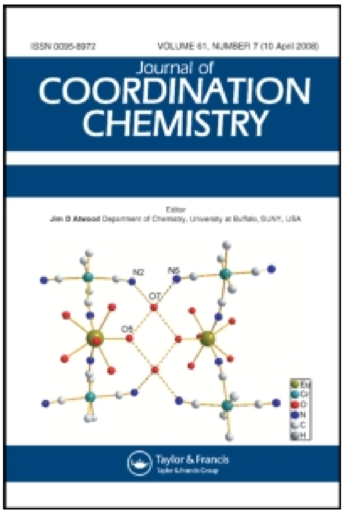

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Synthesis and characterization of a new dimeric polyoxometalate based on Anderson-type polyoxoanions and a trinuclear lanthanide coordination complex

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An unusual compound, $H_5[(C_6NO_2H_4)_4(H_2O)_{15}Nd_3][IMo_6O_{24}]_2 \cdot 13.5H_2O$ (**1**) has been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA), and single crystal X-ray diffraction. Compound **1** consists of two $[IMo_6O_{24}]^{5-}$ units joined by a trinuclear neodymium-pyridine-4-carboxylic acid complex, resulting in a dimeric polyoxometalate, which further interact via weak intermolecular interactions to form a three-dimensional supramolecular framework with channels. To the best of our knowledge, no analogous dimeric polyoxometalate structure composed of an Anderson-type polyoxometalate has been reported in the literature.

Keywords: Anderson-type polyoxoanion; Lanthanide coordination complex; Dimeric polyoxometalate; Supramolecular channel

1. Introduction

Polyoxometalates (POMs) [1–3], as anionic early transition metal oxide clusters, have received much attention, not only because of their potential applications in catalysis, sorption, biology, optical and electromagnetic functional materials, but also for their intriguing variety of architectures and topologies. An intriguing area in this field is the combination of metal cations with POMs to construct new low dimensional POM architectures with particular topologies by self-assembly [4–6]. Several successful strategies have been developed to design POM-based architectures. Pope and coworkers [7] and Müller *et al.* [8], have respectively, reported many very large polyoxotungstate and polyoxomolybdate clusters, and Fukaya and Yamase [9] reported a supramolecular crown-shaped ring architecture composed of lanthanides and $[\alpha\text{-}AsW_9O_{33}]^{9-}$ units. Several dimeric or sandwich-type POMs based on lacunary Keggin and vacant Wells-Dawson polyoxoanions have been reported by Hill and

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coworkers [10] and Kortz and coworkers [11, 12]; a dimeric dumbbell-like compound constructed from Lindquist-type polyoxoanions has also been successfully synthesized [13]. In contrast, the role of Anderson-type polyoxoanions as the basic building block has not been so extensively studied. Thus, it will be of interest to investigate whether this kind of polyoxometalates can be introduced into a dimeric framework by utilizing suitable linkers. More recently, the successful synthesis of two new heteropolymolybdate structures i.e. 6-molybdocobaltate and 6-molybdoaluminate cobalt salts based on Anderson-type polyoxoanions provides further impetus [14].

Lanthanide cations or coordination complexes, in contrast to the widely used 3d-block metal cations, can become important choices as the inorganic linkers in designing novel POM-based architectures. In addition, lanthanide cations may not only exhibit multiple coordination requirements, but also possess potential applications in bioinorganic chemistry, various electronic, magnetic, and photosensitive materials [15–17].

Herein, a novel dimeric POM based on Anderson-type polyoxoanions is reported, $H_5[(C_6NO_2H_4)_4(H_2O)_{15}Nd_3][IMo_6O_{24}]_2 \cdot 13.5H_2O$ (**1**). Compound **1** is composed of two $[IMo_6O_{24}]^{5-}$ building units joined by a trinuclear neodymium-pyridine-4-carboxylic acid complex, resulting in a dimeric polyoxoanion, which further interact with each other via weak intermolecular interactions to form a three-dimensional supramolecular framework with channels. To our knowledge, no analogous dimeric structure composed of an Anderson-type POM has been reported in the literature.

2. Experimental

2.1. *General procedures*

All chemicals were commercially purchased and used without further purification. $Na_5[IMo_6O_{24}] \cdot 3H_2O$ [18] was synthesized according to the literature and characterized by IR spectrum and thermogravimetric analysis (TGA). Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer; I, Mo, and Nd were analyzed on a PLASMA-SPEC(I) inductively coupled plasma (ICP) atomic emission spectrometer. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TGA was performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ C\,min^{-1}$.

2.2. *Preparation*

$Nd(ClO_4)_3$ (0.443 g, 1 mmol) and pyridine-4-carboxylic acid (0.246 g, 2 mmol) were sequentially added to a 40 mL water solution of $Na_5[IMo_6O_{24}] \cdot 3H_2O$ (1.256 g, 1 mmol). The filtrate was kept for 2 weeks at ambient conditions, and purple block crystals of compound **1** were isolated in about 25% yield (based on Nd). Anal. Calcd for $H_5[(C_6NO_2H_4)_4(H_2O)_{15}Nd_3][IMo_6O_{24}]_2 \cdot 13.5H_2O$ (%): I, 7.03; Mo, 31.87; Nd, 11.97; C, 7.97; N, 1.55; H, 2.16. Found: I, 7.24; Mo, 31.60; Nd, 11.69; C 7.88; N, 1.85; H, 2.34. FT-IR data (cm^{-1}): 3390(s), 1639(s), 1581(s), 1464(w), 1411(s), 1110(m), 945(s), 919(s), 688(vs), 626(vs) and 417(s).

2.3. *X-ray crystallography*

A purple single crystal of **1** with dimensions of $0.16 \times 0.14 \times 0.13\,\text{mm}^3$ was mounted inside a glass fiber capillary. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-K_α ($\lambda = 0.71073\,\text{Å}$) at 293 K in the range $3.08^\circ < \theta < 25.00^\circ$. Empirical absorption correction was applied. A total of 30892 (14944 unique, $R_{\text{int}} = 0.0654$) reflections were measured ($-15 \le h \le 15$, $-18 \le k \le 17$, $-29 \le l \le 29$).

The structure of **1** was solved by the direct method and refined by Full-matrix least squares on F^2 using the SHELXTL-97 software [19]. All non-hydrogen atoms in **1** were refined anisotropically. In **1** positions of the hydrogen atoms attached to O1W, O4W, O5W, O6W, O7W, O9W, O10W, O13W and O16W were located from difference maps. Hydrogen atoms attached to carbon atoms and to nitrogen atoms were fixed in ideal positions, and other hydrogen atoms were not located. A summary of the crystallographic data and structural determination for **1** is provided in table 1. Selected bond lengths and angles of **1** are listed in table 2. The atomic coordinates and

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

Empirical formula	$C_{24}H_{78}I_2Mo_{12}N_4Nd_3O_{84.50}$
Formula weight	3612.70
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	13.360(3)
b (Å)	15.960(3)
c (Å)	25.160(5)
α (°)	72.51(3)
β (°)	81.37(3)
γ (°)	71.35(3)
V (Å^3)	4839.4(17)
Z	2
ρ_{calc} (g cm^{-3})	2.479
Absorption coefficient (mm^{-1})	3.831
F (000)	3432
Crystal size (mm)	$0.16 \times 0.14 \times 0.13$
θ Range for data collection (°)	3.08 to 25.00
Limiting indices	$-15 \le h \le 15$, $-18 \le k \le 17$, $-29 \le l \le 29$
Reflections collected	30892
Independent reflections (R_{int})	14944 [R(int) = 0.0654]
Data/restraints/parameters	14944/810/1303
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0683$, $wR_2 = 0.1597$
Indices (all data)	$R_1 = 0.0965$, $wR_2 = 0.1755$
Largest difference peak and hole (e Å^{-3})	1.469 and −1.137

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

I–O$_c$	1.873(9)–1.919(9)	Mo–Oc	2.301(9)–2.410(10)
Mo–Ot	1.687(12)–1.735(12)	Nd–O	2.318(10)–2.614(9)
Mo–Ot′	1.713(10)–1.740(10)	Nd–OH$_2$	2.464(12)–2.628(11)
Mo–Ob	1.888(8)–1.956(10)		
O–I–O$_{cis}$	86.2(4)–93.9(4)	O–Mo–O$_{trans}$	148.4(4)–163.6(4)
O–I–O$_{trans}$	177.2(4)–179.2(4)	O–Nd–O	65.6(4)–151.8(4)
O–Mo–O$_{cis}$	67.3(3)–108.0(5)		

equivalent isotropic displacement parameters for **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary data.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction analysis shows that compound **1** is made up of $[IMo_6O_{24}]^{5-}$ clusters as anions, trinuclear neodymium-pyridine-4-carboxylic acid complexes as cations, water molecules of crystallization and five protons. The $[IMo_6O_{24}]^{5-}$ polyoxoanion is an A-type Anderson structure in which six MoO_6 octahedra arrange hexagonally around the central $\{IO_6\}$ octahedron. Four kinds of oxygen atoms exist in the cluster according to the manner of oxygen coordination, that is the terminal oxygen, Ot, the terminal oxygen linked to Nd^{3+}, Ot′, double-bridging oxygen, Ob, and the central oxygen, Oc. Thus the Mo–O distances can be grouped into four sets: Mo–Ot 1.687–1.735 Å, Mo–Ot′ 1.713–1.740 Å, Mo–Ob 1.888–1.956 Å, Mo–Oc 2.301–2.410 Å. The central I–Oc distances vary from 1.873 to 1.919 Å. The bond angles of $O\text{–}I\text{–}O_{cis}$ range from 86.2 to 93.9° and $O\text{–}I\text{–}O_{trans}$ range from 177.2(4) to 179.2°.

The asymmetric unit in the crystal structure of **1** consists of two crystallographically independent Anderson anions, in which both iodine ions (I1 and I2) occupy special positions, linked up by a trinuclear neodymium-pyridine-4-carboxylic acid complex (figure 1). There are three crystallization-independent neodymium atoms. Nd(1) resides in a distorted monocapped square antiprismatic environment, coordinated by one oxygen atom from one $[IMo_6O_{24}]^{5-}$ unit, two oxygen atoms from the carboxylate groups of two pyridine-4-carboxylic acid molecules and six water molecules. Nd(2) has a bicapped trigonal-prismatic geometry, being defined by one oxygen atom from one $[IMo_6O_{24}]^{5-}$ unit, four oxygen atoms from the carboxylate groups of four pyridine-4-carboxylic acid molecules and three water molecules. Nd(3) also resides in a distorted monocapped square antiprismatic environment, being coordinated by one oxygen atom from one $[IMo_6O_{24}]^{5-}$ unit, two oxygen atoms from the carboxylate

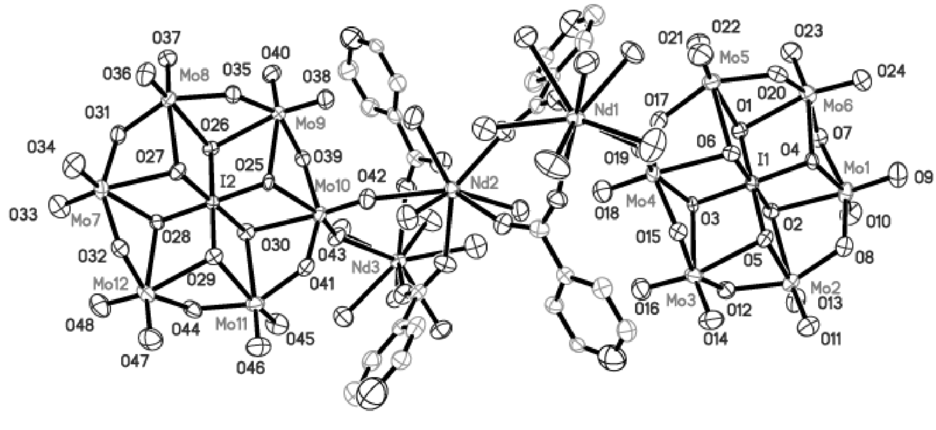

Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at 50% probability. Partial water molecules are omitted for clarity.

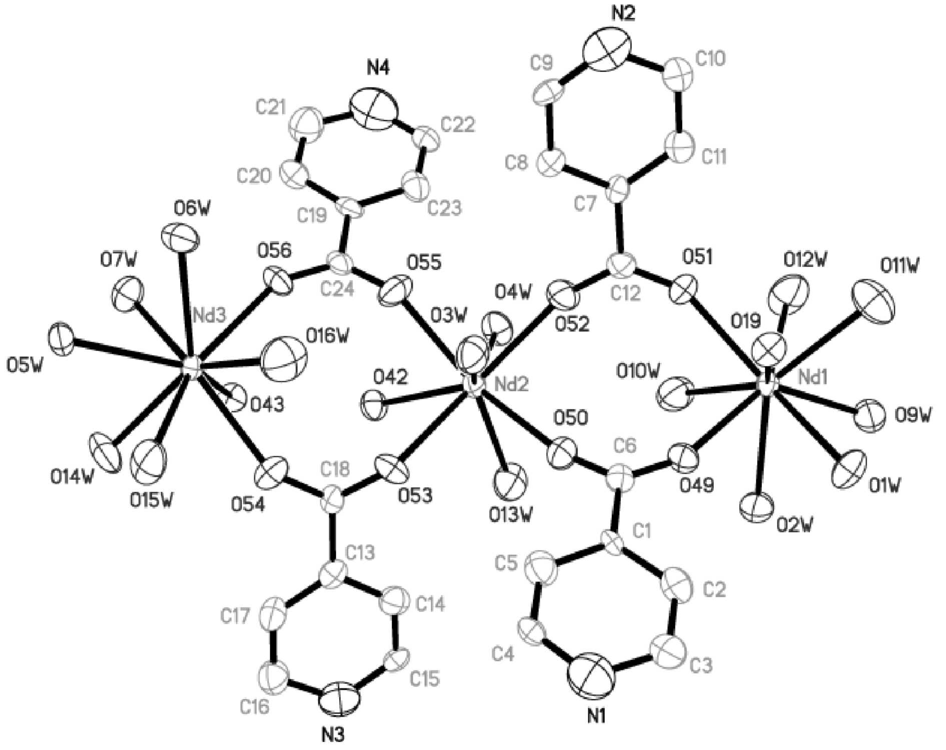

Figure 2. Coordination environment of the trinuclear neodymium-pyridine-4-carboxylic acid complex.

groups of two pyridine-4-carboxylic acid molecules and six water molecules. The bond lengths vary from 2.374 to 2.628 Å for Nd(1)–O, from 2.318 to 2.614 Å for Nd(2)–O, and from 2.420 to 2.599 Å for Nd(3)–O. The average bond length for Nd(1)–O is 2.509 Å, equal to the Nd–O bond length (2.509 Å) in $(CN_3H_6)_2[Nd(H_2O)]_2(C_2O_4)_4 \cdot 3H_2O$ [20], in which the coordinate number is nine and the coordination polyhedron around Nd^{3+} ion is a distorted monocapped square antiprism. The average bond length for Nd(3)–O is 2.516 Å, which is 0.007 Å longer than the Nd–O bond length (2.509 Å) in $(CN_3H_6)_2[Nd(H_2O)]_2(C_2O_4)_4 \cdot 3H_2O$. The average bond length for Nd(2)–O is 2.441 Å, which is shorter than the Nd–O bond length (2.444 Å) in $(dmaH)_2[Nd(dmf)_4(H_2O)][a\text{-}BW_{12}O_{40}] \cdot H_2O$, in which the coordination number is eight and the coordination polyhedron around Nd^{3+} is a distorted square antiprism. The average bond length of Nd–O (CN = 9) is slightly longer than Nd–O (CN = 8). There are four crystallographically independent pyridine-4-carboxylic acid molecules acting as bidentate ligands coordinated to three neodymium atoms (figure 2).

In the structure of **1**, the trinuclear neodymium-pyridine-4-carboxylic acid complex connects two Anderson-type polyoxoanions to construct a dimeric POM. It is noteworthy that one Anderson anion as a bidentate ligand coordinates to two Nd-pyridine-4-carboxylic acid complex fragments via the two terminal oxygen atoms of one MoO_6 octahedron, while the other as a monodentate ligand coordinates to one Nd-pyridine-4-carboxylic acid complex. The dimeric POMs are connected with each other via strong hydrogen-bonding interactions among oxygen atoms of polyoxoanions, organic ligands and coordinated water molecules, to form infinite chains

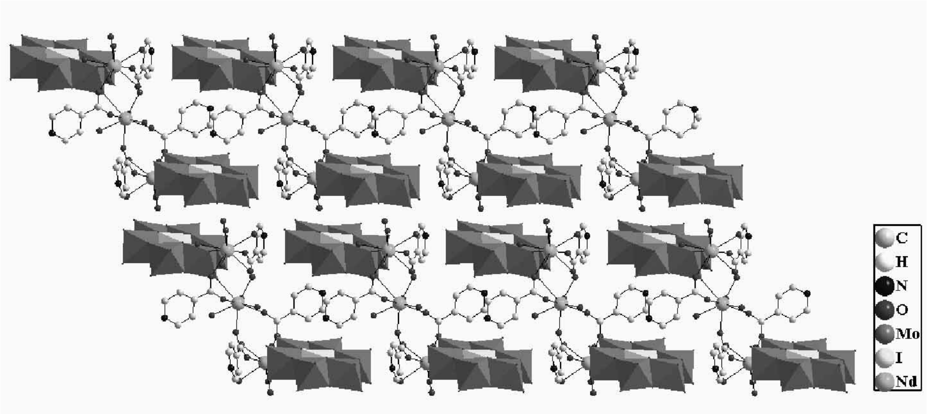

Figure 3. Polyhedral and ball-stick view of the two-dimensional assembly layer in **1**.

(shown in supplementary data). The infinite chains are further held together by other hydrogen bonds yielding a planar sheet (figure 3). A significant feature is the planar sheets are stacked to give a three-dimensional supramolecular framework with one-dimensional channels of nearly 14.0 Å × 5.0 Å along the *a* axis (see figure 4). Lattice water molecules are located in the channels and form multipoint hydrogen bonds with the nearest lattice water molecules, coordinated water molecules and oxygen atoms of polyoxoanions. These strong hydrogen-bonding interactions play an important role in the formation of the three-dimensional supramolecular framework. To the best of our knowledge, compound **1** represents the first example of a dimeric POM architecture based on Anderson-type polyoxoanions.

The bond valence sum (BVS) calculations [21] indicate that I site is in the +7 oxidation state, Nd site is in the +3 oxidation and all Mo sites are in the +6 oxidation in compound **1**. According to the BVS values and the charge balance considerations for compound **1**, there are five protons, and these hydrogen atoms could not be located by the crystal structure analysis [22, 23].

3.2. *FT-IR spectroscopy*

In the IR spectrum of **1**, the characteristic peaks at 945, 919, 688, 626 and 471 $\mathrm{cm^{-1}}$ demonstrate that $[\mathrm{IMo_6O_{24}}]^{5-}$ is an Anderson structure. The peaks at 3390, 1639, 1581, 1464, 1411 and 1110 $\mathrm{cm^{-1}}$ are characteristic of pyridine-4-carboxylic acid molecules (see supplementary data).

3.3. *TGA*

The TGA curve of **1** is shown in figure 5. The TGA curve gives a total weight loss of 28.74% in the range 20–600°C, which agrees with the calculated value of 28.96%. The weight loss of 15.20% at 20–300°C corresponds to the loss of non-coordinated and coordinated water molecules (Calcd 15.45%). The weight loss of 13.54% at 340–600°C arises from decomposition of organic molecules (Calcd 13.51%).

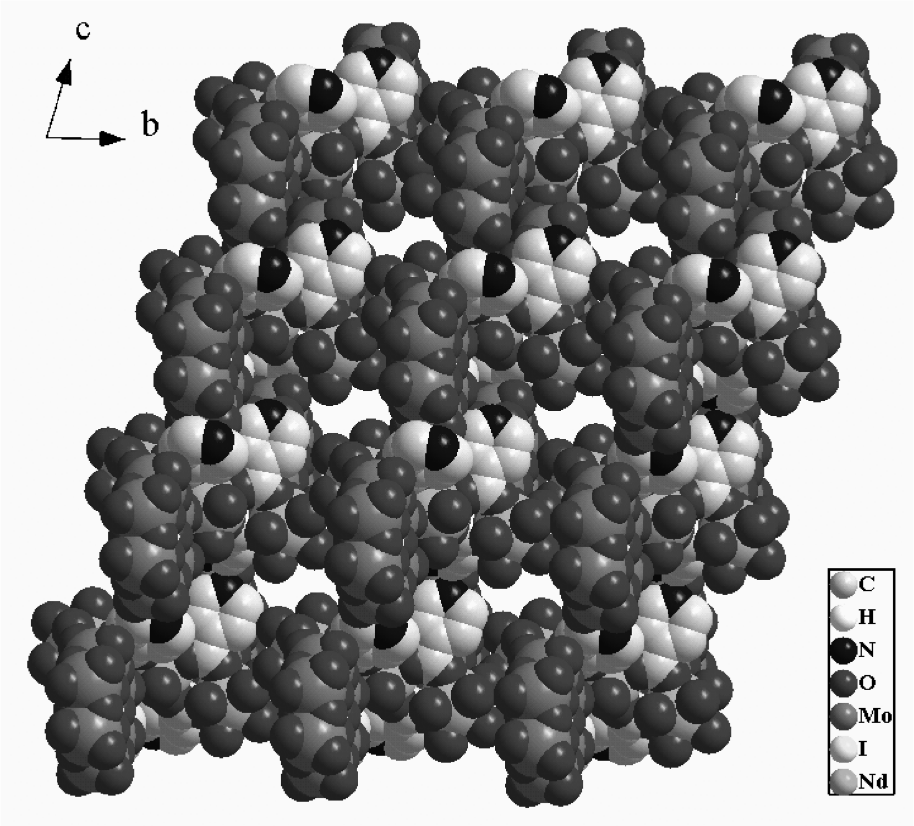

Figure 4. Space-filling diagram of the three-dimensional supramolecular framework of **1**, showing the one-dimensional channels.

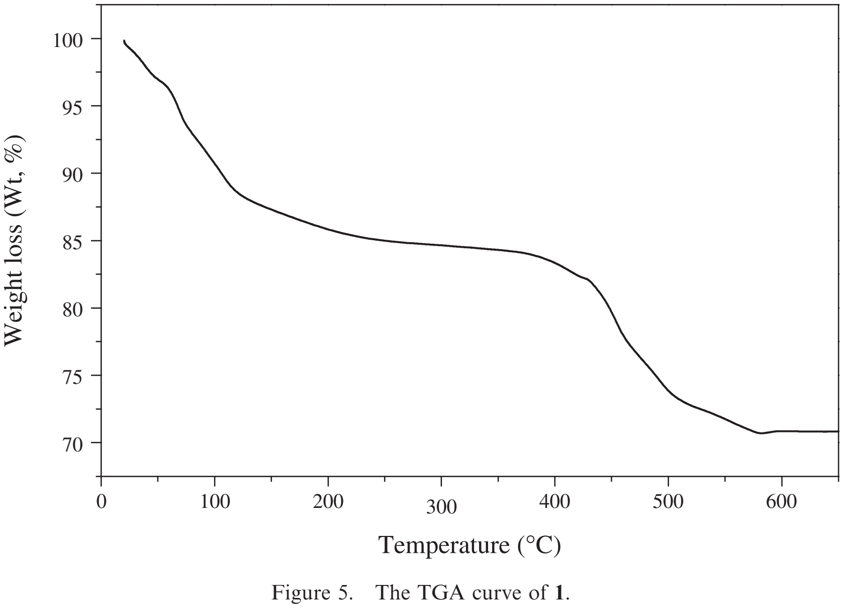

Figure 5. The TGA curve of **1**.

4. Conclusions

In summary, a novel dimeric compound based on the Anderson-type polyoxoanions and lanthanide coordination complexes has been prepared and structurally characterized. The successful synthesis of **1** not only indicates the potential of Anderson-type POMs as building blocks to construct new architecture, but also demonstrates the ability of the POMs to form supramolecular channel frameworks via weak intermolecular interactions. Research is ongoing to prepare novel polymeric frameworks in this subfield and explore their properties.

Supplementary data

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication number CCDC 261151. Copies of available material can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@cdc.cam.ac.uk

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