An Unusual Chain Structure of Decavanadates $V_{10}O_{28}$ Linked by $Zn(en)_2$ Units

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A new decavanadate $[Zn(en)_2]_3[V_{10}O_{28}]\cdot 5H_2O$ (**1**), (en = ethylenediamine) has been hydrothermally synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. It is a structural feature of compound **1** that each $[V_{10}O_{28}]^{6-}$ cluster provides four bridging oxygen atoms of two pairs of opposite $[VO_6]$ octahedra to graft four $[Zn(en)_2]^{2+}$ complexes, observed for the first time for the $[V_{10}O_{28}]^{6-}$ cluster. The resulting array represents the second example of a chain based on these decavanadates linked by transition metal complexes.

Key words: Polyoxometalate, Vanadate, Chain Structure, Hydrothermal Synthesis

Introduction

Over the past decade, polyoxometalates (POMs) have been used as ideal inorganic building blocks for the construction of inorganic–organic hybrid materials, as they exhibit not only a wide variety of robust structural motifs of different sizes and topologies, ranging from closed cages and spherical shells to basket-, bowl-, barrel-, and belt-shaped structures [1], but also have their numerous practical applications and a remarkable range of physical properties [2 – 7]. Currently, widespread interest in POM chemistry is focused on the modification and functionalization of polyoxoanions by transition metal complexes (TMCs) through their terminal or bridging oxygen atoms to extend their structural multiplicity and versatility, leading to novel species with unexpected structures and properties [8 – 14]. Many chemists have paid great attention to the rational design and synthesis of such compounds [15 – 19]. These efforts have achieved significant progress, and many such compounds have been obtained by selecting the appropriate POMs as building blocks, such as Keggin- [20 – 25], Dawson- [26], Anderson- [27, 28], metatungstate- [29 – 31], and octamolybdate-type POMs [32, 33]. However, compared with other POMs, hybrids constructed by decavanadates have been rarely reported so far. It is well known that there are three kinds of decavanadates: (i) $[V_{10}O_{28}]^{6-}$ consists of ten edge-sharing $[VO_6]$ octahedra and exhibits a ball shape structure; (ii) $[V_{10}O_{26}]^{4-}$ consists of eight vertex-sharing VO_4 tetrahedra and two VO_5tetragonal pyramids and shows an oblate spherical structure; (iii) $[V_{10}O_{25}]^{4-}$ consists of VO_4 tetrahedra and VO_5 tetragonal pyramids and shows a layer structure. Especially the ball-shaped $[V_{10}O_{28}]^{6-}$ cluster has drawn more attention than other decavanadate clusters [34 – 45]. For example, a supramolecular intercluster compound $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$ was reported by Jansen *et al.* [46], and a hydrogen bond-supported 3D supramolecular compound $[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_4$ was reported by Kitagawa *et al.* [47]. However, up to now all reported $[V_{10}O_{28}]^{6-}$ compounds have individual units, except

$[(CuL)_{0.5}(H_2L)_{1.5}][H_2V_{10}O_{28}]\cdot 6H_2O$ with a chain of $[V_{10}O_{28}]^{6-}$ clusters [48]. So, the design and synthesis of compounds with chains or higher dimensional structures remain a challenge.

In previous work [49], choosing en molecules, copper cations and $[V_{10}O_{28}]^{6-}$ anions, we have isolated a compound $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]\cdot 12H_2O$ (**2**), in which the decavanadate anions connect $[Cu(en)_2H_2O]^{2+}$ complexes as bidentate ligands with the bridging oxygen atoms forming a discrete structure. Through replacing copper cations by zinc cations, we now obtained a compound $[Zn(en)_2]_3[V_{10}O_{28}]\cdot 5H_2O$ (**1**), which is an unusual example of a chain structure of $[V_{10}O_{28}]^{6-}$ anions, with each of them using four bridging oxygen atoms to bind to $Zn(en)_2$ units.

Experimental

Materials and methods

All reagents were purchased commercially and were used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. V and Zn were analyzed on a Plasm-spec(I) ICP atomic emission spectrometer. The IR spectrum was obtained on an Alpha Centaur FT/IR spectrometer in the 400 – 4000 cm^{-1} region using KBr pellets. The thermogravimetric (TG) analysis was carried out on a Perkin-Elmer TGA7 instrument in air with a heating rate of 10 °C min^{-1}.

Synthesis of $[Zn(en)_2]_3[V_{10}O_{28}]\cdot 5H_2O$

Compound **1** was hydrothermally prepared in 33 % yield (based on Zn). A mixture of 0.58 g $ZnSO_4\cdot 7H_2O$, 0.95 g NH_4VO_3, 0.28 mL en, and 18 mL water in a molar ratio of 1 : 4.1 : 2.1 : 500, was stirred for 2 h at 60 °C. Then the solution was sealed in a 23 mL Teflon-lined autoclave and heated to 180 °C for 4 d with a starting pH of 5.46 adjusted by 6 M HCl. After cooling slowly to room temperature (20 h), light-yellow block-shaped crystals were isolated. The crystals were filtered and dried at room temperature. Anal. for **1** (%): calcd. C 8.30, H 3.55, N 10.57, V 32.03, Zn 12.34; found C 8.22, H 3.61, N 10.37, V 32.10, Zn 12.28.

X-Ray crystallography

Crystallographic data for compound **1** were measured on a Bruker SMART-CCD diffractometer, with monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure of **1** was solved by Direct Methods and refined by a full-matrix least-squares refinement on F^2 using the SHELXTL crystallographic software package [50]. The organic hydrogen atoms were generated geometrically. The hydrogen atoms of the water molecules (O2 and O3) were located from difference Fourier maps. The hydrogen atoms of the half-occupied water molecule (O1) could not be found and were not included into structure factor calculations. The crystal data and numbers pertinent to data collection and structure refinement of **1** are summarized in Table 1.

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

Compound	**1**
Formula	$C_{12}H_{56}N_{12}O_{33}V_{10}Zn_3$
*M*r	1590.23
Crystal size, mm^3	$0.14 \times 0.12 \times 0.12$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	12.9266(6)
b, Å	11.7875(5)
c, Å	16.6458(7)
β, deg	109.386(1)°
V, $Å^3$	2392.56(9)
Z	2
D_{calcd}, g cm^{-3}	2.21
μ(MoK_α), mm^{-1}	3.4
F(000), e	1576.0
hkl range	$-16 \le h \le 17$
	$-13 \le k \le 15$
	$-22 \le l \le 18$
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.663
Refl. measd / unique / R_{int}	5937 / 5869 / 0.0498
Param. refined	323
$R1(F)$ / $wR2(F^2)$[a,b] (all refls.)	0.0829 / 0.1657
GoF (F^2)[c]	1.050
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	1.647 / −0.715

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CCDC 806185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of the structure

Single-crystal X-ray diffraction analysis has revealed that **1** is constructed from $[V_{10}O_{28}]^{6-}$ anions, Zn^{2+} cations and en ligands, as shown in Fig. 1. All V and Zn atoms are in +V and +II oxidation state, respectively, confirmed by bond valence sum (BVS) calculations [51] (the average BVS values are 5.03 for V and 2.19 for Zn) and the charge balance.

The centrosymmetric $[V_{10}O_{28}]^{6-}$ anion consists of five edge-sharing $[VO_6]$ octahedra, similar to the deca-

vanadate structures reported in the literature [34 – 45]. There are two crystallographically independent Zn ions in the structure of **1**: Zn1 is hexa-coordinated in an octahedral geometry by four nitrogen atoms of two en molecules and two oxygen atom of two $V_{10}O_{28}$ clusters, the entire complex having crystallographically imposed inversion symmetry. Zn2 is penta-coordinated in a rectangular pyramidal geometry ($\tau = 0.0885$ for Zn2 [52]) by four nitrogen atoms of two en molecules and one oxygen atom of a $V_{10}O_{28}$ cluster (Figs. 2a and 2b). The bond lengths around the Zn atoms are in the range 2.544 – 2.546 Å (Zn–O) and 1.988 – 2.029 Å (Zn–N); the O–Zn–O angles are of 180° and the N–Zn–N angles are in the range 83.60 – 180.00°. Note that the distance Zn–O (av. 2.545 Å) is shorter than the sum of the van der Waals radii of Zn and O (2.91 Å) [53], implying a long-range coordination bond.

It deserves to be mentioned here that each $[V_{10}O_{28}]^{6-}$ cluster provides four bridge oxygen atoms (O10, O10A, O11, and O11A) of two pairs of opposite $[VO_6]$ octahedra to graft four $[Zn(en)_2]^{2+}$ complexes, which is observed with the decavanadate $[V_{10}O_{28}]^{6-}$ cluster (Fig. 1) for the first time. Another structural feature of **1** is a coordination polymer chain structure which can be described as follows: each $[V_{10}O_{28}]^{6-}$ cluster is bonded to two $Zn2(en)_2$ units forming $[Zn(en)_2]_2[V_{10}O_{28}]$ as a recurring motif, and then each

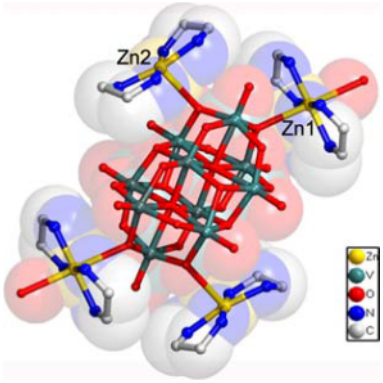

Fig. 1. (color online). View of the structural unit of **1**. All hydrogen atoms and water molecules are omitted for clarity.

$Zn1(en)_2$ unit bridges two $[Zn(en)_2]_2[V_{10}O_{28}]$ blocks to achieve a chain (Fig. 2c), which represents the second example where $[V_{10}O_{28}]^{6-}$ clusters are linked by transition metal complexes. Furthermore, hydrogen-bonding interactions exist between the oxygen atoms of the $[V_{10}O_{28}]^{6-}$ clusters and the hydrogen atoms of the en molecules, with N–H···Od distances in the range of 2.890 – 3.302 Å, forming a 3D supramolecular framework (Fig. 2d).

IR spectrum

The IR spectrum of **1** (Fig. 3, left) exhibits the characteristic bands of the $[V_{10}O_{28}]^{6-}$ structure at 953, and

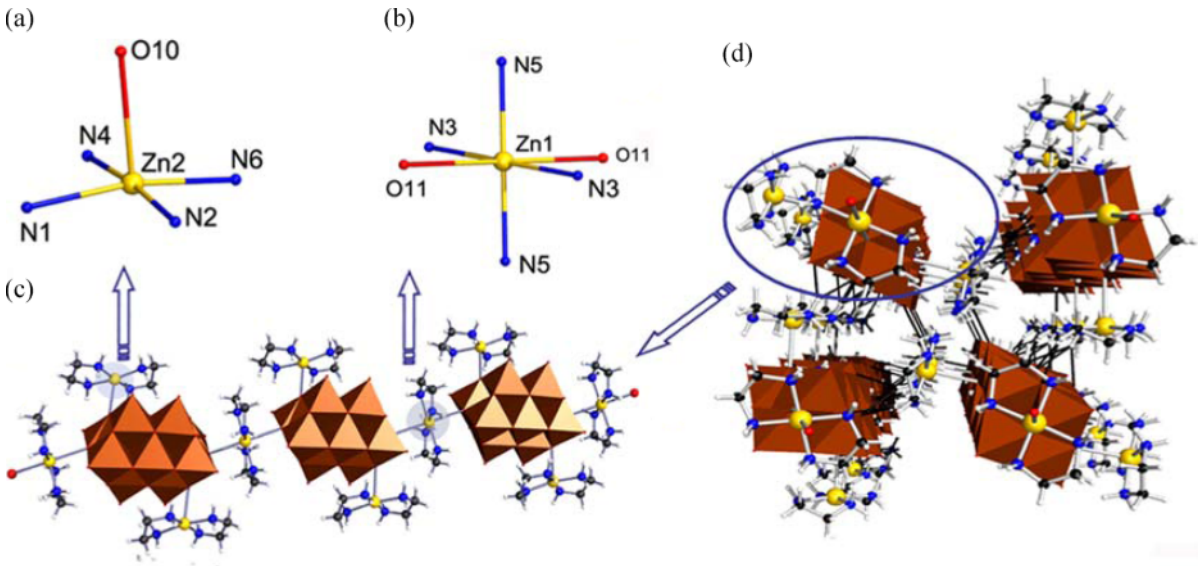

Fig. 2. (color online). Details of the coordination modes of Zn1 (a) and Zn2 (b); diagram of the chain (c) and the 3D supramolecular framework (d). Black bonds represent the hydrogen-bonding interactions in the framework.

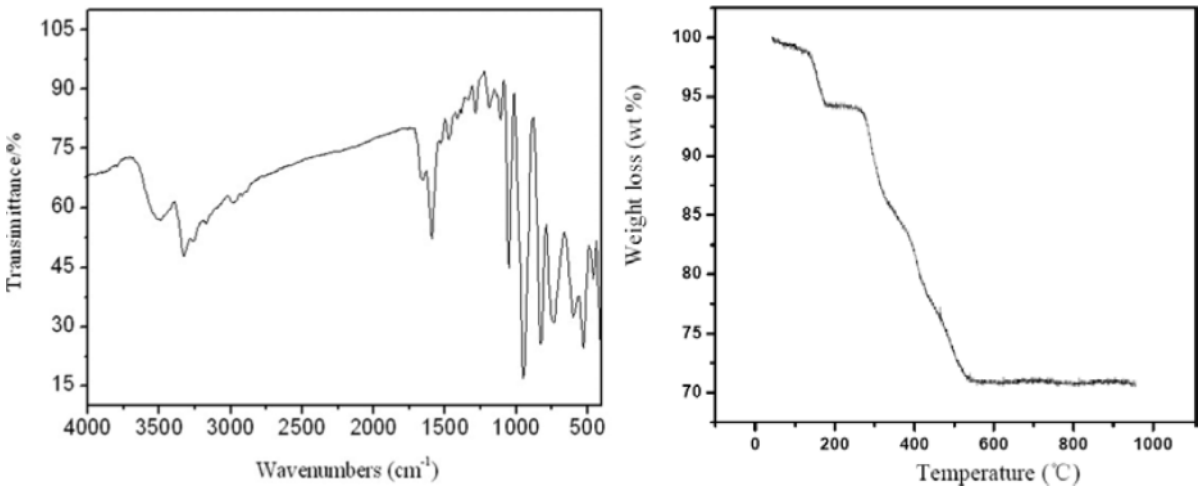

Fig. 3. IR spectrum (left) and TG curve (right) of compound **1**.

826/528 cm^{-1}, which are, respectively, attributed to ν(V–O_t) and ν(V–O_b) [48, 54]. In addition, the peaks in the 1055 – 1606 cm^{-1} region can be assigned to the ethylenediamine molecules, and the peak at 3505 cm^{-1} is attributed to ν(H–O) of water molecules.

Thermal analysis

The TG analysis of **1** was performed in the temperature range of 25 – 1000 °C (Fig. 3, right). The first weight loss of 6.2 % (calcd. 5.6 %) in the temperature range 25 – 175 °C, corresponds to the loss of water molecules. The second weight loss of 22.9 % (calcd. 22.4 %) in the temperature range 175 – 515 °C corresponds to the loss of ethylenediamine ligands. The whole weight loss of 29.1 % is in agreement with the calculated value 28.1 %.

Conclusions

A new chain structure built of decavanadate clusters linked by zinc complexes has been synthesized, which represents the second example of decavanadate $[V_{10}O_{28}]^{6-}$ anions being connected by transition metal complexes into a 1D motif. In this chain, each $[V_{10}O_{28}]^{6-}$ cluster provides four bridging oxygen atoms to bind $[Zn(en)_2]^{2+}$ complexes, indicating that the bridging oxygen atoms are more active than the terminal oxygen atoms in this coordinative interaction. This concept may be useful for further design of decavanadates with transiton metal complexes. The successful synthesis of this compound will inspire us in expanding our work to include high-dimensional frameworks based on the $[V_{10}O_{28}]^{6-}$ cluster *via* the introduction of other kinds of metal cations and organonitrogen ligands. More work in this field is underway.

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