	0.0063 (19)
C5	0.019 (3)	0.019 (3)	0.025 (3)	0.001 (2)	−0.003 (2)	0.000 (2)
N5	0.027 (2)	0.023 (2)	0.026 (2)	0.0044 (19)	0.0021 (19)	0.0009 (19)
C7	0.020 (3)	0.012 (2)	0.024 (3)	0.000 (2)	−0.002 (2)	0.006 (2)
C8	0.017 (3)	0.019 (3)	0.031 (3)	0.001 (2)	−0.004 (2)	0.001 (2)

H3a	0.2679 (5)	0.4632 (3)	0.5467 (3)	0.0268 (13)*		
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H12a	0.6733 (5)	0.5550 (3)	0.2756 (3)	0.0311 (14)*		
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O4W	0.4380 (6)	0.2923 (4)	0.2784 (3)	0.052 (2)	0.808 (12)	
O5W	0.4666 (14)	0.1886 (16)	0.2587 (11)	0.087 (10)	0.38 (2)	
H2Wb	0.369 (8)	0.511 (5)	0.001 (5)	0.09 (3)*		

Atomic displacement parameters (Å²)

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O2W	0.043 (3)	0.031 (2)	0.039 (3)	0.0042 (18)	−0.008 (2)	−0.004 (2)
O1	0.045 (2)	0.030 (2)	0.035 (2)	−0.0033 (18)	0.0055 (19)	0.0099 (18)
O6	0.024 (2)	0.036 (2)	0.026 (2)	0.0014 (16)	0.0001 (16)	−0.0091 (17)
O7	0.022 (2)	0.042 (2)	0.023 (2)	0.0017 (16)	0.0008 (16)	−0.0056 (17)
O5	0.0170 (19)	0.030 (2)	0.033 (2)	0.0022 (15)	0.0027 (15)	−0.0006 (17)
O11	0.028 (2)	0.040 (2)	0.037 (2)	0.0035 (17)	−0.0088 (19)	0.0011 (18)
O4	0.039 (2)	0.020 (2)	0.032 (2)	0.0009 (16)	−0.0099 (18)	−0.0064 (17)
O3	0.039 (2)	0.026 (2)	0.039 (2)	−0.0049 (17)	0.0118 (18)	0.0013 (18)
O10	0.032 (2)	0.026 (2)	0.036 (2)	−0.0004 (16)	−0.0075 (17)	0.0036 (18)
N1	0.024 (2)	0.020 (2)	0.025 (2)	0.0070 (18)	0.0023 (18)	0.0051 (18)
O9	0.036 (2)	0.030 (2)	0.041 (2)	0.0021 (17)	−0.0080 (18)	0.0104 (19)
O2	0.071 (3)	0.032 (2)	0.037 (2)	−0.017 (2)	−0.005 (2)	0.0023 (19)
N3	0.010 (2)	0.024 (2)	0.029 (2)	−0.0024 (17)	−0.0006 (17)	0.0053 (19)
N6	0.020 (2)	0.028 (2)	0.030 (3)	0.0008 (18)	0.0015 (19)	0.0065 (19)
N4	0.021 (2)	0.022 (2)	0.021 (2)	0.0023 (18)	−0.0030 (17)	0.0020 (19)
O12	0.053 (3)	0.037 (3)	0.061 (3)	0.012 (2)	−0.032 (2)	−0.001 (2)
N2	0.020 (2)	0.028 (2)	0.027 (2)	0.0016 (18)	0.0004 (18)	0.0063 (19)
C5	0.019 (3)	0.019 (3)	0.025 (3)	0.001 (2)	−0.003 (2)	0.000 (2)
N5	0.027 (2)	0.023 (2)	0.026 (2)	0.0044 (19)	0.0021 (19)	0.0009 (19)
C7	0.020 (3)	0.012 (2)	0.024 (3)	0.000 (2)	−0.002 (2)	0.006 (2)
C8	0.017 (3)	0.019 (3)	0.031 (3)	0.001 (2)	−0.004 (2)	0.001 (2)

Non-porous three-dimensional of $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$

Weerinradah Tapala,[a]* Pimchanok Tapangpan[b] and Apinpus Rujiwatra[b]

[a]Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand, and [b]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

Correspondence email: weerinradah@mju.ac.th

Abstract

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Keywords: coordination polymer; lanthanide; triazine; TTHA, crystal structure

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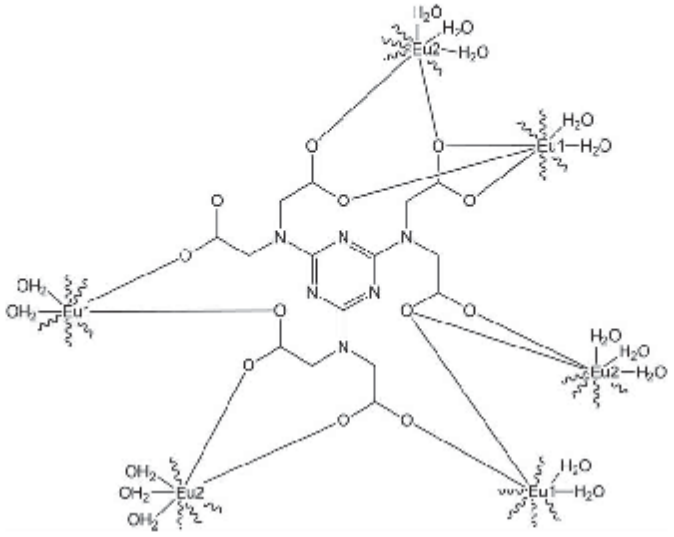

1. Chemical context

Interest in coordination polymers of lanthanides (LnCPs) particularly those with multi-dimensional frameworks has been continually growing, owing to their fascinating framework architectures and unique properties. A wide variety of potential functions, *e.g.* gas storage, sensing, catalysis and proton conductivity, has been reported (Roy *et al.*, 2014; Jiao *et al.*, 2019). To fabricate new multi-dimensional LnCPs, the use of polypodal ligands is a common strategy (Lin *et al.*, 2014). Here, 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA) was employed due to its availability of as many as six flexible $(CH_2COOH)_2$ arms and also its capability to promote supramolecular assembly *via* hydrogen bonding and π-π stacking interactions. Based on a survey of the Cambridge Structural Database (version 5.41, Nov 2019; Groom *et al.*, 2016), there are less than twenty LnCPs fabricated using H_6TTHA as a ligand (Zhu *et al.*, 2009; Surinwong *et al.*, 2013;

Mao *et al.*, 2013; Zhang *et al.*, 2014; Yotnoi *et al.*, 2015; Feng *et al.*, 2019). With the use of H_6TTHA, a new $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$ ($TTHA^{6-}$ = 1,3,5-triazine-2,4,6-triamine hexaacetate) (**I**) was synthesized as a contaminated phase of $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Zhu *et al.*, 2009). Single crystal structure, framework architecture and topology as well as the weak interactions analysis of **I** are reported herein.

2. Structural commentary

Crystal structure of **I** crystallizes in the monoclinic space group $P2_1/n$. Its asymmetric unit contains forty non-hydrogen atoms, including two crystallographically unique Eu^{III} ions, one fully deprotonated $TTHA^{6-}$, four coordinated water molecules and one crystallizing water molecule (Fig. 1). Eu1 adopts a ninefold coordination of a distorted tricapped trigonal prismatic geometry, *i.e.* *TPRS*-$\{Eu1O_9\}$, which is delineated by seven O atoms from three $TTHA^{6-}$ (O1, O4, O5, O6, O8, O9 and O12) and two O atoms from the coordinated water molecules (O1W and O2W). Eu2 is, on the other hand, eightfold coordinated to eight O atoms from three $TTHA^{6-}$ (O3, O5, O7, O8, O10 and O11) and two O atoms of the coordinated water molecules, *i.e.* $\{Eu2O_8\}$. The coordination geometry about the Eu2 is however poorly defined because of the two water molecules disorder over three crystallographic sites with approximate occupancies of 0.81 (O4W), 0.38 (O5W) and 0.81 (O6W). The Eu—O and Eu—OW distances are in the ranges of 2.2567 (1) − 2.6436 (1) and 2.2990 (0) − 2.5985 (0) Å, respectively. These distances are consistent with the values reported for the other LnCPs of H_6TTHA (Zhu *et al.*, 2009; Surinwong *et al.*, 2013; Mao *et al.*, 2013; Zhang *et al.*, 2014; Yotnoi *et al.*, 2015; Feng *et al.*, 2019).

The ninefold $\{Eu1O_9\}$ and the eightfold $\{Eu2O_8\}$ units are bridged by O5 and O8 of the O5–C5–O6 and O7–C7–O8, respectively, through the μ_2-η^1:η^2 coordination mode to form an edge-sharing $\{Eu_2O_{15}\}$ dimer (Fig. 2). The distance between Eu1 and Eu2 in the same dimer is 4.1129 (1) Å. The three-dimensional framework of **I** can be regarded as being constructed using this $\{Eu_2O_{15}\}$ dimeric motif each of which is connected to eleven neighboring equivalents through four $TTHA^{6-}$ linkers. Four different modes of coordination are exhibited (Fig. 3), *i.e.* the monodentate μ_1-η^0:η^1 (O1–C1–O2), the bridging μ_2-η^1:η^1 (*syn-syn*, O3–C4–O4 and O11–C9–O12), the bridging μ_2-η^1:η^1 (*syn-anti*, O9–C11–O10) and the chelating/bridging μ_2-η^1:η^2 (O5–C5–O6 and O7–C7–O8). The distances between centroids of the two neighboring dimers are varied from 5.8959 (1) to 13.0014 (2) Å. **I** and $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Zhu *et al.*, 2009) are closely similar in view of their crystal structures both of which are constructed from the dimeric motifs. The coordination about the Eu^{III}, modes of the coordination of $TTHA^{6-}$ as well as the crystallizing water content are however different. The dimer of **I** is made up of the ninefold $\{Eu1O_9\}$ and the eightfold $\{Eu2O_8\}$ units whereas the dimer of $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ is constructed solely from two ninefold $\{EuO_9\}$ units. Regarding modes of coordination, there are only three modes exhibited by $TTHA^{6-}$ in $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$, *i.e.* the chelating μ_1-η^1:η^1, the bridging μ_2-η^1:η^1 (*syn-syn*) and the chelating/bridging μ_2-η^1:η^2, the latter two of which are also found in **I**. The bridging μ_2-η^1:η^1 (*syn-anti*) and the monodentate μ_1-η^0:η^1 exhibited by $TTHA^{6-}$ in **I**, however, do not exist in $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$. According to the as-described variances, the framework of **I** is denser in nature occupying no void space compared to $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (*ca* 33% void), which may be accounted for the higher synthesis temperature of **I**. Similar phenomena has been reported (Sinchow *et al.*, 2019).

3. Supramolecular features

Hydrogen bonding interactions in the crystal structures of **I** were analyzed using *PLATON* (Spek, 2009) and evaluated on the basis of the distances between the possible donor (D) and acceptor (A) atoms if H atoms could not be located (Table 1). The offset parallel displaced π-π interaction between the triazine rings was measured and the centroid-centroid distance and angle are 4.422 Å and 52.2°, respectively (Fig. 4).

4. Topology

Topology of the three-dimensional framework of **I** was analyzed using TOPOS software (Blatov, 2004). If both the $\{Eu_2O_{15}\}$ dimer and the $TTHA^{6-}$ linker are considered as nodes, the frameworks of **I** can be simplified to a uninodal four-connected **crb** net with a point symbol of $\{4.6^5\}$ (Blatov *et al.*, 2014) (Fig. 5). This is different from the **pts** net of the porous $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ framework (Zhu *et al.*, 2009).

5. Database survey

There are 9 structures in the Cambridge Structural Database (CSD version 5.41 up to May 2020; Groom *et al.*, 2016) containing only $TTHA^{6-}$. They can be classified into 4 isostructural groups: $[Ln_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Ln = Sm, Eu, Tb, Gd and Dy) (Zhu *et al.*, 2009; Surinwong *et al.*, 2013), $[Yb_2(TTHA)]$ (Zhu *et al.*, 2009) $[Tb_2(TTHA)(H_2O)_2]\cdot 1.5H_2O$ (Mao *et al.*, 2013) and $[Tb_4(TTHA)_2(H_2O)_4]\cdot 7H_2O$ (Feng *et al.*, 2019). Including the secondary ligand and the heterometal cases results in 7 more structures of 4 isostructural groups: $[Ln_4(TTHA)_2(pzac)(H_3O)_2(H_2O)]\cdot 5H_2O$ (Ln = Pr and Nd), $[Sm_4(TTHA)_4(pzac)_{0.5}(H_3O)(H_2O)_{7.5}]\cdot 4H_2O$) and $[Ln_4(HTTHA)_2(SO_4)(H_2O)_4]\cdot 5H_2O$ (Ln = Pr and Nd, $pzac^{2-}$ = 2,5-dioxo-piperazine-1,4-diacetate) (Yotnoi *et al.*, 2015), and $[M_3Tb_2(TTHA)_2(H_2O)_6]\cdot 10H_2O$ (*M* = Zn and Co) (Zhang *et al.*, 2014).

6. Synthesis and crystallization

The H_6TTHA was synthesized following the method described in the literature (Karuehanon *et al.*, 2012). The colorless block crystals of **I** were obtained as a contaminated phase of the reaction between H_6TTHA (0.142 g, 0.300 mmol) and $Eu(NO_3)_3\cdot 5H_2O$ (0.202 g, 0.600 mmol) in 10.00 ml of deionized water under an autogenous pressure generated at 180 °C for 2 days. The reaction was carried out in a 23 ml Teflon-lined autoclave. The main phase of the reaction was notably the previously reported $[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O$ (Zhu *et al.*, 2009).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The disorder of the two water molecules over three crystallographic sites could be clearly seen in the electron-density map and was refined using the SUMP command providing occupancies of 0.81 (O4W), 0.38 (O5W) and 0.81 (O6W).

fig1.tif

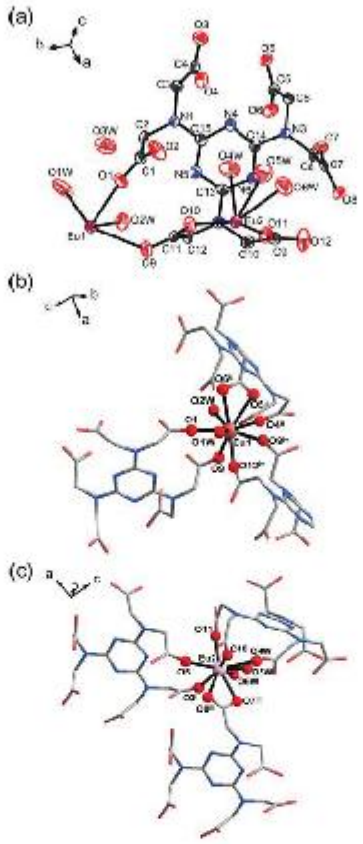

Figure 1

[Views of (*a*) an extended asymmetric unit of **I** drawn using 50% probability ellipsoids and the coordination environments about (*b*) Eu1 and (*c*) Eu2. (Symmetry codes: (i) $1/2 + x, 1/2 - y, -1/2 + z$; (ii) $1/2 - x, 1/2 + y, 1/2 - z$; (iii) $-1/2 + x, 1/2 - y, -1/2 + z$; (iv) $1.5 - x, 0.5 + y, 0.5 - z$)]

fig2.tif

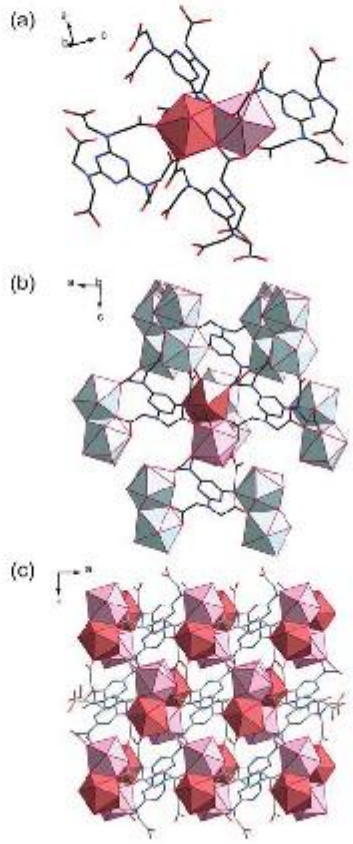

Figure 2
[Views of (*a*) an edge-sharing of {Eu1O_9} and {Eu2O_8} units, (*b*) coordination environment of the dimer and (*c*) the three-dimensional framework of **I**]

fig3.tif

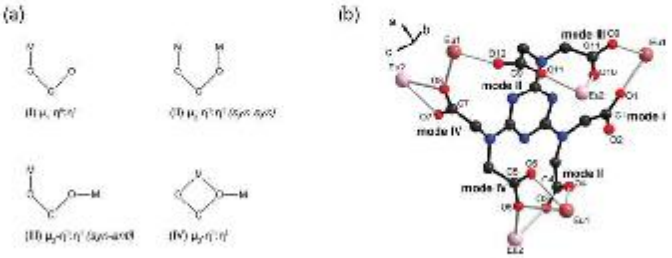

Figure 3

[Views of (*a*) coordination modes at each –COO⁻ pendant, and (*b*) spatial arrangement of $TTHA^{6-}$ in **I**]

fig4.tif

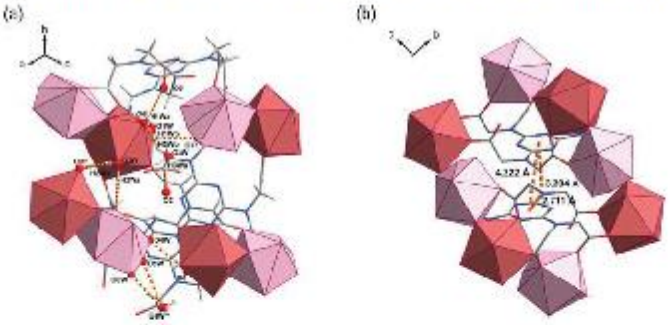

Figure 4

[Views of (*a*) the hydrogen-bonding interactions and (*b*) the Π–Π interactions in **I**]

fig5.tif

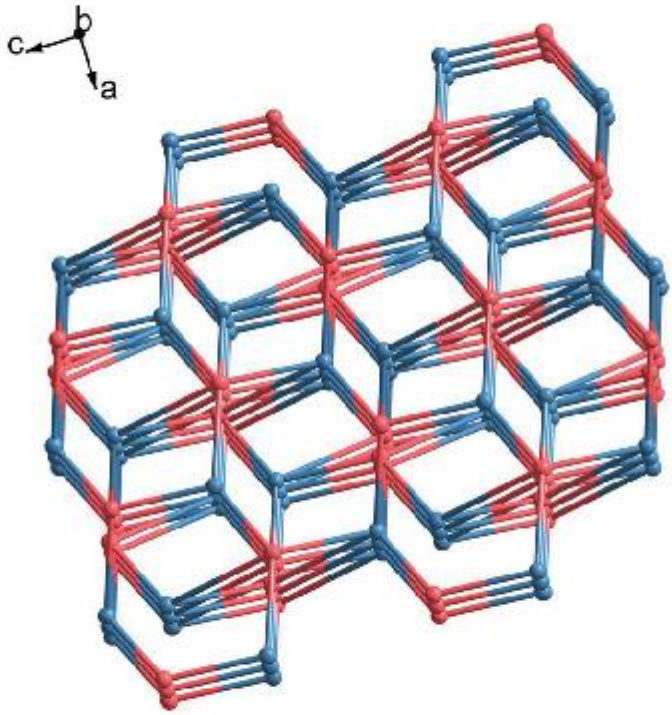

Figure 5
[Topological representation of the four-connected **crb** net of **I**]

Table 1
Experimental details

Crystal data	
Chemical formula	$C_{15}H_{16}Eu_2N_6O_{16}\cdot H_2O$
M_r	858.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	9.8332 (2), 14.9924 (3), 15.6429 (4)
β (°)	89.914 (2)
V (Å^3)	2306.12 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.49
Crystal size (mm)	0.22 × 0.08 × 0.05

Data collection	
Diffractometer	SuperNova, Single source at offset/far, HyPix3000
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.058, 0.082
No. of measured, independent and observed [$I \geq 2u(I)$] reflections	15065, 4578, 3930
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.077, 1.04
No. of reflections	4578
No. of parameters	380
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.35, −1.41

Computer programs: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018), ShelXT (Sheldrick, 2015), olex2.refine 1.3 (Bourhis *et al.*, 2015), Olex2 1.3 (Dolomanov *et al.*, 2009).

Table 2

Hydrogen-bond geometry (Å, º)

Symmetry codes: (i) 0.5-x, 0.5+y, 0.5-z; (ii) 1-x, 1-y, 1-z; (iii) 1-x, 1-y, -z; (iv) 0.5-x, -0.5+y, 0.5-z.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1Wa···O2^{i}	0.87 (3)	2.20 (3)	2.20 (3)	126 (5)
O1W—H1Wb···O7^{ii}	0.87 (3)	2.38 (4)	2.831 (6)	113 (4)
O2W—H2Wb···O9^{iii}	0.80 (8)	2.16 (8)	2.927 (6)	160 (8)
O2W—H2Wa···O10	0.882 (6)	2.356 (6)	3.184 (6)	156.3 (5)
O3W—H3Wa···O2	0.85 (5)	2.05 (5)	2.820 (6)	149 (6)
O3W—H3Wb···O6^{i}	0.85 (6)	2.20 (6)	2.935 (6)	144 (6)
O4W···O6	.	.	2.9555 (1)	.
O5W···O3W^{iv}	.	.	3.1021 (1)	.
O6W···O3W^{iv}	.	.	2.7786 (1)	.

Acknowledgements

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supporting information

Non-porous three-dimensional of $[Eu_2(TTHA)(H_2O)_4]\cdot H_2O$

Weerinradah Tapala,* Pimchanok Tapangpan and Apinpus Rujiwatra

Computing details

Data collection: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: olex2.refine 1.3 (Bourhis *et al.*, 2015); molecular graphics: Olex2 1.3 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.3 (Dolomanov *et al.*, 2009).

(I)

Crystal data

$C_{15}H_{16}Eu_2N_6O_{16}\cdot H_2O$	$F(000) = 1649.554$
$M_r = 858.27$	$D_x = 2.472$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc (x-z,y,z)	Cell parameters from 9673 reflections
$a = 9.8332$ (2) Å	$\theta = 1.9$–$27.4°$
$b = 14.9924$ (3) Å	$\mu = 5.49$ mm^{-1}
$c = 15.6429$ (4) Å	$T = 293$ K
$\beta = 89.914$ (2)°	Block, clear light colourless
$V = 2306.12$ (9) Å^3	0.22 × 0.08 × 0.05 mm
$Z = 4$	

Data collection

SuperNova, Single source at offset/far, HyPix3000 diffractometer	Absorption correction: multi-scan *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
ω scans	$T_{min} = 0.058$, $T_{max} = 0.082$
	15065 measured reflections
	4578 independent reflections
	3930 reflections with $I \geq 2u(I)$
	$R_{int} = 0.046$
	$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
	$h = -12 \rightarrow 12$
	$k = -18 \rightarrow 18$
	$l = -19 \rightarrow 20$

Refinement

Refinement on F^2	$wR(F^2) = 0.077$
Least-squares matrix: full	$S = 1.04$
$R[F^2 > 2\sigma(F^2)] = 0.034$	4578 reflections

380 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.003$
27 constraints	$\Delta\rho_{max} = 1.35$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{min} = -1.41$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Eu1	0.41159 (2)	0.671969 (16)	0.111938 (16)	0.02055 (9)	
Eu2	0.55377 (2)	0.263665 (17)	0.142748 (16)	0.02206 (9)	
O8	0.9318 (3)	0.1872 (2)	0.5074 (2)	0.0246 (8)	
O2W	0.3349 (4)	0.5213 (3)	0.0456 (3)	0.0375 (10)	
H2Wa	0.3782 (4)	0.4783 (3)	0.0728 (3)	0.0563 (15)*	
O1	0.3299 (4)	0.5862 (2)	0.2209 (2)	0.0365 (10)	
O6	0.3399 (4)	0.1785 (2)	0.4199 (2)	0.0291 (9)	
O7	0.8067 (4)	0.2406 (2)	0.6105 (2)	0.0289 (9)	
O5	0.2150 (3)	0.1913 (2)	0.5359 (2)	0.0268 (8)	
O11	0.7445 (4)	0.2587 (2)	0.2227 (2)	0.0349 (10)	
O4	0.1269 (4)	0.3311 (2)	0.4245 (2)	0.0306 (9)	
O3	0.0711 (4)	0.3631 (2)	0.5591 (2)	0.0347 (9)	
O10	0.5464 (4)	0.4153 (2)	0.1613 (2)	0.0315 (9)	
N1	0.3151 (4)	0.4793 (3)	0.4252 (3)	0.0230 (9)	
O9	0.5883 (4)	0.5538 (2)	0.1203 (2)	0.0359 (9)	
O2	0.2458 (4)	0.4529 (3)	0.2524 (2)	0.0467 (11)	
N3	0.5728 (4)	0.2376 (3)	0.5053 (3)	0.0211 (9)	
N6	0.6639 (4)	0.3384 (3)	0.4100 (3)	0.0257 (10)	
N4	0.4449 (4)	0.3613 (3)	0.4743 (2)	0.0212 (9)	
O12	0.9072 (4)	0.2251 (3)	0.3117 (3)	0.0505 (12)	
N2	0.7286 (4)	0.4307 (3)	0.2998 (3)	0.0251 (10)	
C5	0.3313 (5)	0.1927 (3)	0.4983 (3)	0.0213 (11)	
N5	0.5218 (4)	0.4584 (3)	0.3614 (3)	0.0252 (10)	
C7	0.8146 (5)	0.2064 (3)	0.5381 (3)	0.0186 (10)	
C8	0.6891 (5)	0.1807 (3)	0.4881 (3)	0.0224 (11)	
H8a	0.6652 (5)	0.1196 (3)	0.5019 (3)	0.0268 (14)*	
H8b	0.7100 (5)	0.1832 (3)	0.4276 (3)	0.0268 (14)*	
C2	0.3006 (5)	0.5530 (3)	0.3667 (3)	0.0261 (12)	
H2a	0.2191 (5)	0.5859 (3)	0.3818 (3)	0.0313 (14)*	
H2b	0.3774 (5)	0.5929 (3)	0.3741 (3)	0.0313 (14)*	
C15	0.4311 (5)	0.4316 (3)	0.4214 (3)	0.0221 (11)	
O1W	0.3275 (6)	0.7731 (3)	0.2298 (3)	0.082 (2)	
H1Wa	0.361 (6)	0.8263 (12)	0.223 (3)	0.123 (3)*	
H1Wb	0.360 (6)	0.757 (3)	0.2789 (7)	0.123 (3)*	
C1	0.2920 (5)	0.5273 (3)	0.2735 (3)	0.0271 (12)	
C11	0.6057 (5)	0.4888 (3)	0.1699 (3)	0.0225 (11)	
C4	0.1337 (5)	0.3780 (3)	0.4894 (4)	0.0262 (12)	
C9	0.8324 (5)	0.2806 (4)	0.2766 (3)	0.0278 (12)	
C3	0.2184 (5)	0.4633 (3)	0.4931 (3)	0.0223 (11)	

H3a	0.2679 (5)	0.4632 (3)	0.5467 (3)	0.0268 (13)*		
H3b	0.1562 (5)	0.5135 (3)	0.4948 (3)	0.0268 (13)*		
O3W	0.0396 (4)	0.5107 (4)	0.1402 (3)	0.0595 (13)		
H3Wa	0.107 (4)	0.480 (5)	0.158 (4)	0.089 (2)*		
H3Wb	0.073 (6)	0.545 (4)	0.102 (4)	0.089 (2)*		
C14	0.5601 (5)	0.3160 (3)	0.4619 (3)	0.0208 (11)		
C13	0.6336 (5)	0.4083 (3)	0.3597 (3)	0.0230 (11)		
C6	0.4558 (5)	0.2069 (4)	0.5539 (3)	0.0243 (11)		
H6a	0.4786 (5)	0.1513 (4)	0.5821 (3)	0.0291 (14)*		
H6b	0.4346 (5)	0.2504 (4)	0.5978 (3)	0.0291 (14)*		
C10	0.8537 (5)	0.3780 (3)	0.2965 (3)	0.0268 (12)		
H10a	0.9133 (5)	0.4034 (3)	0.2534 (3)	0.0321 (15)*		
H10b	0.8996 (5)	0.3829 (3)	0.3512 (3)	0.0321 (15)*		
O6W	0.5054 (7)	0.1195 (5)	0.2188 (4)	0.058 (3)	0.813 (18)	
C12	0.7056 (5)	0.5047 (3)	0.2422 (3)	0.0259 (12)		
H12a	0.6733 (5)	0.5550 (3)	0.2756 (3)	0.0311 (14)*		
H12b	0.7922 (5)	0.5217 (3)	0.2173 (3)	0.0311 (14)*		
O4W	0.4380 (6)	0.2923 (4)	0.2784 (3)	0.052 (2)	0.808 (12)	
O5W	0.4666 (14)	0.1886 (16)	0.2587 (11)	0.087 (10)	0.38 (2)	
H2Wb	0.369 (8)	0.511 (5)	0.001 (5)	0.09 (3)*		

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.01904 (15)	0.02013 (15)	0.02250 (16)	−0.00103 (10)	−0.00126 (11)	0.00239 (10)
Eu2	0.01851 (15)	0.02344 (16)	0.02425 (16)	0.00033 (10)	−0.00295 (11)	0.00003 (11)
O8	0.0137 (18)	0.031 (2)	0.029 (2)	0.0041 (15)	−0.0024 (14)	−0.0020 (16)
O2W	0.043 (3)	0.031 (2)	0.039 (3)	0.0042 (18)	−0.008 (2)	−0.004 (2)
O1	0.045 (2)	0.030 (2)	0.035 (2)	−0.0033 (18)	0.0055 (19)	0.0099 (18)
O6	0.024 (2)	0.036 (2)	0.026 (2)	0.0014 (16)	0.0001 (16)	−0.0091 (17)
O7	0.022 (2)	0.042 (2)	0.023 (2)	0.0017 (16)	0.0008 (16)	−0.0056 (17)
O5	0.0170 (19)	0.030 (2)	0.033 (2)	0.0022 (15)	0.0027 (15)	−0.0006 (17)
O11	0.028 (2)	0.040 (2)	0.037 (2)	0.0035 (17)	−0.0088 (19)	0.0011 (18)
O4	0.039 (2)	0.020 (2)	0.032 (2)	0.0009 (16)	−0.0099 (18)	−0.0064 (17)
O3	0.039 (2)	0.026 (2)	0.039 (2)	−0.0049 (17)	0.0118 (18)	0.0013 (18)
O10	0.032 (2)	0.026 (2)	0.036 (2)	−0.0004 (16)	−0.0075 (17)	0.0036 (18)
N1	0.024 (2)	0.020 (2)	0.025 (2)	0.0070 (18)	0.0023 (18)	0.0051 (18)
O9	0.036 (2)	0.030 (2)	0.041 (2)	0.0021 (17)	−0.0080 (18)	0.0104 (19)
O2	0.071 (3)	0.032 (2)	0.037 (2)	−0.017 (2)	−0.005 (2)	0.0023 (19)
N3	0.010 (2)	0.024 (2)	0.029 (2)	−0.0024 (17)	−0.0006 (17)	0.0053 (19)
N6	0.020 (2)	0.028 (2)	0.030 (3)	0.0008 (18)	0.0015 (19)	0.0065 (19)
N4	0.021 (2)	0.022 (2)	0.021 (2)	0.0023 (18)	−0.0030 (17)	0.0020 (19)
O12	0.053 (3)	0.037 (3)	0.061 (3)	0.012 (2)	−0.032 (2)	−0.001 (2)
N2	0.020 (2)	0.028 (2)	0.027 (2)	0.0016 (18)	0.0004 (18)	0.0063 (19)
C5	0.019 (3)	0.019 (3)	0.025 (3)	0.001 (2)	−0.003 (2)	0.000 (2)
N5	0.027 (2)	0.023 (2)	0.026 (2)	0.0044 (19)	0.0021 (19)	0.0009 (19)
C7	0.020 (3)	0.012 (2)	0.024 (3)	0.000 (2)	−0.002 (2)	0.006 (2)
C8	0.017 (3)	0.019 (3)	0.031 (3)	0.001 (2)	−0.004 (2)	0.001 (2)

119	C2	0.025 (3)	0.020 (3)	0.034 (3)	0.007 (2)	0.001 (2)	0.002 (2)
120	C15	0.029 (3)	0.022 (3)	0.015 (3)	0.001 (2)	−0.005 (2)	0.000 (2)
121	O1W	0.163 (6)	0.034 (3)	0.050 (3)	−0.003 (3)	0.056 (4)	0.003 (2)
122	C1	0.028 (3)	0.024 (3)	0.030 (3)	−0.001 (2)	0.001 (2)	0.003 (3)
123	C11	0.024 (3)	0.020 (3)	0.024 (3)	0.006 (2)	0.004 (2)	0.001 (2)
124	C4	0.020 (3)	0.020 (3)	0.039 (3)	0.004 (2)	−0.002 (2)	0.003 (3)
125	C9	0.026 (3)	0.034 (3)	0.023 (3)	−0.001 (3)	−0.003 (2)	0.006 (3)
126	C3	0.026 (3)	0.019 (3)	0.022 (3)	0.000 (2)	0.002 (2)	−0.002 (2)
127	O3W	0.048 (3)	0.072 (4)	0.059 (3)	−0.017 (2)	0.002 (2)	0.015 (2)
128	C14	0.017 (3)	0.020 (3)	0.025 (3)	0.001 (2)	−0.004 (2)	−0.001 (2)
129	C13	0.022 (3)	0.025 (3)	0.022 (3)	−0.004 (2)	−0.001 (2)	0.001 (2)
130	C6	0.019 (3)	0.027 (3)	0.028 (3)	−0.002 (2)	−0.002 (2)	0.007 (2)
131	C10	0.018 (3)	0.034 (3)	0.028 (3)	0.002 (2)	−0.001 (2)	0.001 (2)
132	O6W	0.056 (4)	0.049 (5)	0.071 (5)	−0.007 (3)	0.002 (3)	0.016 (4)
133	C12	0.026 (3)	0.023 (3)	0.030 (3)	−0.002 (2)	−0.003 (2)	0.006 (2)
134	O4W	0.053 (4)	0.065 (5)	0.039 (3)	−0.011 (3)	0.001 (3)	−0.003 (3)
135	O5W	0.055 (10)	0.12 (2)	0.087 (13)	0.027 (9)	0.010 (8)	0.042 (14)

136 *Geometric parameters (Å, °)*

137	Eu1—O8^{i}	2.429 (3)	N3—C8	1.451 (6)
138	Eu1—O2W	2.599 (4)	N3—C14	1.363 (6)
139	Eu1—O1	2.280 (3)	N3—C6	1.453 (6)
140	Eu1—O6^{ii}	2.525 (4)	N6—C14	1.346 (6)
141	Eu1—O5^{ii}	2.644 (4)	N6—C13	1.344 (6)
142	Eu1—O4^{ii}	2.481 (3)	N4—C15	1.347 (6)
143	Eu1—O9	2.485 (4)	N4—C14	1.335 (6)
144	Eu1—O12^{i}	2.289 (4)	O12—C9	1.240 (6)
145	Eu1—C5^{ii}	2.965 (5)	N2—C13	1.365 (6)
146	Eu1—O1W	2.526 (4)	N2—C10	1.462 (6)
147	Eu2—O8^{iii}	2.543 (3)	N2—C12	1.448 (6)
148	Eu2—O7^{iii}	2.483 (4)	C5—C6	1.517 (7)
149	Eu2—O5^{iv}	2.399 (3)	N5—C15	1.354 (6)
150	Eu2—O11	2.257 (4)	N5—C13	1.332 (6)
151	Eu2—O3^{iv}	2.313 (3)	C7—C8	1.512 (7)
152	Eu2—O10	2.293 (4)	C8—H8a	0.9700
153	Eu2—C7^{iii}	2.902 (5)	C8—H8b	0.9700
154	Eu2—O6W	2.513 (6)	C2—H2a	0.9700
155	Eu2—O4W	2.445 (5)	C2—H2b	0.9700
156	Eu2—O5W	2.299 (14)	C2—C1	1.510 (7)
157	O8—C7	1.280 (5)	O1W—H1Wa	0.8698
158	O2W—H2Wa	0.8815	O1W—H1Wb	0.8705
159	O2W—H2Wb	0.79 (7)	C11—C12	1.517 (7)
160	O1—C1	1.263 (6)	C4—C3	1.528 (7)
161	O6—C5	1.248 (6)	C9—C10	1.509 (7)
162	O7—C7	1.245 (6)	C3—H3a	0.9700
163	O5—C5	1.286 (5)	C3—H3b	0.9700
164	O11—C9	1.253 (6)	O3W—H3Wa	0.8498

165	O4—C4	1.237 (6)	O3W—H3Wb	0.8504
166	O3—C4	1.272 (6)	C6—H6a	0.9700
167	O10—C11	1.254 (6)	C6—H6b	0.9700
168	N1—C2	1.443 (6)	C10—H10a	0.9700
169	N1—C15	1.347 (6)	C10—H10b	0.9700
170	N1—C3	1.445 (5)	C12—H12a	0.9700
171	O9—C11	1.258 (6)	C12—H12b	0.9700
172	O2—C1	1.250 (6)		
173				
174	O2W—Eu1—O8^{i}	87.65 (12)	C5—O6—Eu1^{vii}	97.8 (3)
175	O1—Eu1—O8^{i}	148.20 (12)	C7—O7—Eu2^{v}	96.6 (3)
176	O1—Eu1—O2W	72.91 (13)	Eu2^{viii}—O5—Eu1^{vii}	109.21 (12)
177	O6^{iii}—Eu1—O8^{i}	117.67 (11)	C5—O5—Eu1^{vii}	91.3 (3)
178	O6^{iii}—Eu1—O2W	70.73 (12)	C5—O5—Eu2^{viii}	154.2 (3)
179	O6^{iii}—Eu1—O1	79.94 (12)	C9—O11—Eu2	159.9 (4)
180	O5^{iii}—Eu1—O8^{i}	67.41 (11)	C4—O4—Eu1^{vii}	138.0 (3)
181	O5^{iii}—Eu1—O2W	66.98 (12)	C4—O3—Eu2^{viii}	131.6 (3)
182	O5^{iii}—Eu1—O1	123.37 (12)	C11—O10—Eu2	150.5 (3)
183	O5^{iii}—Eu1—O6^{ii}	50.26 (10)	C15—N1—C2	117.6 (4)
184	O4^{iii}—Eu1—O8^{i}	80.20 (11)	C3—N1—C2	121.8 (4)
185	O4^{iii}—Eu1—O2W	134.40 (13)	C3—N1—C15	120.1 (4)
186	O4^{iii}—Eu1—O1	131.29 (12)	C11—O9—Eu1	132.9 (3)
187	O4^{iii}—Eu1—O6^{ii}	76.57 (11)	C14—N3—C8	119.2 (4)
188	O4^{iii}—Eu1—O5^{ii}	67.76 (11)	C6—N3—C8	122.3 (4)
189	O9—Eu1—O8^{i}	70.43 (11)	C6—N3—C14	117.4 (4)
190	O9—Eu1—O2W	66.71 (12)	C13—N6—C14	112.3 (4)
191	O9—Eu1—O1	78.72 (12)	C14—N4—C15	113.3 (4)
192	O9—Eu1—O6^{iii}	136.32 (11)	C9—O12—Eu1^{vi}	158.1 (4)
193	O9—Eu1—O5^{ii}	117.03 (11)	C10—N2—C13	117.8 (4)
194	O9—Eu1—O4^{ii}	143.53 (12)	C12—N2—C13	120.6 (4)
195	O12^{i}—Eu1—O8^{i}	82.84 (14)	C12—N2—C10	121.6 (4)
196	O12^{i}—Eu1—O2W	137.50 (14)	O6—C5—Eu1^{vii}	57.5 (3)
197	O12^{i}—Eu1—O1	94.58 (15)	O5—C5—Eu1^{vii}	63.0 (3)
198	O12^{i}—Eu1—O6^{iii}	148.50 (14)	O5—C5—O6	120.3 (5)
199	O12^{i}—Eu1—O5^{iii}	141.80 (13)	C6—C5—Eu1^{viii}	177.9 (3)
200	O12^{i}—Eu1—O4^{iii}	84.52 (14)	C6—C5—O6	122.2 (4)
201	O12^{i}—Eu1—O9	71.07 (14)	C6—C5—O5	117.3 (4)
202	C5^{ii}—Eu1—O8^{i}	93.05 (12)	C13—N5—C15	112.9 (4)
203	C5^{ii}—Eu1—O2W	67.93 (13)	O8—C7—Eu2^{v}	61.1 (3)
204	C5^{ii}—Eu1—O1	102.17 (13)	O7—C7—Eu2^{v}	58.2 (2)
205	C5^{ii}—Eu1—O6^{iii}	24.64 (11)	O7—C7—O8	119.2 (4)
206	C5^{ii}—Eu1—O5^{iii}	25.69 (11)	C8—C7—Eu2^{v}	173.6 (3)
207	C5^{ii}—Eu1—O4^{iii}	69.05 (13)	C8—C7—O8	118.9 (4)
208	C5^{ii}—Eu1—O9	132.02 (13)	C8—C7—O7	121.7 (4)
209	C5^{ii}—Eu1—O12^{i}	153.56 (14)	C7—C8—N3	113.4 (4)
210	O1W—Eu1—O8^{i}	135.32 (13)	H8a—C8—N3	108.9 (2)
211	O1W—Eu1—O2W	135.94 (15)	H8a—C8—C7	108.9 (2)
212	O1W—Eu1—O1	71.24 (14)	H8b—C8—N3	108.9 (3)

213	O1W—Eu1—O6^{ii}	78.52 (17)	H8b—C8—C7	108.9 (3)
214	O1W—Eu1—O5^{ii}	114.73 (16)	H8b—C8—H8a	107.7
215	O1W—Eu1—O4^{ii}	62.63 (14)	H2a—C2—N1	108.5 (2)
216	O1W—Eu1—O9	128.17 (16)	H2b—C2—N1	108.5 (3)
217	O1W—Eu1—O12^{i}	70.41 (19)	H2b—C2—H2a	107.5
218	O1W—Eu1—C5^{iii}	95.65 (18)	C1—C2—N1	115.0 (4)
219	O7^{iii}—Eu2—O8^{iii}	51.35 (10)	C1—C2—H2a	108.5 (3)
220	O5^{iv}—Eu2—O8^{iii}	69.54 (11)	C1—C2—H2b	108.5 (3)
221	O5^{iv}—Eu2—O7^{iii}	120.75 (12)	N4—C15—N1	118.3 (4)
222	O11—Eu2—O8^{iii}	149.77 (12)	N5—C15—N1	115.5 (4)
223	O11—Eu2—O7^{iii}	157.82 (13)	N5—C15—N4	126.2 (4)
224	O11—Eu2—O5^{iv}	81.18 (13)	H1Wa—O1W—Eu1	109.6
225	O3^{iv}—Eu2—O8^{iii}	78.56 (12)	H1Wb—O1W—Eu1	110.6
226	O3^{iv}—Eu2—O7^{iii}	86.28 (12)	H1Wb—O1W—H1Wa	103.3
227	O3^{iv}—Eu2—O5^{iv}	77.80 (12)	O2—C1—O1	124.0 (5)
228	O3^{iv}—Eu2—O11	103.02 (13)	C2—C1—O1	115.7 (5)
229	O10—Eu2—O8^{iii}	78.66 (12)	C2—C1—O2	120.3 (5)
230	O10—Eu2—O7^{iii}	91.19 (12)	O9—C11—O10	123.4 (5)
231	O10—Eu2—O5^{iv}	80.21 (12)	C12—C11—O10	121.4 (4)
232	O10—Eu2—O11	89.37 (13)	C12—C11—O9	115.2 (4)
233	O10—Eu2—O3^{iv}	152.66 (13)	O3—C4—O4	125.3 (5)
234	C7^{iii}—Eu2—O8^{iii}	26.15 (11)	C3—C4—O4	122.6 (5)
235	C7^{iii}—Eu2—O7^{iii}	25.23 (11)	C3—C4—O3	112.1 (5)
236	C7^{iii}—Eu2—O5^{iv}	95.66 (13)	O12—C9—O11	122.2 (5)
237	C7^{iii}—Eu2—O11	172.92 (13)	C10—C9—O11	119.3 (5)
238	C7^{iii}—Eu2—O3^{iv}	82.37 (13)	C10—C9—O12	118.4 (5)
239	C7^{iii}—Eu2—O10	83.83 (13)	C4—C3—N1	117.9 (4)
240	O6W—Eu2—O8^{iii}	123.64 (16)	H3a—C3—N1	107.8 (3)
241	O6W—Eu2—O7^{iii}	83.65 (17)	H3a—C3—C4	107.8 (3)
242	O6W—Eu2—O5^{iv}	134.1 (2)	H3b—C3—N1	107.8 (2)
243	O6W—Eu2—O11	82.30 (16)	H3b—C3—C4	107.8 (3)
244	O6W—Eu2—O3^{iv}	64.8 (2)	H3b—C3—H3a	107.2
245	O6W—Eu2—O10	141.9 (2)	H3Wb—O3W—H3Wa	104.5
246	O6W—Eu2—C7^{iii}	104.30 (17)	N6—C14—N3	116.4 (4)
247	O4W—Eu2—O8^{iii}	116.89 (16)	N4—C14—N3	116.5 (4)
248	O4W—Eu2—O7^{iii}	74.15 (15)	N4—C14—N6	127.1 (5)
249	O4W—Eu2—O5^{iv}	149.52 (16)	N2—C13—N6	116.2 (4)
250	O4W—Eu2—O11	84.89 (16)	N5—C13—N6	127.7 (4)
251	O4W—Eu2—O3^{iv}	132.01 (16)	N5—C13—N2	116.1 (4)
252	O4W—Eu2—O10	72.63 (17)	C5—C6—N3	112.6 (4)
253	O4W—Eu2—C7^{iii}	94.93 (16)	H6a—C6—N3	109.1 (3)
254	O4W—Eu2—O6W	69.7 (3)	H6a—C6—C5	109.1 (3)
255	O5W—Eu2—O8^{iii}	128.5 (4)	H6b—C6—N3	109.1 (3)
256	O5W—Eu2—O7^{iii}	77.5 (4)	H6b—C6—C5	109.1 (3)
257	O5W—Eu2—O5^{iv}	158.8 (4)	H6b—C6—H6a	107.8
258	O5W—Eu2—O11	81.7 (4)	C9—C10—N2	114.4 (4)
259	O5W—Eu2—O3^{iv}	94.1 (7)	H10a—C10—N2	108.7 (3)
260	O5W—Eu2—O10	112.0 (6)	H10a—C10—C9	108.7 (2)

O5W—Eu2—C7^{iii}	102.6 (4)	H10b—C10—N2	108.7 (3)
O5W—Eu2—O6W	30.1 (5)	H10b—C10—C9	108.7 (3)
O5W—Eu2—O4W	39.5 (6)	H10b—C10—H10a	107.6
Eu2^{v}—O8—Eu1^{vi}	111.58 (12)	C11—C12—N2	116.4 (4)
C7—O8—Eu1^{vi}	151.4 (3)	H12a—C12—N2	108.2 (3)
C7—O8—Eu2^{v}	92.8 (3)	H12a—C12—C11	108.2 (3)
H2Wa—O2W—Eu1	107.5	H12b—C12—N2	108.2 (3)
H2Wb—O2W—Eu1	114 (6)	H12b—C12—C11	108.2 (3)
H2Wb—O2W—H2Wa	95 (6)	H12b—C12—H12a	107.3
C1—O1—Eu1	169.9 (3)		
Eu1^{vi}—O8—C7—Eu2^{v}	−149.3 (8)	Eu2^{viii}—O3—C4—C3	−131.1 (4)
Eu1^{vi}—O8—C7—O7	−146.4 (6)	Eu2—O10—C11—O9	121.6 (7)
Eu1^{vi}—O8—C7—C8	38.0 (6)	Eu2—O10—C11—C12	−58.0 (7)
Eu1—O1—C1—O2	−36 (2)	O8—C7—C8—N3	−153.3 (4)
Eu1—O1—C1—C2	146 (2)	O1—C1—C2—N1	−154.4 (4)
Eu1^{viii}—O6—C5—O5	6.0 (3)	O6—C5—C6—N3	23.3 (5)
Eu1^{viii}—O6—C5—C6	−177.5 (3)	O7—C7—C8—N3	31.2 (5)
Eu1^{viii}—O5—C5—O6	−5.7 (3)	O5—C5—C6—N3	−160.1 (4)
Eu1^{viii}—O5—C5—C6	177.7 (2)	O11—C9—C10—N2	39.0 (5)
Eu1^{viii}—O4—C4—O3	−29.5 (5)	O4—C4—C3—N1	−13.2 (6)
Eu1^{viii}—O4—C4—C3	151.9 (5)	O3—C4—C3—N1	168.1 (4)
Eu1—O9—C11—O10	82.5 (4)	O10—C11—C12—N2	0.3 (5)
Eu1—O9—C11—C12	−97.8 (4)	N1—C2—C1—O2	27.7 (5)
Eu1^{vi}—O12—C9—O11	164.1 (10)	N1—C15—N4—C14	176.4 (5)
Eu1^{vi}—O12—C9—C10	−12.6 (11)	N1—C15—N5—C13	−179.2 (4)
Eu1^{viii}—C5—O5—Eu2^{viii}	−143.4 (5)	O9—C11—C12—N2	−179.4 (4)
Eu2^{v}—O8—C7—O7	2.9 (3)	N3—C14—N6—C13	169.9 (4)
Eu2^{v}—O8—C7—C8	−172.7 (2)	N3—C14—N4—C15	−171.8 (4)
Eu2^{v}—O7—C7—O8	−2.9 (3)	N6—C14—N4—C15	6.9 (6)
Eu2^{v}—O7—C7—C8	172.5 (2)	N6—C13—N2—C10	−0.8 (5)
Eu2^{viii}—O5—C5—O6	−149.1 (7)	N6—C13—N2—C12	179.7 (4)
Eu2^{viii}—O5—C5—C6	34.2 (7)	N6—C13—N5—C15	−0.9 (6)
Eu2—O11—C9—O12	154.2 (10)	N4—C15—N5—C13	−1.5 (6)
Eu2—O11—C9—C10	−29.2 (10)	O12—C9—C10—N2	−144.3 (5)
Eu2^{viii}—O3—C4—O4	50.1 (5)	N2—C13—N5—C15	179.0 (4)

Symmetry codes: (i) −x+3/2, y+1/2, −z+1/2; (ii) −x+1/2, y+1/2, −z+1/2; (iii) x−1/2, −y+1/2, z−1/2; (iv) x+1/2, −y+1/2, z−1/2; (v) x+1/2, −y+1/2, z+1/2; (vi) −x+3/2, y−1/2, −z+1/2; (vii) −x+1/2, y−1/2, −z+1/2; (viii) x−1/2, −y+1/2, z+1/2.

Hydrogen-bond geometry (Å, °)

Symmetry codes: (i) 0.5-x, 0.5+y, 0.5-z; (ii) 1-x, 1-y, 1-z; (iii) 1-x, 1-y, -z; (iv) 0.5-x, -0.5+y, 0.5-z.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*Wa*···O2^{i}	0.87 (3)	2.20 (3)	2.20 (3)	126 (5)
O1*W*—H1*Wb*···O7^{ii}	0.87 (3)	2.38 (4)	2.831 (6)	113 (4)
O2*W*—H2*Wb*···O9^{iii}	0.80 (8)	2.16 (8)	2.927 (6)	160 (8)
O2*W*—H2*Wa*···O10	0.88 (1)	2.36 (1)	3.184 (6)	156 (1)
O3*W*—H3*Wa*···O2	0.85 (5)	2.05 (5)	2.820 (6)	149 (6)

O3*W*—H3*Wb*···O6	0.85 (6)	2.20 (6)	2.935 (6)	144 (6)
O4*W*···O6			2.9555 (1)	
O5*W*···O3*W*^{iv}			3.1021 (1)	
O6*W*···O3*W*^{v}			2.7786 (1)	

other supporting information

Crystallographic Information File. t0h0363.cif

Structure factors. t0h0363Isup2.hkl