A Composite Based on {VO₃}ₙⁿ⁻ Chain Containing Two Different Types of Organic Ligands

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The composite compound, [Cu(1,10-phen)(en)H₂O][Cu(en)₂]₀.₅[V₃O₉] (1,10-phen = 1,10-phenanthroline, en = ethylenediamine) (**1**) has been prepared by solution diffusion method. Compound **1** consists of one 1D {VO₃}ₙⁿ⁻ chain formed by corner-sharing VO₄ tetrahedra and two different types of cations [Cu(1,10-phen)(en)H₂O]²⁺ and [Cu(en)₂]²⁺. The adjacent 1D {VO₃}ₙⁿ⁻ chain are further bridged by [Cu(en)₂]²⁺ complexes through Cu···O weak interactions to form a 2D network.

Key Words: Polyoxometalates, Polyoxovanadates, Network, Cluster.

INTRODUCTION

Polyoxometalates (POMs) are a large family of anionic metal-oxygen clusters made up of early transition metals[1,2]. As one of most outstanding subclass in polyoxometalate chemistry, polyoxovanadates (POVs) has generated significant interest owing to their intriguing structural diversity and potential applications in the fields of catalysis[3,4] and lithium batteries[5,6]. Up to now, a number of polyoxovanadate clusters containing the {VO₃}ₙⁿ⁻ chain have been reported[7-10], such as, [Cu(dien)V₂O₆·H₂O][11], [Cu(bipy)₂V₂O₆][12], [M(dpa)V₂O₆] (M = Zn, Cu)[7] and [M(bipy)(H₂O)(V₂O₆)][13]. To the best of our knowledge, the reported polyoxovanadate clusters based on {VO₃}ₙⁿ⁻ chains[7-13] are synthesized under hydrothermal conditions and contain one type of organic ligand, however, no analogous compound containing mixed organic ligands have been reported. In this context, we simultaneously employ 1,10-phenanthroline and ethylenediamine to synthesize novel polyoxometalates with mixed organic ligands. Fortunately, we obtained a new compound, [Cu(1,10-phen)(en)H₂O] [Cu(en)₂]₀.₅[V₃O₉] (**1**).

EXPERIMENTAL

K₇HNb₆O₁₉·13H₂O was prepared according to procedures in the literature[14] and confirmed by IR spectrum. Other reagents were purchased from commercial sources and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded on a Nicolet 170SXFT/IR spectrometer using KBr pellets in the range of 4000-400 cm⁻¹.

Preparation of compound 1: 4 mL dimethyl sulfoxide solution containing Cu(NO₃)₂·3H₂O (0.2 mmol), 1,10-phenanthroline (0.4 mmol) and 0.1 mL ethylenediamine, 4 mL mixed solvent of DMSO/H₂O (1:1, volume ratio) and 4 mL H₂O solution containing K₇HNb₆O₁₉·13H₂O (0.1 mmol) and NaVO₃·2H₂O (0.63 mmol) were dropped slowly in a 20 mL test tube in sequence. The test tube was sealed with film and left at room temperature. After three months, blue crystals of [Cu(1,10-phen)(en)H₂O][Cu(en)₂]₀.₅[V₃O₉] (**1**) were obtained in a yield of 23 % (based on V). Anal. calcd. (%) for compound **1**: C, 27.33; H, 2.56; N, 11.95. Found (%): C, 27.45; H, 2.47; N, 11.82.

Crystal data for compound **1** were collected at 296(2) K on Bruker APEX-II CCD detector with graphite monochromatic MoKₐ radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares on F² using the SHELXTL-97 program package[15,16]. All of the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were added according to theoretical models in compound. The crystal data and structure refinement for compound **1** was summarized in Table-1. Selected bond lengths (Å) and angles (°) for compound **1** were listed in Table-2. CCDC number 818755.

RESULTS AND DISCUSSION

The single crystal X-ray diffraction analysis revealed that compound **1** is composed of one [V₃O₉]³⁻ cluster, two discrete cations [Cu(1,10-phen)(en)H₂O]²⁺ and [Cu(en)₂]²⁺ (Fig. 1). All the V atoms display tetrahedral coordination geometry, which

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR COMPOUND 1

Formula	$C_{16}H_{18}Cu_{1.5}N_6O_{10}V_3$
Formula weight	702.5
Crystal system	Monoclinic
Space group	P21/c
a (Å)	7.3850(4)
b (Å)	17.6108(10)
c (Å)	19.2592(9)
β (°)	106.837(2)
Volume (Å^3)	2397.4(2)
Z	2
D_c (Mg/m^3)	1.946
μ (mm^{-1})	2.504
θ range (°)	1.60-25.00
Limiting indices	$-8 \le h \le 8$, $-12 \le k \le 20$, $-22 \le l \le 20$
Reflection collected	11559
Independent reflections	4168 (R_{int} = 0.0268)
R_1, ωR_2 [I >2σ(I)]	0.0361, 0.1125
R1, ωR_2 (all data)	0.0451, 0.1322

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

TABLE-2
SELECTED BOND DISTANCES (Å) AND
BOND ANGLES (°) FOR COMPOUND 1

Bond	d (Å)	Angle	ω (°)
V(1)-O(1)	1.635(4)	O(1)-V(1)-O(2)	108.9(2)
V(1)-O(3)	1.802(3)	O(2)-V(1)-O(3)	110.13(18)
V(2)-O(3)	1.820(3)	O(2)-V(1)-O(8)	108.13(18)
V(2)-O(5)	1.629(3)	O(5)-V(2)-O(4)	108.30(19)
V(3)-O(6)#2	1.806(3)	O(4)-V(2)-O(3)	107.77(16)
V(3)-O(8)	1.795(3)	O(4)-V(2)-O(6)	106.64(15)
Cu(1)-N(3)	2.006(3)	O(9)-V(3)-O(7)	107.8(2)
Cu(1)-N(1)	2.020(3)	O(7)-V(3)-O(8)	110.90(18)
Cu(1)-O(1W)	2.210(3)	O(7)-V(3)-O(6)#2	109.68(16)
Cu(2)-N(5)#1	2.003(4)	V(1)-O(3)-V(2)	133.08(18)
Cu(2)-N(6)#1	1.996(3)	V(3)-O(8)-V(1)	141.4(2)
V(1)-O(2)	1.637(4)	O(1)-V(1)-O(3)	108.91(18)
V(1)-O(8)	1.805(3)	O(1)-V(1)-O(8)	108.49(18)
V(2)-O(4)	1.641(3)	O(3)-V(1)-O(8)	112.20(16)
V(2)-O(6)	1.824(3)	O(5)-V(2)-O(3)	110.28(17)
V(3)-O(7)	1.644(3)	O(5)-V(2)-O(6)	110.85(17)
V(3)-O(9)	1.616(3)	O(3)-V(2)-O(6)	112.79(14)
Cu(1)-N(4)	2.018(4)	O(9)-V(3)-O(8)	108.77(17)
Cu(1)-N(2)	2.040(4)	O(9)-V(3)-O(6)#2	109.02(17)
Cu(2)-N(5)	2.003(4)	O(8)-V(3)-O(6)#2	110.59(16)
Cu(2)-N(6)	1.996(3)	–	–

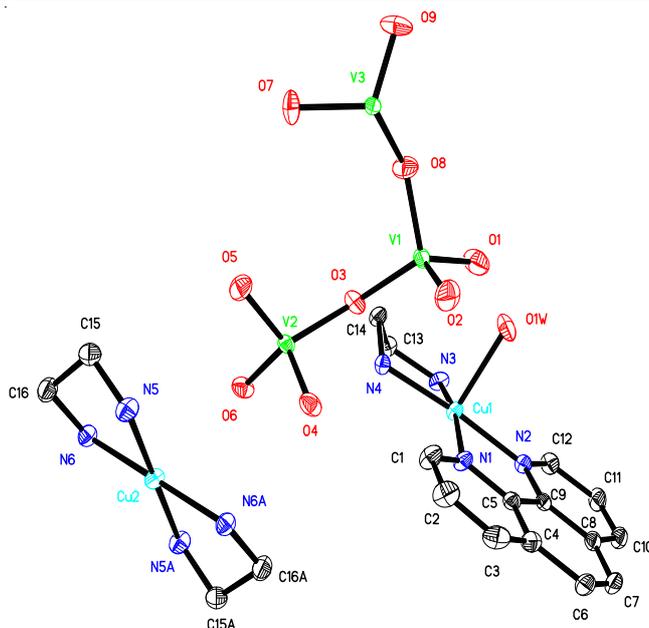Symmetry codes for compound 1: #1 -x,-y-1,-z-1; #2 x+1,y,z; #3 x-1,y,z.

Fig. 1. Molecular structure unit of compound 1 showing the atom labeling scheme. All the H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30 % probability level

There are two crystallographic independent Cu atoms (Cu1 and Cu2) exhibiting different coordination geometry. The Cu1 atom in the discrete cation [Cu(1)(1,10-phen)(en)H$_2$O]$^{2+}$ exhibits a square-pyramidal coordination geometry, defined by two nitrogen atoms from one 1,10-phen molecule (Cu-N = 2.020(3) and 2.040(4) Å), two nitrogen atoms from one en molecule (Cu-N = 2.006(3) and 2.018(4) Å) and one oxygen atom from O1W with Cu-O distance of 2.210(3) Å. To our best of knowledge, the Cu atom simultaneously coordinated to different types of organic ligands has rarely been reported[19]. The Cu2 atom in the discrete cation [Cu(2)(en)$_2$]$^{2+}$ displays a nearly square-planar geometry, coordinated by four nitrogen atoms from two en molecules with Cu-N distances of 1.996(3) and 2.003(4) Å. We surmised that the employment of two different organic ligands was a key factor to form such a novel structure, for it not only helped to modulate the basicity of reaction system but also might meet with the coordination requirement of the central metal ions.

An unusual feature of compound 1 is that the adjacent 1D chains are bridged by [Cu(en)$_2$]$^{2+}$ complexes through Cu···O weak interactions (Cu2···O6 = 2.8762(30) Å) to yield a 2D network (Fig. 2). The {VO$_3$}$_n^{n-}$ chains in compound 1 are similar to the chains in [Cu(H$_2$O)(C$_5$H$_{14}$N$_2$)$_2$][VO$_3$]$_2$(C$_5$H$_{14}$N$_2$ = 2,2-dimethyl propyldiamine)[18]. But different from compound 1, the adjacent chains in the literature[18] are linked by the hydrogen bonding interactions between the [Cu(H$_2$O)(C$_5$H$_{14}$N$_2$)$_2$]$^{2+}$ and {VO$_3$}$_n^{n-}$ chains. In addition, another prominent feature of compound 1 is that two [Cu(en)$_2$]$^{2+}$ complexes and two [V$_3$O$_9$]$^{3-}$ clusters from two neighboring chains form a {Cu$_2$V$_6$O$_8$} ring.

As shown in Fig. 3, the IR spectra of compound 1 exhibits intensity bands in the range of 1583-1054 cm^{-1}, which are attributed to the characteristic peaks of 1,10-phen and en ligands. The peaks in the region 997-925 cm^{-1} are assigned to ν(V=O). The bands between 536 and 856 cm^{-1} are ascribed to ν$_{as}$(V-O-V) for bridging oxo-groups[20].

are further corner-sharing to each other to form a 1D {VO$_3$}$_n^{n-}$ infinite chain. The V-O distances and O-V-O bond angles are in the range of 1.616(3)-1.824(3) Å and 106.64(15)-112.79(14)°, respectively, indicating that the VO$_4$ tetrahedra are distorted to some extent. These bond lengths and bond angles fall in the normal ranges and are in agreement with the corresponding ones in the literature[17]. The V-O-V bond angles are in the range of 129.03(18)-141.4(2)°, which is comparable to the corresponding values in the literature[7]. The shortest V-V separation distance of 3.3222(9) Å is too long for the formation of bonding interactions[18]. In the structure of 1, all the terminal oxygen atoms (O1, O2, O4, O5, O7 and O9) are directed out of the chain, as observed in other chains[18].

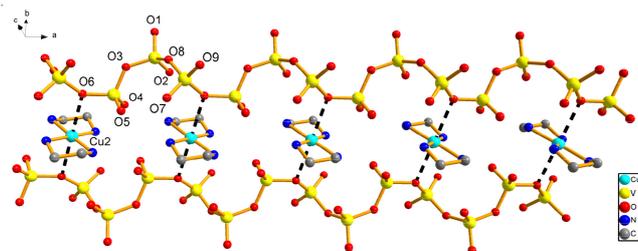Fig. 2. Ball/stick representation of the 2D network in **1**. The dashed lines denote the Cu⋯O weak interactions
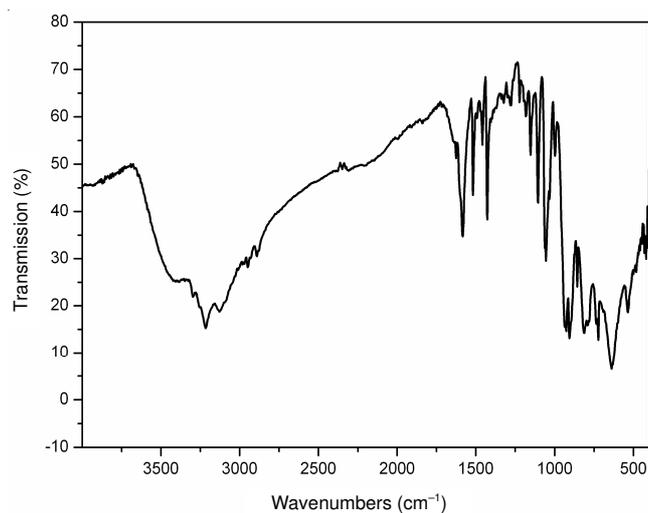

Fig. 3. Infrared spectrum of compound **1** in the 4000-400 cm^{-1} region

Conclusion

In summary, a polyoxovanadate containing two different types of organic ligands has been synthesized by the solution diffusion method and structurally characterized. Compound **1** possess a 1D {VO$_3$}$_n^{n-}$ infinite chain and the adjacent chains are linked by the [Cu(en)$_2$]$^{2+}$ complexes through the weak Cu⋯O interactions to generate a 2D network. The successful preparation of compound 1 demonstrates that it is a useful strategy to employ more than one type of organic ligands to construct the novel polyoxovanadate structure.

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