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A Novel Coordination Polymer Based on Decavanadate Units Linked by Copper(II) Ethylenediamine Complexes

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Summary: A novel coordination polymer$[\{Cu(en)_2\}(V_{10}O_{28})]_n \cdot 2n[Cu(en)_2(H_2O)] \cdot 2n(H_3BO_3) \cdot 2n(H_2O)$ was obtained by hydrothermal reaction. The compound crystallizes in the monoclinic crystal system, in the C2/c space group, with a = 26.490 (3) Å; b = 11.6558 (11) Å; c = 19.8426 (19) Å; β = 124.011 (1)°; V = 5078.6(8) Å^3. The solid structure is formed by polymeric chains, $[Cu(en)_2(H_2O)]^{2+}$ cations, and boric acid and water solvate molecules, stabilized through a multiple hydrogen bond network.

Keywords: copper(II); decavanadate; hydrothermal; infinite chain; Inorganic polymer

Introduction

The field of Inorganic Polymers or Coordination Polymers has been extensively studied, due to their importance in applications in materials science. Among inorganic polymers, three important subgroups can be mentioned: i) metal-organic frameworks (MOFs), ii) hybrid organo-inorganic frameworks and iii) functionalized polyoxometalates (POMs).

The first is basically formed by systems made of transition metal cations bridged by organic ligands, giving rise to structures showing different dimensionalities. The second subgroup comprises inorganic lattices, which are modified by the coordination of transition metal complexes. The third corresponds to extended systems built up by the functionalization of polyoxometalates with coordination complexes. For all the three groups the diversity of structures and dimensionalities that can be obtained, are function of the coordination plasticity, the oxidation state and the nature of the transition metal cation, and are also function of the characteristics of the organic ligand, such as coordination centres, basicity, flexibility, among others.

Copper is a first row transition metal which has centred a great attention in many chemistry groups around the world, due to its coordination plasticity. Several MOFs based on copper can be mentioned, which are based on one type of organic ligand[1,2] or on two types of organic ligands.[3–6] The number of different types of ligands and the topology of the coordination centres of each ligand will determine the dimensionality of the obtained polymer.

A hybrid organo-inorganic system can be understood as the mixture of an inorganic part with organic molecules. A literature investigation about hybrid organo-inorganic extended systems shows that authors define as a hybrid organo-inorganic material, as an extended inorganic lattice which is functionalized with coordination compounds. An important

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class of hybrid organo-inorganic materials are the VPO inorganic lattices (VPO: acronym for frameworks based on vanadium-phosphorus-oxygen) due to their application in catalysis, for example in the oxidation of butane.[7] Moreover, these kind of materials functionalized with copper compounds have been studied due to their structural diversity and magnetic properties.[8–14] In some cases the organic ligand acts as a compensating charge agent (counter-cation),[8] or as a linker and a counter-cation.[9] Capping ligands, such as 2,2′-bipyridine and 1,10-phenantroline, can avoid the condensation of the oxides to form a 3D framework giving rise to lower dimensional solids (1D or 2D).[10–12] On the other hand, the use of bridging ligands such as 4,4′-bipyridine can produce an increase in the final dimensionality of the solid, i.e. bridging 1D inorganic chains into 2D layer structures.[13] There are also examples of VPO inorganic lattices, functionalized by coordination complexes without an organic ligand.[14]

Functionalized polyoxometalates (POMs) give rise to a great variety of materials. Three groups can be mentioned: i) the functionalization with metal cations, or with organic ligands, or with coordination compounds, giving rise to extended or polymeric species, and sometimes also called ‘‘hybrid organo-inorganic’’,[15–20] ii) nano-composites formed by the interaction of POMs with organic polymers[21] and iii) materials formed by direct interaction of two different POMs with organic molecules to give an extended system.[22]

Most of the reported work related to functionalization of polyoxometalates corresponds to heteronuclear POMs. Some of this literature informs systems in which the coordination complex ($Cu(en)_2^{2+}$) appears as a charge compensating agent in the solid.[23–25] Other many examples show that the functionalization with $Cu(en)_2^{2+}$ gives rise to chains (1D structures)[26,27] or layers (2D structures)[28–30] and also 3D structures.[30]

There is an increase in the interest in the POMs as building blocks for ‘‘creating highly sophisticated functional hierarchical systems with multiple interdependent functionalities’’.[31] Within this group vanadium based homometalic polioxometalates are an important family of compounds due to their magnetic properties.[32] It has been shown that large size vanadium clusters permit to stabilize lower valent vanadium ions, giving rise to mixed valence (V(IV)/V(V) species.[33]

In this paper we present the synthesis and structural characterization of a novel coordination polymer based on decavanadate units linked by copper(II)-ethylenediamine complexes $[Cu(en)_2(H_2O)]_2$-$[\{Cu(en)_2\}(V_{10}O_{28})] \cdot 2(H_3BO_3) \cdot 2(H_2O)$ **(1)**.

Experimental Part

Synthesis

The reaction mixture of NH_4VO_3 (1.85 mmoles), $Na_2B_4O_7 \cdot 10H_2O$ (4.94 mmole), $Cu(NO_3)_2 \cdot 3H_2O$ (1.85 mmole), 1,10-phenantroline (1.85 mmole), ethylenediamine (1.24 mmole) and water (1.5 mL) was heated hydrothermally in a Teflon Lined Parr reactor at 170 °C for 72 hours. The initial and final pH values of the reaction mixture were 9.0 and 8.7 respectively. After cooling down the reaction mixture, a purple precipitate was filtered off and the mother liquor was left a week at room temperature, for slow evaporation. Red single crystals were obtained, and used for X-ray crystal structure determination. The purple solid was not suitable for single crystal X-ray diffraction, and the powder X-ray diffractogram showed a different pattern from that of the red crystals. An approximately 5% yield, calculated from vanadium, was obtained.

X-ray Diffraction

An X-ray diffraction quality crystal of **(1)** was picked up from the synthesis vessel and glued on the tip of a capillary glass. Data collection was done on a Bruker Smart APEX2 system[34] at 293 K. SAINT[35] was used for data reduction, while SHELXS[36] included in the Bruker package, was used to solve the structure by direct methods. Subsequent Fourier difference synthesis and refinement allowed location of all non-H atoms. Hydrogen atom positions were calculated after each cycle of least-squares refinement, assigning 0.97Å to the C–H, 0.90Å to the N–H and 0.82Å to the O–H bond lengths respectively. U_{iso}(H) values were set equal to $1.2\,U_{eq}$ of the parent carbon and nitrogen atom, while $1.5\,U_{eq}$ was used for hydrogen atoms of the boric acid molecules. The exception are the water hydrogen atoms, which were located in the Fourier difference map in the final stages of refinement, while the hydrogen atoms of the boric acid molecules, which were located in the Fourier Map, and then refined using the parent atom riding model. U_{eq}'s but no coordinates were subsequently refined for water hydrogen atoms. Additional crystallographic and refinement details are given in Table 1.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-776143. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB21EZ, UK (Fax: int. code +44 (123) 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1.
Crystal parameters and refinement details for $[Cu(en)_2(V_{10}O_{28})]_n \cdot 2n[Cu(en)_2(H_2O)] \cdot 2n\ H_2O \cdot 2n\ H_3BO_3$ O_3 (**1**).

Empirical formula	$C_{12}H_{62}B_2Cu_3N_{12}O_{38}V_{10}$
Formula weight	1704.41
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	A = 26.490 (3) Å b = 11.6558 (11) Å c = 19.8426 (19) Å β = 124.011 (1)°
Volume	5078.6 (8) Å^3
Z	4
Density (calculated)	2.229 kg m^{-3}
Absorption coefficient	3.09 mm^{-1}
F(000)	2686
Crystal size	0.29 × 0.16 × 0.13 mm^3
Theta range for data collection	1.85 to 25.06
Index ranges	$-31 \leq h \leq 30$ $-13 \leq k \leq 13$ $23 \leq l \leq 23$
Reflections collected	15522
Independent reflections	4491 reflections
R	0.034
Goodness-of-fit on F^2	1.06
Max and Min El. diff eÅ^{-3}	0.73 and −0.58 eÅ^{-3}

Structural Characterization

Table 2 presents selected bond and intermetallic distances and selected angles for compound **(1)**.

The structure is constructed around a central $[Cu(en)_2(V_{10}O_{28})]_n^{2n-}$ covalent chain (see Figure 1), running along (001), defined by alternating $[Cu(en)_2]^{2+}$ and $[V_{10}O_{28}]^{6-}$ units. Each copper(II)-bis-ethylenediamine fragment displays an axially elongated octahedral coordination environment (4 + 2) with four short Cu-N distances (Cu2–N5, 2.025 (3)Å and Cu2–N6, 1.993(3)Å). The symmetry of both the vanadate $[V_{10}O_{28}]^{6-}$ anion and the $[Cu(en)_2]^{2+}$ cation is C_i. The anionic chains are parallel and are far enough to not show any direct bonding interaction between them. The inter-chain space is filled by charge balancing $[Cu(en)_2(H_2O)]^{2+}$ cations and solvate water and boric acid molecules.

As aforementioned, charge counterbalance is provided by $[Cu(en)_2(H_2O)]^{2+}$

Table 2.
Selected bond and intermetallic distances (Å) and angles (°) for $[Cu(en)_2(V_{10}O_{28})]_n \cdot 2n[Cu(en)_2(H_2O)] \cdot 2n\ H_2O \cdot 2n\ H_3BO_3$ (**1**).

Selected Bond Distances (Å)			
Cu1–N1	1.989 (4)	Cu1–N2	2.001 (3)
Cu1–N3	1.988 (3)	Cu1–N4	2.035 (4)
Cu1–O2w	2.530 (3)	Cu2–O7	2.621 (1)
Cu2–N6	1.993 (3)	Cu2–N5	2.025 (3)
V1–V1^{i}	3.0619 (10)	V1–V2	3.1062 (7)
V1–V2^{i}	3.1145 (8)	V1–V3	3.0733 (7)
V2–V3	3.1857 (7)	V2–V5^{i}	3.0864 (8)
V3–V4	3.0708 (8)	V3–V5	3.1634 (7)
V4–V4^{i}	3.0534 (11)	V4–V5	3.1033 (8)
Selected Angles (°)			
N3–Cu1–N1	170.04 (15)	N3–Cu1–O2w	90.30 (13)
N3–Cu1–N2	94.79 (14)	N1–Cu1–O2w	99.59 (14)
N1–Cu1–N2	85.18 (16)	N2–Cu1–O2w	83.68 (14)
N3–Cu1–N4	83.17 (17)	N4–Cu1–O2w	92.96 (14)
N1–Cu1–N4	97.41 (18)	N6–Cu2–O7	88.80 (10)
N2–Cu1–N4	176.07 (14)		

Symmetry code: i −x, y, −z + 1/2.

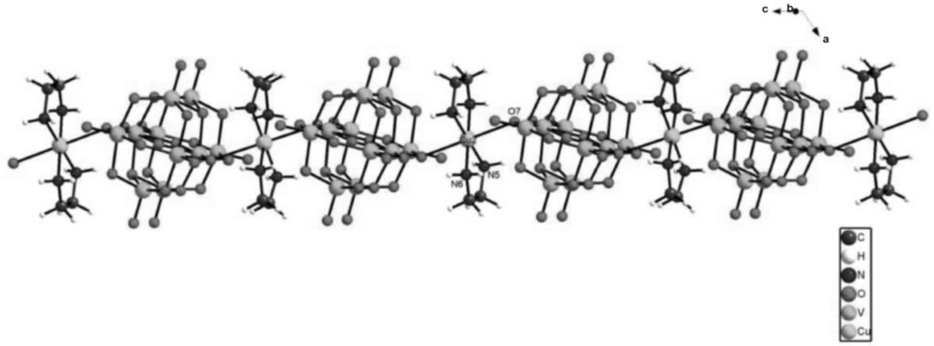

Figure 1.
Chain formed by decavanadate units linked by $[Cu(en)_2]^{2+}$ complex units along the *c* axis.

cations (see Figure 2). These cations can be conveniently described as having a slightly distorted square base pyramid ($\tau = 0.11$) as coordination geometry, with four nitrogen donor atoms from two ethylenediamine molecules in the basal plane, and a water molecule at the apical position. It is important to stress that the cations are not covalently nor coordinatively bonded to any chain or solvate molecule in the lattice. Both the solvate boric acid and water molecules are connected to each other and to the rest of the network, through hydrogen bonding. A summary of the most relevant intermolecular interactions are shown in Figure 3 and given in Table 3.

Results and Discussion

The initial goal of this work was to obtain borovanadate anions, linked by mixed ligand copper(II) complexes, containing 1,10-phenantroline and ethylenediamine. However, boron was not condensated to the oxovanadium groups, remaining in the crystalline lattice as solvate boric acid molecules. On the other hand, 1,10-phenantroline did not form copper complexes, neither appeared as protonated countercations or solvate molecules. Literature reports the compound with formula $[Cu(2,2'\text{-}bipy)_2]_2[H_2V_{10}O_{28}] \cdot (2,2'\text{-}bipy) \cdot H_2O$ where the diimine ligand appears forming a complex and also is present as a solvate molecule.[37] There is another example in literature, where copper forms complexes with 1,10-phenatroline, but the reaction conditions did not permit the bonding of these complexes to the decavanadate anions. Therefore the copper complexes act only as compensating cations in the solid structure.[38]

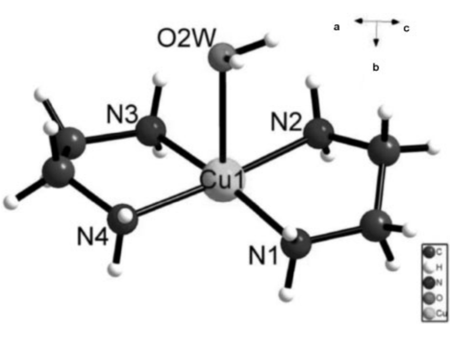

Figure 2.
Counterbalancing $[Cu(en)_2(H_2O)]^{2+}$ cation.

The polymeric species discussed in this work presents a structure consisting of $(V_{10}O_{28})^{6-}$, linked by $Cu(en)_2^{2+}$ cations forming infinite chains running along the *c* crystallographic axis (Figure 1). The distance between the copper atom and the axial oxygen atom from the decavanadate anion is 2.621 Å. The decavanadate anion obtained in this work is completely non protonated. There are examples in the literature, where the obtained decavanadate unit is protonated in the solid structure. Rakovsky et al. reported a triprotonated decavanadate species,[38] while Zheng et al. reported a tetraprotonated anion present in the solid.[39]

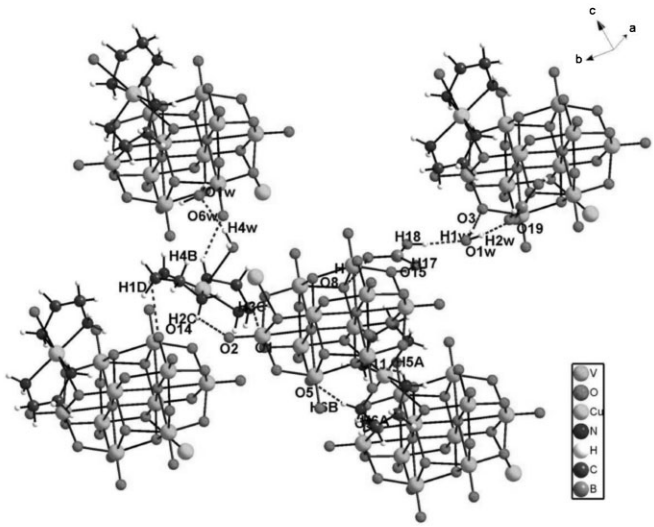

Figure 3.
Hydrogen-bond scheme for $[Cu(en)_2(V_{10}O_{28})]_n \cdot 2n[Cu(en)_2(H_2O)] \cdot 2nH_2O \cdot 2n\ H_3BO_3$ (**1**).

In both cases the decavanadate units are not bonded to other building blocks, which can be due to the protonation of the anion. In our framework the non protonated clusters are bonded to the $Cu(en)_2^{2+}$ building blocks. On the other hand, all the V-O distances correspond to unprotonated groups.[38,39]

The use of ligands which act as bridges, such as pyrazine (pyr) and 2-pyrazinecarboxylate (2pzc) can produce polymeric structures, based only on the secondary metal (copper) and the organic ligands, leading the decavanadates to act as counteranions between infinite chains[40] or in the pores of 2D layers.[39] Wang et al. reported polymeric chains formed by $Cu(H_2O)_4^{2+}$ complexes bridged by pyrazine molecules, which grow along the *b* crystallographic axis.[40] The structure is stabilized by hydrogen bonds between the chains and decavanadate anions in the inter-chain space. Zheng et al. reported a polymeric material which corresponds to a 2D structure formed by the alternated coordination of trans-$Cu(H_2O)_2^{2+}$ octahedral units and square planar copper atoms.[39] The octahedrally coordinated copper atoms contain two water molecules in the axial positions, and in the equatorial plane two nitrogen atoms from different 2pzc molecules, and two oxygen atoms also corresponding to carboxylate groups from different ligands. The square planar copper atom is bridged to the other copper centre through the same carboxylate group. Therefore the pyrazinecarboxylate ligand acts as a bidentate ligand in the square planar copper centres. The other two coordination positions of the square planar copper centres correspond to nitrogen atoms from de 2pzc ligand. The tetraprotonated decavanadate anions are

Table 3.
Hydrogen-bond geometry for $[Cu(en)_2(V_{10}O_{28})]_n \cdot 2n[Cu(en)_2(H_2O)] \cdot 2n\ H_2O \cdot 2n\ H_3BO_3$ (**1**).(Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1D...O14^{iii}	0.90	2.60	3.032 (4)	110
N2—H2C...O2^{i}	0.90	2.62	3.029 (4)	109
N3—H3C...O1	0.90	2.60	3.052 (4)	112
N4—H4B...O6^{iv}	0.90	2.28	3.050 (4)	144
N5—H5A...O11^{ii}	0.90	2.45	3.045 (3)	124
N6—H6A...O9	0.90	2.27	3.000 (4)	139
N6—H6B...O5^{v}	0.90	2.12	2.996 (4)	164
O2w—H4w...O1w^{iv}	0.85	2.05	2.890 (5)	169
O17—H17...O15^{i}	0.82	2.03	2.818 (3)	161
O19—H19...O8	0.82	1.92	2.708 (5)	164
O18—H18...O1w^{vi}	0.82	1.99	2.788 (4)	164
O1w—H1w...O3	0.85	1.92	2.765 (4)	175
O1w—H2w...O19	0.93	1.93	2.871 (4)	166

Symmetry codes: ^{i} −x, y, −z + 1/2; ^{ii} −x, −y + 1, −z; ^{iii} −x, y + 1, −z + 1/2; ^{iv} −x + 1/2, −y + 3/2, −z + 1; ^{v} x, −y + 1, z − 1/2; ^{vi} −x + 1/2, y − 1/2, −z + 1/2.

hydrogen bonded to the layer structure. The rectangular cavity, where the anions are located, is formed by four octahedrally coordinated copper centres at the corners, and four tetracoordinated copper atoms in the centre of the four edges.

The number of reported systems formed by decavanadate and copper complexes is very limited. This work presents a discussion of the few examples mentioned above. The compound in this paper, is the first reported polymeric species based on the functionalization of a non protonated decavanadate anion with copper complexes with diamine ligands.

Conclusion

Under the hydrothermal reaction condition used, the condensation of vanadate and borates did not occur. The generation of unprotonated decavanadate anions during the hydrothermal reaction, permitted their functionalization to produce a polymeric structure.

The reported polymeric material presents two different types of copper complexes in the crystalline framework. The first corresponds to a tetracoordinated copper, acting as a building block in the infinite chains. The second corresponds to pentacoordinated $[Cu(en)_2(H_2O)]^{2+}$ isolated countercations between the chains.

The stabilization of the structure in the solid is due to the hydrogen bonds from the $[Cu(en)_2(H_2O)]^{2+}$ isolated counteractions to the vanadate units, and the boric acid and water molecules, which are also present in the inter-chain space, also hydrogen bonded to the decavanadates.

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