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Article

Three-dimensional Samarium(III) Coordination Polymer With 1,2,4,5-Benzenetetracarboxylicylate Ligand and Ethylenediammonium Cation: Synthesis, Infrared Spectroscopy Characterization, Thermal Analyses, and Crystal Structure

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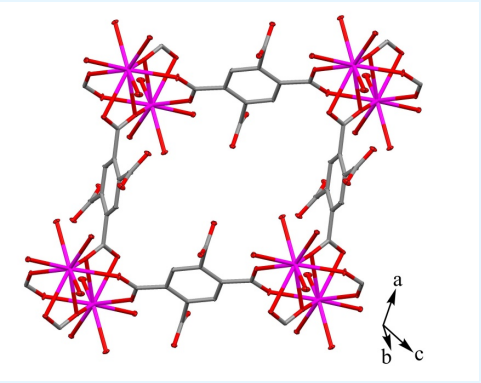
Abstract: A new three-dimensional samarium(III) coordination polymer, $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (**1**) ($BTEC^{4-}$ is 1,2,4,5-benzenetetracarboxylicylate and H_2en^{2+} is ethylenediammonium), was prepared from the reaction of $SmCl_3.6H_2O$ and $[H_2en]_2[BCT].2H_2O$ in water and in an ice bath. Suitable crystals of this complex for crystal structure determination were obtained by slow evaporation of the produced colorless solution at room temperature. Complex **1** was characterized by elemental analysis, FT-IR spectroscopy and single-crystal X-ray crystallography. The X-ray crystallography analysis shows that this compound is a three-dimensional polymer and the Sm(III) cation is nine-coordinated in a distorted tri-capped trigonal prismatic configuration by nine O atoms from four BTEC anions and four coordinated water molecules. Also, the thermal stability of **1** was studied by thermogravimetric and differential thermal analyses.

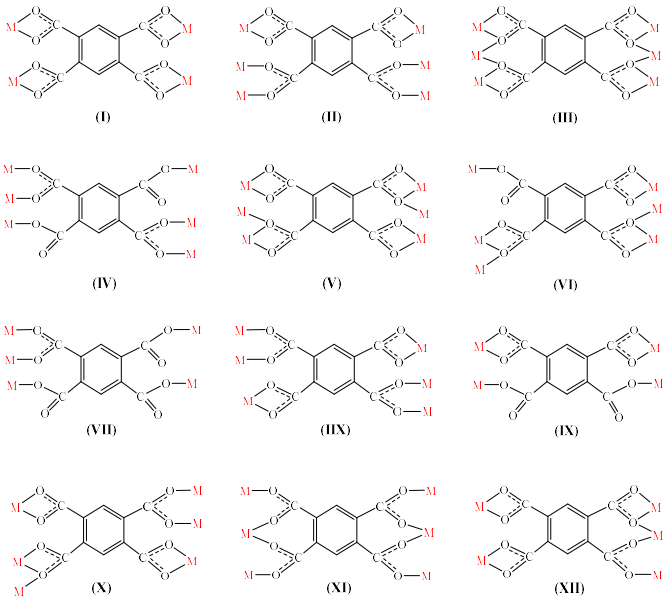


Keywords: Sm(III), 1,2,4,5-Benzenetetracarboxylicylate, Crystal structure, Thermal gravimetric, Differential thermal analyses

1. INTRODUCTION

In recent years the synthesis of one, two and three-dimensional lanthanide(III) coordination polymers have been of great interest due to their potential applications in magnetism, gas adsorption and gas storage, as luminescence materials, sensors, molecular recognition, ion exchange and catalyst.[1-8] Furthermore, lanthanide(III) carboxylate coordination polymers have attracted considerable attention due to their intriguing structures and properties.[9-16] Coordination polymers (CPs) are normally linked by coordinative bonds or some other weak chemical interactions. The automatic self-assemble is the main synthesis procedure of these compounds.[17-20] On the other hand, 1,2,4,5-benzenetetracarboxylicylate ($BTEC^{4-}$) is a good flexible multidentate ligand that is important in the domain of three-dimensional coordination polymers. This multidentate ligand with four carboxylate groups, which are placed in pairs side by side on the benzene ring, can bond through eight oxygen atoms to the lanthanide(III) ions in different directions (Scheme 1). The aromatic ring can stabilize the crystal structure via π-stacking interactions. These structural properties are important in the design of self-assembled coordination polymers, porous coordination polymers (PCPs) and metal-organic frameworks (MOFs). To date, numerous lanthanide(III) based coordination polymers involving this ligand have been synthesized and their crystal structure have been determined by X-ray crystallography.[21-28]

In recent years from the reaction of proton transfer ligand of $[H_2en]_2[BTEC].2H_2O$ with $Cu(NO_3)_2.3H_2O$, we prepared the complex $\{[Cu(\mu_4\text{-}BCT)(H_2en)].2.5H_2O\}_n$.[29,30] The crystal structure of this compound was determined by X-ray crystallography. Continuing these researches, we wish to report herein the synthesis and crystal structure of a new three-dimensional coordination polymer of $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (**1**). Structural studies on this complex were performed by elemental analysis, X-ray crystallography and FT-IR spectroscopic technique. Also, the thermal stability of complex **1** was studied by thermogravimetric and differential thermal analyses.



Scheme 1. The possible binding modes of $BTEC^{4-}$ to lanthanide(III) ions

2. EXPERIMENTAL

Materials and Physical Methods

All chemicals were purchased from Merck. Infrared spectrum (4000-300 cm^{-1}) of solid sample was taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. Thermal behavior was measured with a STA 503 Bähr apparatus. $[H_2en]_2[BTEC].2H_2O$ ligand was prepared according to a procedure described previously.[29]

The X-ray crystallography measurements for single crystal of $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (**1**) was made on a Bruker APEX II CCD area detector diffractometer at 298 K (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). The structure of this complex was solved by SHELX-97 and absorption correction was done using the SADABS program.[31] Some software including Bruker APEX II (data collection and cell refinement), Bruker SHELXTL (data reduction), and WinGX (publication material) were properly used.[32-35] The ORTEP and crystal packing diagram for title complex were drawn with the Mercury 2.4 program.[36]

Synthesis of $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (1)

A solution of $[H_2en]_2[BTEC].2H_2O$, (0.12 g, 0.29 mmol) in water (100 mL) was added to a solution of the $SmCl_3.6H_2O$ (0.11 g, 0.29 mmol) in water (50 mL) without stirring, in an ice bath. This solution was left to evaporate slowly at room temperature. After three days, block colorless crystals of the title compound were isolated (yield 0.12g, 76.92%; m.p. > 300 °C). FT-IR (KBr, cm^{-1}) 3430m, 3258br, 2986w, 1607s, 1563s, 1503m, 1413s, 1381s,1362m, 1280w, 1138m, 1106w, 1053w, 1011w, 882w, 841w, 818m, 775m, 721m, 676m, 589s, 523s, 441m, 372m. Anal. Calcd. for $C_{11}H_{19}NO_{14}Sm$ (%): C, 24.48; H, 3.52; N, 2.59; O, 41.51. Found: C, 24.39; H, 3.50; N, 2.57; O, 41.71.

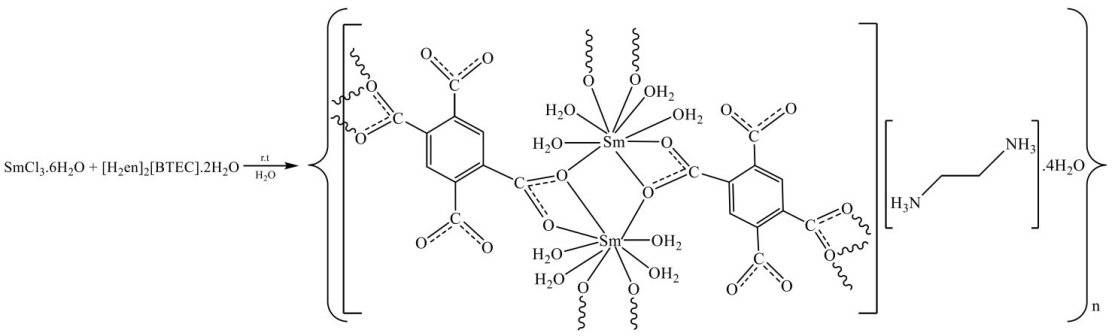
3. RESULTS AND DISCUSSION

Synthesis of $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (1)

Complex **1** was obtained from the reaction of one equivalent of $[H_2en]_2[BTEC].2H_2O$ with one equivalent of $SmCl_3.6H_2O$ in water, without stirring and in an ice bath. Suitable crystals of this complex were obtained for X-ray crystallography measurement by slow evaporation of aqueous solution at room temperature. The synthetic route of this complex is shown in Scheme 2.

Spectroscopic characterization of $\{[Sm(\mu_2\text{-}BTEC)(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (1)

FT-IR absorption bands of **1** are listed in the experimental section. In the infrared spectrum for this complex, the medium and weak absorption band at around 3430 and 2986 cm^{-1} are assigned to the N–H and C–H stretching vibrations, respectively for the ethylenediammonium. The broad absorption band present at around 3258 cm^{-1} is assigned to ν(O-H). The medium absorption bands observed in the range 1503-1280 cm^{-1} are assigned to ν(C=C) vibrations and the medium to strong absorption bands in the region 869-721 cm^{-1} are assigned to the deformation vibrations of δ(C=C=C) in the benzene rings.[37,38] The strong absorption bands at 1607 and 1413 cm^{-1} are assigned as $\nu_{as}(COO)_{un\text{-}coord}$ and $\nu_s(COO)_{un\text{-}coord}$ and the absorption strong bands at 1563 and 1381 cm^{-1} are assigned as $\nu_{as}(COO)_{coord}$ and $\nu_s(COO)_{coord}$, respectively. The frequency difference Δν [Δν = $\nu_{as}(COO)$-$\nu_s(COO)$] is correlated with the coordination mode of a carboxylate ligand.



Scheme 2. The preparation method of **1**

The Δν differences [$\Delta\nu = \nu_{as}(COO)_{un\text{-}coord}\text{-}\nu_s(COO)_{un\text{-}coord}$] and [$\Delta\nu = \nu_{as}(COO)_{coord}\text{-}\nu_s(COO)_{coord}$] are 194 and 182 cm^{-1}, respectively. These Δν values are comparable to those of un-coordinated and bridged carboxylate complexes.[39-42] The absorption bands present in the 372-441 cm^{-1} regions are assigned as Sm-$O_{carbxylate}$ and Sm-O_{water} stretching vibrations.[9]

Thermal studies of {[Sm(μ$_2$-BTEC)(H$_2$O)$_4$](H$_2$en)$_{0.5}$.2H$_2$O}$_n$ (1)

The thermal stability of **1** have been determined on single-crystalline samples between 30-900 °C in an air atmosphere with a heating rate of 10 °C min^{-1} by thermogravimetric analyses (TGA) and differential thermal analyses (DTA). The TGA curve (Figure 1) shows a three-step thermal decomposition. The first step between 75 and 135 °C with a mass loss of 6.8% corresponds to the loss of two water solvent molecules (calcd. 6.67%). The second step is between 150 and 320 °C, with a mass loss of 12.4%, corresponding to the loss of one ethylenediammonium cation (calcd. 11.5%). In the last one step between 330 and 790 °C, the four coordinated water molecules and one 1,2,4,5-benzenetetracarboxylicylate anion are lost and the framework decomposes. The final residual weight is 31.8% corresponding to 0.5Sm_2O_3 (calcd. 32.3%). The DTA curve of **1** displays five distinct endothermic peaks at 112, 162, 312, 510 and 576 °C.

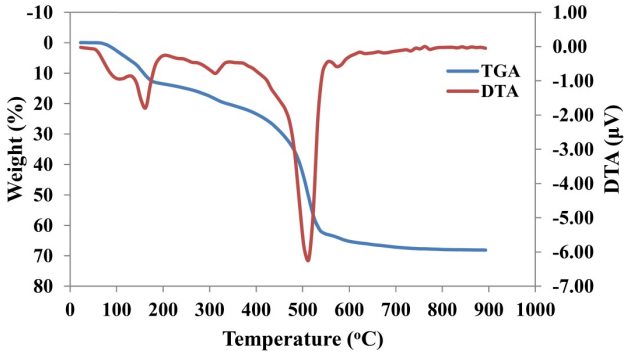


Figure 1. Thermal behavior of **1**.

Description of the molecular structure of {[Sm(μ$_2$-BTEC)(H$_2$O)$_4$](H$_2$en)$_{0.5}$.2H$_2$O}$_n$ (1)

Crystallographic data for **1** are given in Table 1 and the selected bond lengths and angles are presented in Table 2. The ORTEP view with the numbering schemes for compound **1** is shown in Figure 2. The asymmetric unit of the title compound contains one Sm(III) cation, two half of 1,2,4,5-benzenetetracarboxylicylate anion ($BTEC^{4-}$), one half of ethylenediammonium cation and four coordinated and two solvent water molecules. In this complex, each Sm(III) cation is nine-coordinated in a distorted tri-capped trigonal prismatic configuration (Figure 3a) by nine O atoms from two μ-η^1-η^1-η^1-η^1-BTCE anions, two μ-η^1-η^2-η^1-η^2-BTEC anions and four coordinated water molecules. As depicted in Figure 3b, two $BTEC^{4-}$ anions coordinated to Sm(III) with different coordination modes. One of them acts as bridged μ-η^1-η^1-η^1-η^1-BTEC ligand and is coordinated to the four Sm(III) cation from four η^1-O atoms and the other one acts as bridged μ-η^1-η^2-η^1-η^2-BTEC ligand between the four Sm(III) cations through two η^1-O and two η^1-η^2-O atoms. These different modes have caused the formation of square cavities, which are placed at the vertices of this square with binuclear clusters of samarium with a distance of 4.052(1)Å (Figure 3c). Finally, these clusters formed 3D polymers through $BTEC^{4-}$ anion ligands. The value of Sm…Sm separation (4.052(1) Å) in cluster of this complex is almost shorter than the reported in a dimeric Sm(III) complex of $[Sm_2(HBidc)_3(H_2O)]_n$, (4.1008 Å) ($Bidc^{2-}$ is 1H-benzimidazole-5,6-dicarboxylicylate).[43] The Sm–$O_{carboxylate}$ bond lengths are in the range of 2.4228(18) to 2.607(2) Å and the Sm–O_{water} distances are in the range of 2.4132(2) to 2.4756(19) Å. The Sm–$O_{carboxylate}$ and Sm–O_{water} distances are agree with that reported bond distances for in Sm(III) carboxylate coordination polymer complexes.[9,28,43]

Table 1. Crystallographic and structure refinement data for **1**

Empirical formula	$C_{11}H_{19}NO_{14}Sm$
Formula weight	539.63
Temperature/K	293(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size/mm^3	0.40 × 0.35 × 0.30
a/Å	10.077(2)
b/Å	10.179(2)
c/Å	10.446(2)
α/°	100.02(3)
β/°	109.72(3)
γ/°	111.59(3)
Z	2
Volume/Å^3	881.7(3)
Density (calc.)/g cm^{-1}	2.032
F(000)	532
θ ranges for data collection	2.20-27.90
Index ranges	-13<=h<=12 -13<=k<=13 -13<=l<=13
Data collected	8648
Unique data (R_{int})	4128, 0.0297
Parameters, restrains	310, 0
Goodness-of-fit on F^2	1.155
Final R_1, wR_2 (Obs. data)	0.0185, 0.0492
Final R_1, wR_2 (All data)	0.0190, 0.0494
Largest diff. peak and hole/e.Å^{-3}	0.577 and -0.899 e.Å^{-3}
CCDC	2363002

Table 2. Bond distances (Å) and bond angles (°) for **1**

Sm1-O1	2.451(2)	O2-Sm1-O5	113.14(8)
Sm1-O2	2.417(3)	O2-Sm1-O9	140.15(7)
Sm1-O3	2.4756(19)	O2-Sm1-O10	138.16(7)
Sm1-O4	2.440(3)	O2-Sm1-O6^{i}	76.66(8)
Sm1-O5	2.4132(18)	O2-Sm1-O9^{i}	73.82(7)
Sm1-O9	2.535(2)	O3-Sm1-O4	78.08(9)
Sm1-O10	2.607(2)	O3-Sm1-O5	149.26(7)
Sm1-O6^{i}	2.4228(18)	O3-Sm1-O9	122.44(7)
Sm1-O9^{i}	2.4607(19)	O3-Sm1-O10	73.75(7)
O1-Sm1-O2	68.56(8)	O3-Sm1-O6^{i}	74.83(7)
O1-Sm1-O3	82.74(7)	O3-Sm1-O9^{i}	137.56(7)
O1-Sm1-O4	71.02(9)	O4-Sm1-O5	76.18(9)
O1-Sm1-O5	73.24(7)	O4-Sm1-O9	86.96(9)
O1-Sm1-O9	142.87(7)	O4-Sm1-O10	62.94(9)
O1-Sm1-O10	131.42(7)	O4-Sm1-O6^{i}	130.40(9)
O1-Sm1-O6^{i}	142.69(7)	O4-Sm1-O9^{i}	144.25(8)
O1-Sm1-O9^{i}	109.64(7)	O5-Sm1-O9	72.64(7)
O2-Sm1-O3	73.77(8)	O5-Sm1-O10	108.29(7)
O2-Sm1-O4	132.86(9)		

Symetry code: (i) 1-x,1-y,2-z

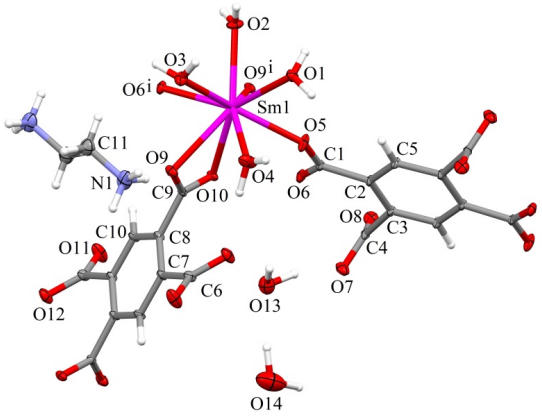


Figure 2. The molecular structure of {[Sm(μ_2-BTEC)$(H_2O)_4$]$(H_2en)_{0.5}.2H_2O$}$_n$ (**1**), with the atom-numbering scheme. The ellipsoids are show in 30% probability displacement level. Symmetry code: (i) 1-x,1-y,2-z.

The crystal packing diagram for 1 is shown in Figure 4. The extensive N-H...O, O-H···O and C-H···O hydrogen bonds (Table 3), formed between ethylenediammonium cation, carboxylate groups of 1,2,4,5-benzenetetra-carboxylicylate ligands, coordinated and non-coordinated water molecules were found in the crystal structure of **1** (Figure 3).

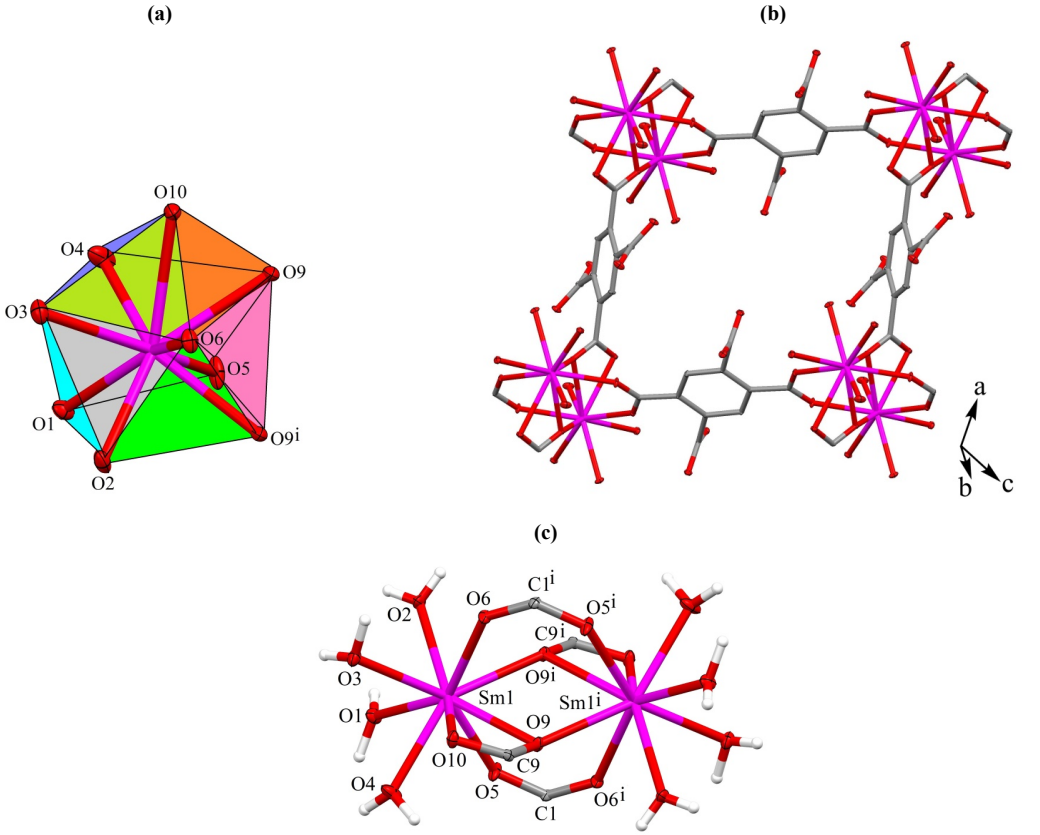


Figure 3. (a) Local coordination environment of Sm(III) in **1**. (b) Tetrameric ring of **1**. Solvent water molecules and ethylenediammonium cation have been omitted for clarity. (c) The binuclear cluster in **1**. Symmetry code: (i) 1-x,1-y,2-z.

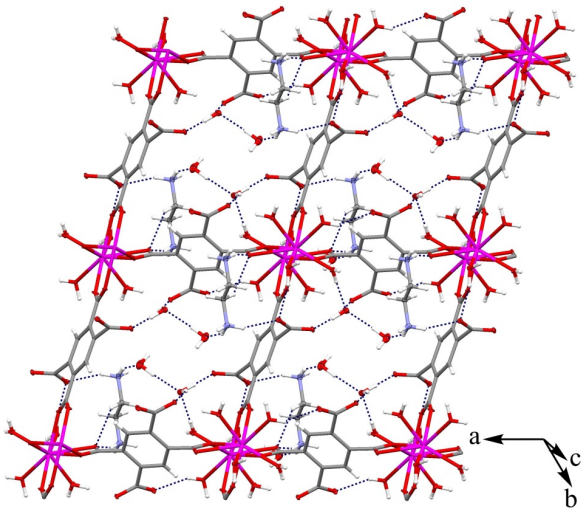


Figure 4. The packing diagram of **1**. Inter and intramolecular N-H···O, O-H···O and C-H···O hydrogen bonds are shown as dashed lines.

4. CONCLUSION

In this work, a new three-dimensional samarium(III) coordination polymer, $\{[Sm(\mu_2\text{-BTEC})(H_2O)_4](H_2en)_{0.5}.2H_2O\}_n$ (**1**), has been synthesized by the reaction of $SmCl_3.6H_2O$ and $[H_2en]_2[BCT].2H_2O$ in water, in an ice bath and characterized by elemental analysis, FT-IR spectroscopy and single-crystal X-ray crystallography. The X-ray crystallography analysis shows that this compound is a three-dimensional polymer and the Sm(III) cation is nine-coordinated in a distorted tri-capped trigonal prismatic configuration by nine O atoms from two μ-η^1-η^1-η^1-η^1-BTCE anions, two μ-η^1-η^2-η^1-η^2-BTEC anions and four coordinated water molecules. Furthermore, the thermal stability of **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

CONFLICTS OF INTEREST

There are no conflicts to declare.

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