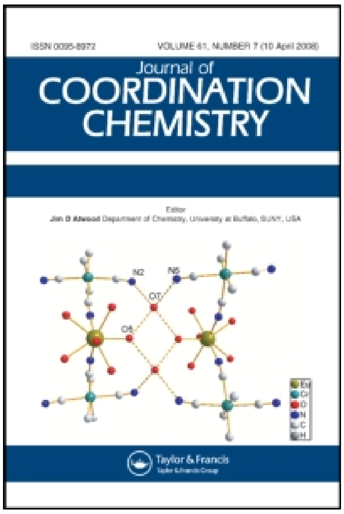

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Synthesis and structure of a novel one-dimensional vanadate constructed from tetravanadate clusters linked via copper-organic complex moieties: $[\{Cu(phen)(H_2O)\}_2V_4O_{12}]$

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Synthesis and structure of a novel one-dimensional vanadate constructed from tetravanadate clusters linked via copper–organic complex moieties: $[\{Cu(phen)(H_2O)\}_2V_4O_{12}]$

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A novel organic–inorganic hybrid copper vanadate $[\{Cu(phen)(H_2O)\}_2V_4O_{12}]$ (**1**) (phen = 1,10-phenanthroline) was synthesized by the hydrothermal reaction of V_2O_5, $CuCl_2 \cdot 2H_2O$, phen and water. Complex **1** was characterized by elemental analyses, XPS spectrum, TG analysis, IR spectrum and single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, $a = 7.7715(16)$ Å, $b = 9.3157(19)$ Å, $c = 10.887(2)$ Å, $\alpha = 89.35(3)^\circ$, $\beta = 69.63(3)^\circ$, $\gamma = 76.41(3)^\circ$, $V = 716.1(3)$ Å^3, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, and $R(F) = 0.0648$. The title compound contains a novel double-chain ribbon constructed from tetravanadate clusters linked through copper–organic complex fragments. To the best of our knowledge, compound **1** represents the first example of one-dimensional vanadium oxide complexes constructed from tetranuclear $V_4O_{12}^{4-}$ clusters linked via metal–organic complex moieties.

Keywords: Organic–inorganic hybrid; Tetravanadate; Hydrothermal synthesis; Crystal structure

1. Introduction

Organic–inorganic hybrid materials attract interest owing to their potential applications in catalysis, electron conductivity, magnetism and photochemistry, as well as their intriguing structural features [1, 5–17]. Polyoxometalates (POMs) as metal oxide clusters with nanosizes and abundant topologies, are of interest in the fields of catalysis and material science, as well as in biology, magnetism, nonlinear optics and medicine [2–4]. Therefore, the functionality of organic–inorganic hybrid materials based on POMs can be multiplied by the incorporation of organic and inorganic counterparts into one structural unit [1, 5]. In recent years, the rational design of inorganic–organic

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hybrid POMs has been achieved through defining their architectures and it has contributed to increased understanding of the methods to control synergistic interactions between organic and inorganic chemical compositions [6]. An important advance in this field has been to realize that the organic components act as ligands either directly coordinated to the inorganic scaffoldings or to secondary metal centers [7, 8]. As concluded in a review by Zubieta and co-workers, inorganic vanadium oxides can be modified efficiently by metal–organic complexes to generate hybrid materials with attractive prospects [6b]. During studies of such materials, a large variety of organic–inorganic hybrid materials belonging to the {MxLy/V/O} system (M = transition metal, L = organic ligand, $x:y = 1:1$, $1:2$ or $1:3$) have been isolated [6–11].

As an important subclass of the family of oxovanadium compounds, the organic–inorganic hybrid tetravanadate clusters have been widely studied [9–17]. Discrete cyclo-tetravanadate clusters are one of the common structural types, such as $[Zn(bipy)_3]_2V_4O_{12} \cdot 11H_2O$ [9], $[Zn(bipy)_2]_2V_4O_{12}$ [9], $[Zn(phen)_2]_2V_4O_{12} \cdot H_2O$ [9], $[Ni(bipy)_3V_4O_{12}] \cdot 11H_2O$ [10], and $[H_2pn][Mn_2(C_2O_4)(V_4O_{12})]$ [11], in which the transition metal complexes are supported on the cyclo-tetravanadate skeletons or act as charge balance cations. Another typical structure is two-dimensional (2D) layered tetravanadates, such as $[H_2N(CH_2)_4NH_2]V_4O_9$ [12], $[NH_3(CH_2)_3NH_3]V_4O_{10}$ [13], α-, β-$[H_3N(C_2H_4)_2NH_3]_2V_4O_{10}$ [14], α-, β-$[H_3NCH_2CH_2NH_3]V_4O_{10}$ [14], and $[VO_2(terpy)]V_4O_{10}$ [15]. These layered vanadium oxides share a common structural feature, acting as 'host' materials, and organic amines or cationic guests are accommodated between the anionic oxide layers. However, tetravanadate with a one-dimensional (1D) chainlike structure is rare [16, 17]. To our knowledge, 1D vanadate complexes constructed from V_4O_{12} tetravanadate clusters and metal–organic complex moieties have not been observed. In this work, we report the hydrothermal synthesis and crystal structure of a 1D vanadium oxide complex, $[\{Cu(phen)(H_2O)\}_2V_4O_{12}]$ (**1**), constructed from two subunits, V_4O_{12} tetramer rings and $[Cu(phen)(H_2O)]^{2+}$ fragments.

2. Experimental

2.1. *General procedures*

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Cu and V were determined by a Leaman inductively coupled plasma (ICP) spectrometer. XPS analysis was performed on a VG ESCALABMK II spectrometer with an Mg-Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}.

2.2. *Preparation*

In a typical synthesis procedure for **1**, a mixture of V_2O_5 (0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.5 mmol), phen (0.5 mmol) and H_2O (7 mL) was stirred for 30 min in air. The mixture was sealed in a 15 mL Teflon-lined autoclave and heated at 170°C for 144 h. Then the autoclave was cooled at 10°C h^{-1} to room temperature. The resulting blue block crystals **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: ca 60% based on vanadium). Elemental analyses of the blue crystals are consistent with the stoichiometry $C_{12}H_{10}CuN_2O_7V_2$. The elemental analyses Found: C, 31.51; H, 2.28; Cu, 13.64; N, 6.13; V, 22.26%; Calcd for $C_{12}H_{10}CuN_2O_7V_2$: C, 31.36; H, 2.19; Cu, 13.83; N, 6.09; V, 22.17%. IR spectrum (cm^{-1}): 3061(m), 1622(m), 1585(m), 1517(s), 1427(s), 1345(w), 1225(w), 1143(m), 1106(w), 978(s), 943(s), 918(s), 900(m), 871(m), 852(s), 837(w), 825(m), 813(m), 771(s), 723(m), 644(w), 509(w), 426(w).

2.3. *X-ray crystallography*

The structure of compound **1** was determined by single crystal X-ray diffraction. A blue single crystal of **1** with dimensions $0.43 \times 0.26 \times 0.21\ mm^3$ was mounted on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer (using Rapid Auto program) with Mo-Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $2.26 < \theta < 27.93°$. Empirical absorption correction (multiscan) was applied. The structure was solved by the direct method and refined by the full-matrix least squares on F^2 using the SHELXTL-97 software [18]. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions, and those attached to oxygen atoms were not located. A total of 3514 (2786 unique, $R_{int} = 0.0662$) reflections were measured. Structure solution and refinement based on 2786 independent reflections with $I > 2\sigma(I)$ and 217 parameters gave $R_1(wR_2) = 0.0648$ (0.1618) $\{R_1 = \sum ||F_o| - |F_C|| / \sum |F_o|;\ wR_2 = \sum [w(F_o^2 - F_C^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$.

A summary of crystal data and structure refinement for compound **1** is provided in table 1. Selected bond lengths and angles are listed in table 2. The atomic coordinates and equivalent isotropic displacement parameters for **1** are given in table 3.

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

Empirical formula	$C_{12}H_{10}CuN_2O_7V_2$
Formula weight	459.64
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 7.7715(16)$, $\alpha = 89.35(3)$ $b = 9.3157(19)$, $\beta = 69.63(3)$ $c = 10.887(2)$, $\gamma = 76.41(3)$
Volume (Å^3)	716.1(3)
Z	2
D_c ($g\,cm^{-3}$)	2.132
Absorption coefficient (mm^{-1})	2.790
θ range for data collection (°)	2.26 to 27.93
Reflections collected	3514
Independent reflections	2786 [$R(int) = 0.0662$]
Data/restraints/parameters	2786/0/217
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0648$, $wR_2 = 0.1618$
R indices (all data)	$R_1 = 0.0780$, $wR_2 = 0.1714$

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

Cu(1)–O(6)	2.049(4)	Cu(1)–N(1)	2.080(4)
Cu(1)–OW1	2.012(4)	Cu(1)–O(1)#1	1.960(4)
Cu(1)–N(2)	2.130(5)	V(1)–O(4)	1.780(5)
V(1)–O(3)	1.607(4)	V(1)–O(5)	1.783(4)
V(1)–O(6)	1.639(4)	V(2)–O(2)	1.595(4)
V(2)–O(5)	1.761(4)	V(2)–O(1)	1.700(4)
V(2)–O(4)#2	1.763(5)		
OW1–Cu(1)–O(6)	89.44(17)	O(1)#1–Cu(1)–OW1	106.33(18)
O(1)#1–Cu(1)–N(1)	113.57(17)	O(1)#1–Cu(1)–O(6)	96.87(16)
OW1–Cu(1)–N(1)	139.79(19)	O(6)–Cu(1)–N(1)	90.66(17)
O(6)–Cu(1)–N(2)	163.74(17)	O(1)#1–Cu(1)–N(2)	98.65(17)
N(1)–Cu(1)–N(2)	78.70(17)	OW1–Cu(1)–N(2)	90.83(19)
O(3)–V(1)–O(5)	109.8(2)	O(3)–V(1)–O(6)	107.6(2)
O(6)–V(1)–O(5)	108.7(2)	O(3)–V(1)–O(4)	110.1(3)
O(4)–V(1)–O(5)	108.3(2)	O(6)–V(1)–O(4)	112.4(2)
O(2)–V(2)–O(4)#2	109.9(3)	O(2)–V(2)–O(1)	108.8(2)
O(1)–V(2)–O(4)#2	109.6(2)	O(2)–V(2)–O(5)	106.2(2)
O(5)–V(2)–O(4)#2	110.4(2)	O(1)–V(2)–O(5)	111.79(19)

Symmetry transformations used to generate equivalent atoms: #1: $x+1, y, z$; #2: $-x+1, -y+1, -z+1$; #3: $x-1, y, z$.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	10202(1)	8687(1)	3052(1)	21(1)
V(1)	7091(1)	6476(1)	4374(1)	24(1)
V(2)	3456(1)	6208(1)	3526(1)	24(1)
O(6)	9020(5)	6907(4)	3414(4)	29(1)
OW1	7911(6)	9910(5)	4482(5)	40(1)
O(5)	5809(5)	6092(5)	3393(4)	36(1)
O(4)	7585(6)	4888(6)	5236(5)	48(1)
O(3)	5847(7)	7884(5)	5398(5)	48(1)
O(2)	3560(6)	5589(5)	2135(4)	36(1)
O(1)	2124(5)	7985(4)	3850(4)	30(1)
N(2)	11022(6)	10637(5)	2292(4)	26(1)
N(1)	11177(6)	8136(5)	1040(4)	27(1)
C(12)	11923(7)	10458(6)	972(5)	27(1)
C(11)	11985(7)	9114(6)	303(5)	28(1)
C(10)	10886(9)	11887(7)	2911(6)	37(1)
C(9)	11694(10)	13001(7)	2281(8)	45(2)
C(8)	12645(9)	12808(7)	967(7)	40(1)
C(7)	12760(8)	11514(7)	244(6)	34(1)
C(6)	13668(9)	11238(7)	−1140(7)	44(2)
C(5)	13720(9)	9989(9)	−1771(6)	46(2)
C(4)	12895(8)	8887(7)	−1067(6)	32(1)
C(3)	12928(9)	7533(8)	−1655(6)	43(2)
C(2)	12089(9)	6557(7)	−892(6)	39(1)
C(1)	11234(8)	6879(6)	456(6)	32(1)

3. Results and discussion

3.1. *Structure description*

The asymmetric unit of **1** (figure 1) shows two crystallographically independent V atoms and one crystallographically independent Cu atom. The V(1) site exhibits

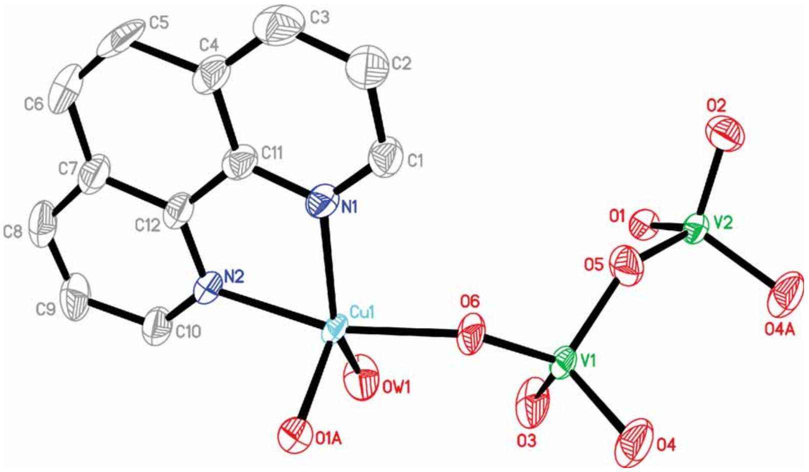

Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at 50% probability. H atoms are omitted for clarity.

a distorted tetrahedral coordination geometry with a terminal and three bridging oxygen atoms, two of which are linked with two V(1) atoms and another one linked with Cu(1). In the {V(2)O_4} unit, three oxygen atoms bridge two V(1) atoms and one Cu atom, and the fourth oxygen atom is terminal. Three kinds of oxygen atoms exist in the V_4O_{12} tetramer rings according to the manner of oxygen coordination, that is the terminal oxygen Ot, double-bridging oxygen Ob, the bridging oxygen linked to Cu^{2+} Ob′. Thus the V–O distances can be grouped into three sets: V–Ot 1.595(4)–1.607(4) Å, V–Ob, 1.761(4)–1.783(4) Å, and V–Ob′ 1.639(4)–1.700(4) Å. Generally the fewer metal atoms that share the oxygen atoms, the shorter the V–O bonds (i.e., one < two < three). The V–O distances of compound **1** display the anticipated trend. The bond angles of O–V–O range from 106.2(2) to 112.4(2)°. Each Cu^{II} is ligated by two nitrogen atoms (Cu–N 2.080(4) and 2.130(5) Å) from a phen ligand, one aqua oxygen atom (Cu–OW 2.012(4) Å) and one bridging oxygen atom (Cu–O 2.049(4) Å) linked with V(1) at equatorial positions, and completed by a bridging oxygen atom (Cu–O 1.960(4) Å) linked with V(2) at the apical positions to furnish a square pyramidal geometry.

Single-crystal X-ray diffraction analysis reveals that compound **1** consists of a novel double-chain ribbon along the *a*-axis, as shown in figure 2. Each ribbon is composed of alternating V_4O_{12} tetramer rings and $[Cu(phen)(H_2O)]^{2+}$ fragments, which are linked by corner-sharing oxygen atoms. To our knowledge, compound **1** represents the first example of 1D vanadate complexes constructed from V_4O_{12} tetravanadate clusters linked through metal–organic complex fragments.

There are two types of supramolecular interactions in **1**, hydrogen bonding and aromatic π–π stacking interactions. First, the phen ligands between adjacent ribbons are arranged in an off-set fashion with a plane-to-plane separation of 3.4–3.5 Å, indicating strong aromatic π–π stacking interactions [19]. Thus, the adjacent chains of **1** are extended into 2D supramolecular arrays on the {011} plane (figure 3). Second, the C(3)$\cdots$O(3), C(5)$\cdots$O(3), C(9)$\cdots$O(2), and OW1$\cdots$O(1) distances are 3.287, 3.338, 3.069 and 2.678 Å (table S6), respectively, indicating hydrogen bonding

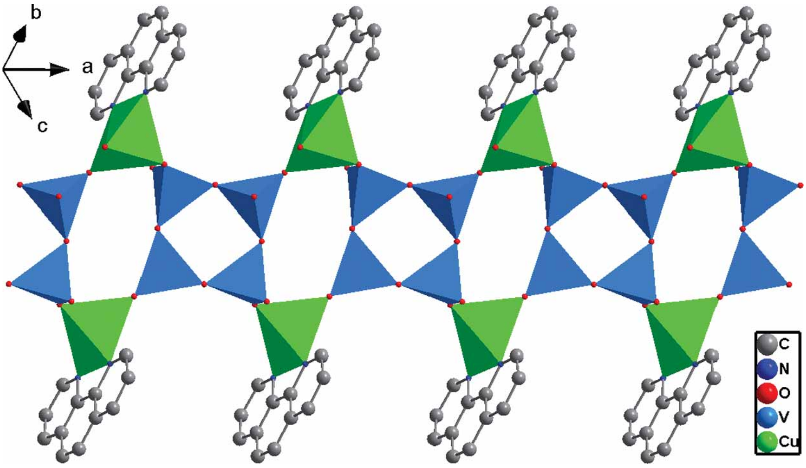

Figure 2. View of the organic–inorganic double-chain ribbon in **1**.

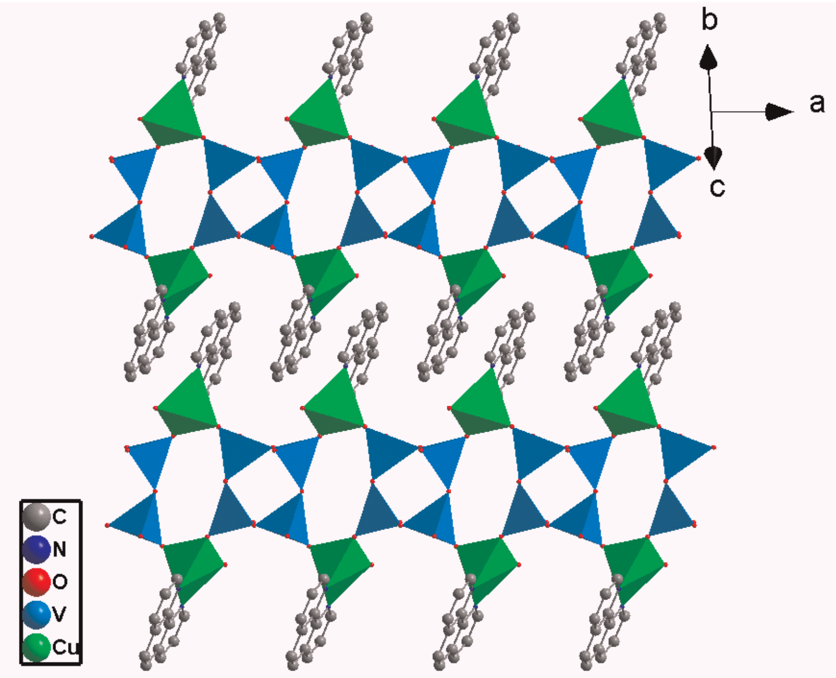

Figure 3. The polyhedron representation of the 2D supramolecular arrays of **1**, showing the aromatic π–π stacking interactions.

interactions [20]. Therefore, the 2D supramolecular arrays are further extended by hydrogen bonding interactions into three-dimensional (3D) supramolecular architecture (figures 4 and S2).

The bond valence sum calculations [21] indicate that all V sites are in the +5 oxidation state in **1**. This result is also supported by the XPS measurement of **1** in

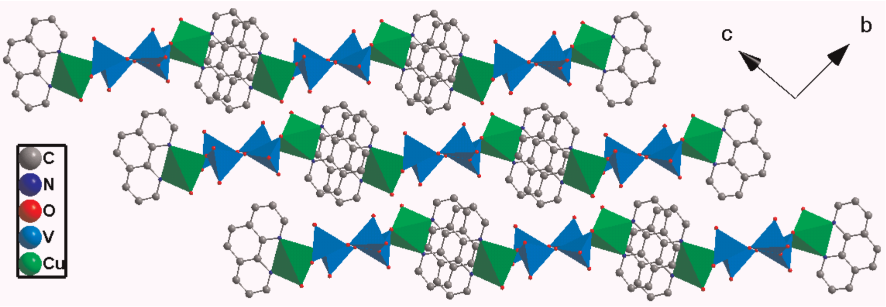

Figure 4. The packing arrangement of compound **1** with 3D structure, viewed along the *a* axis direction.

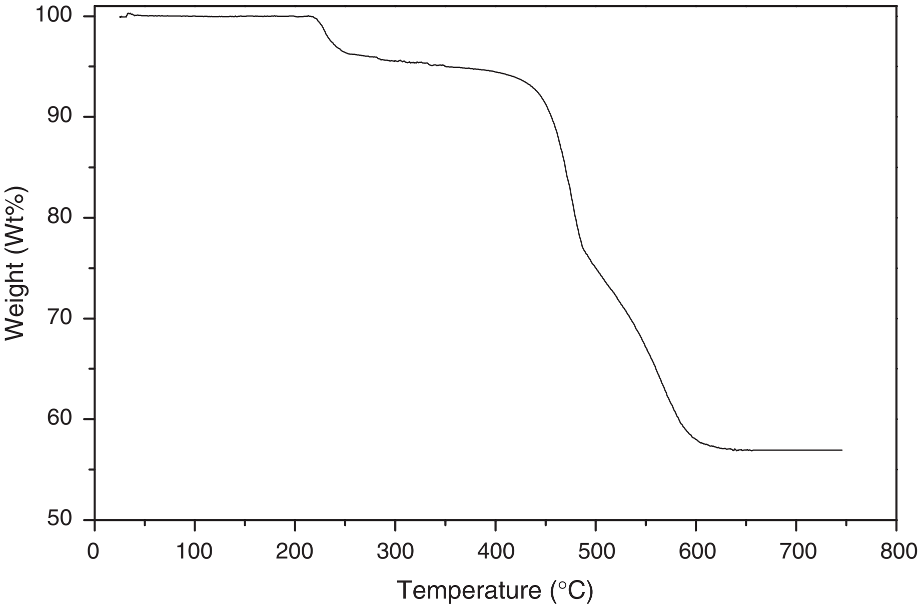

Figure 5. The TG curve of compound **1**.

the energy regions of V_{2p}. The XPS spectrum shows one peak at 516.6 eV as shown in figure S3, attributable to V^{5+} [22]. The bond valence analysis also shows that the Cu site is in the +2 oxidation state. These results are consistent with charge balance considerations.

3.2. *FT-IR spectroscopy*

In the infrared spectrum of compound **1** (as shown in figure S1), the strong bands at 978, 943, 918, 900, 852, 771 and 723 $\mathrm{cm^{-1}}$ could be due to the $\nu(V{=}O)$ or $\nu(V–O–V)$ vibrations [8a]. Bands in the 1622–1143 $\mathrm{cm^{-1}}$ regions in the infrared spectrum are attributed to the characteristic peaks of phen groups [8b].

3.3. *Thermal analysis*

The TG curve of compound **1** (figure 5) exhibits three steps of weight loss. The first weight loss occurs in the range of 215–275°C, corresponding to the release of coordinated water molecules. The observed weight loss (3.99%) is consistent with the calculated value (3.92%). The second weight loss is 17.96% from 295 to 485°C, the third is 20.62% in the temperature range 485–640°C, both assigned to the loss of phen groups. The observed weight loss in the second and third step (38.58%) is in agreement with the calculated value (39.21%). The sample does not lose weight at temperatures higher than 640°C. The thermal stability of compound **1** is comparable to those of other vanadates decorated with transition-metal–ligand functional units [8, 23]. However, compared with other metal–organic coordination polymers containing phen ligand [24], the thermal stability of compound **1** is significantly higher, in accord with the fact that organic–inorganic hybrid products are usually stable. The inorganic {V/O} backbone increases the thermal stability of metal–organic complexes.

4. Conclusions

In summary, we have prepared the first 1D vanadate complex constructed from V_4O_{12} tetravanadate clusters linked *via* metal–organic complex fragments. The successful isolation of **1** further confirms the observation that the transition metal complex moieties may profoundly influence the structure of the vanadium oxide framework.

Supplementary material

CCDC reference number: 261157.

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