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Hydrothermal syntheses, crystal structures and magnetic properties of two inorganic–organic hybrid materials: $[\{Cu(phen)\}_2(V^{V}O_2)_2V^{IV}O_2(H_2O)(PO_4)_2]$ and $[V_4O_7(2,2'\text{-}bpy)_2(HPO_4)_2]$ (phen = 1,10-phenathroline, bpy = bipyridine)

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Abstract

Two two-dimensional inorganic–organic hybrid materials formulated as $[\{Cu(phen)\}_2(V^{V}O_2)_2V^{IV}O_2(H_2O)(PO_4)_2]$ **1** and $[V_4O_7(2,2'\text{-}bpy)_2(HPO_4)_2]$ **2** have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Both crystallize in the triclinic space group $P\bar{1}$ (no. 2), with cell parameters $a = 8.118(3)$, $b = 9.272(3)$, $c = 10.348(5)$ Å, $\alpha = 96.71(1)$, $\beta = 100.97(1)$, $\gamma = 104.66(1)°$, $V = 728.5(5)$ Å^3, $Z = 1$ for **1** and $a = 8.402(4)$, $b = 9.270(5)$, $c = 9.676(7)$ Å, $\alpha = 97.10(1)$, $\beta = 110.29(1)$, $\gamma = 98.92(1)°$, $V = 685.4(7)$ Å^3, $Z = 1$ for **2**. The structure of **1** is analogous to that of $[\{Cu(phen)\}_2(V^{V}O_2)_3(OH)(PO_4)_2]$ (**1′**) and consists of $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chains that are bridged by $\{(VO_2)(PO_4)\}_2$ 4-membered rings via oxygen atoms into a two-dimensional network. Compounds **1** and **1′** are isostructural but the oxidization states of vanadium atoms in them are not fully same. Thus, **1** and **1′** are relatively rare examples of all V(V) and V(V)/V(IV) mixed valence analogues in the solid state. Compound **2** is also relatively uncommon and features 2,2′-bipy ligands directly coordinated to vanadium atoms. The structure of **2** is constructed by 4-, 6- and 8-membered rings and is topologically relevant to $[V_3O_7(phen)]$. The temperature-dependent magnetic susceptibility of **1** shows alternating ferro- and antiferromagnetic interactions.

Keywords: Vanadium; Organic–inorganic hybrid; Magnetic properties; Hydrothermal

1. Introduction

Inorganic frameworks are highly attractive in the search for new materials because of stability and superior electronic, magnetic and optical properties [1], while organic and coordination compounds built upon molecular building-blocks hold great promises for processability, flexibility, structural diversity, and geometrical control [2]. Incorporation of the two counterparts into a single structure may generate organic–inorganic hybrid composites that enhance or combine the useful properties [3]. The role of organic molecules in the organic–inorganic hybrid composites has been realized in zeolite [4], MCM-41 class [5], transition metal phosphate or phosphonate [6], biomineralization [7] and molybdenum and vanadium oxides [8]. While the organic components are conventionally introduced as charge-compensating and space-filling constituents, they may also act as ligands coordinated to oxide scaffolding or secondary metal ions. The fields of hybrid composites to vanadium oxides mainly concentrate on the following aspects: (a) layered vanadium oxides with interlayer organic cations [9]; (b) discrete cluster-like, one- and two-dimensional vanadium oxide substructure decorated with or linked by secondary-metal complex fragments [10,11]; (c) oxovanadium phosphate or phosphonate with charge-compensating organic cations [12]; (d) vanadium oxides

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with organic ligands directly coordinated [13,14]. Recently, an important advance on hybrid vanadium oxides has been the study of solid-state coordination chemistry of oxovanadium phosphate or phosphonate [15–17]. In this paper, we present two new solid-state coordination complexes of oxovanadium phosphate, namely $[\{Cu(phen)\}_2(V^{V}O_2)_2V^{IV}O_2(H_2O)(PO_4)_2]$ **1** and $[V_4O_7(2,2'\text{-bpy})_2(HPO_4)_2]$ **2**, where phen = 1,10-phenanthroline and 2,2′-bpy = 2,2′-bipyridine.

2. Experimental

All syntheses were carried out in 23 mL Teflon-lined reactor under autogenous pressure with a filling capacity of 50%. The C, H, N microanalyses were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer. Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K at a magnetic field of 1 T on polycrystalline samples with a Maglab System 2000 magnetometer. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$, where χ_m is the molar magnetic susceptibility. The experimental susceptibilities were corrected for the Pascal's constants.

2.1. Synthesis

$[\{Cu(phen)\}_2(V^{V}O_2)_2V^{IV}O_2(H_2O)(PO_4)_2]$ **(1)**. A mixture of V_2O_5 (0.09 g), $Cu(OAc)_2 \cdot H_2O$ (0.10 g), phen (0.16 g), H_3PO_4 (0.20 g, 85%) and H_2O (10 mL) in the molar ratio of 1:1:1.8:3.5:1112 was stirred in air for 20 min and transferred into 23 mL Teflon-lined stainless steel reactor and heated at 160°C for 108 h. Black crystals of **1** (35%) and minor blue crystals $[\{Cu(phen)\}(VO_2)(PO_4)]$[16a] (4%) were recovered after filtration off, washing and dried in air. Anal: Calc. For **1** $C_{24}H_{18}Cu_2N_4O_{15}P_2V_3$: C, 30.53; H, 1.92; N, 5.93. Found: C, 30.37; H, 1.99; N, 5.86. IR (KBr, cm^{-1}): 3605 (w), 3438 (m), 3052 (w), 2924 (w), 1628 (w), 1583 (m), 1426 (s), 1342 (w), 1222 (w), 1056 (s), 1025 (s), 996 (s), 956 (s), 852 (s), 722 (m), 519 (w), 480 (w).

$[V_4O_7(2,2'\text{-bpy})_2(HPO_4)_2]$ **(2)**. A mixture of V_2O_5 (0.09 g), $Cu(OAc)_2 \cdot H_2O$ (0.05 g), 2,2′-bpy (0.15 g), H_3PO_4 (0.20 g) and H_2O (10 mL) in the molar ratio of 1:0.5:1.9:3.5:1112 was stirred in air for 20 min and transferred into 23 mL Teflon-lined stainless steel reactor and heated at 170°C for 144 h. The resulting product was filtered off, washed with deionized water and dried in air. Black crystals of **2** were recovered in 60% yield based on vanadium. Anal: Calc. For **2** $C_{20}H_{18}N_4O_{15}P_2V_4$: C, 25.38; H, 1.42; N, 4.93. Found: C, 25.17; H, 1.29; N, 4.86. IR (KBr, cm^{-1}): 3418 (bs), 3061 (w), 1620 (m), 1581 (m), 1425 (s), 1305 (w), 1081 (s), 1003 (s), 946 (s), 848 (s), 722 (s), 649 (w), 503 (m).

2.2. X-ray crystallography

Data collection were performed at 293 K on a Siemens R3m diffractometer (Mo*K*α, $\lambda = 0.71073$ Å). Lorentz-polarization and absorption corrections were applied. The structures were solved with direct methods (SHELXS-97) [18] and refined with full-matrix least-squares technique (SHELXL-97) [19]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. In all cases, all non-hydrogen atoms were refined anistropically. Hydrogen atoms of organic ligands were geometrically placed. The crystallographic data for **1** and **2** are listed in Table 1. Selected interatomic distances and angles for **1** and **2** are given in Table 2.

CCDC 193582 and 193583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1
Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{24}H_{18}Cu_2N_4O_{15}P_2V_3$	$C_{20}H_{18}N_4O_{15}P_2V_4$
F_w	944.26	820.08
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.118(3)	8.402(4)
b (Å)	9.272(3)	9.270(5)
c (Å)	10.348(5)	9.676(7)
α (deg)	96.71(1)	97.10(1)
β (deg)	100.97(1)	110.29(1)
γ (deg)	104.66(1)	98.92(1)
V (Å^3)	728.5(5)	685.4(7)
Z	1	1
ρ_{calc} (g cm^{-3})	2.152	1.987
$F(000)$	467	408
μ (mm^{-1})	2.558	1.521
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Max. and Min.	0.3858 and 0.3388	0.742 and 0.568
Data/restrains/parameters	3516/0/236	3298/0/206
Goodness-of-fit on F^2	1.062	1.048
R_1[a]	0.0404	0.0536
wR_2[b]	0.1131	0.1330

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

Table 2
Selected bond distances (Å) and bond angles (deg) for **1** and **2**

Compound **1**

	Bond distances		Bond distances
Cu(1)–O(2)	1.957(3)	V(1)–O(1)	2.388(5)
Cu(1)–O(4)	1.975(2)	V(2)–O(8)	1.612(3)
Cu(1)–N(1)	2.008(3)	V(2)–O(7)	1.617(3)
Cu(1)–N(2)	2.027(3)	V(2)–O(6)^c	1.861(3)
Cu(1)–O(4)^a	2.305(2)	V(2)–O(5)	1.871(3)
V(1)–O(2)	1.647(3)	P(1)–O(4)	1.523(2)
V(1)–O(3)^b	1.832(3)	P(1)–O(3)	1.527(3)
V(1)–O(2)^b	1.954(3)	P(1)–O(6)	1.552(3)
V(1)–O(3)	2.147(3)	P(1)–O(5)	1.555(3)

	Bond angles		Bond angles
O(2)–Cu(1)–O(4)	89.4(1)	O(3)–V(1)–O(1)	72.0(1)
O(2)–Cu(1)–N(1)	94.5(1)	O(8)–V(2)–O(7)	108.6(2)
O(4)–Cu(1)–N(1)	171.7(1)	O(8)–V(2)–O(6)^c	111.2(1)
O(2)–Cu(1)–N(2)	161.9(1)	O(7)–V(2)–O(6)^c	110.2(1)
O(4)–Cu(1)–N(2)	92.0(1)	O(8)–V(2)–O(5)	108.2(1)
N(1)–Cu(1)–N(2)	82.1(1)	O(7)–V(2)–O(5)	109.8(1)
O(2)–Cu(1)–O(4)^a	101.4(1)	O(6)^c–V(2)–O(5)	108.9(1)
O(4)–Cu(1)–O(4)^a	80.1(1)	O(4)–P(1)–O(3)	112.5(1)
N(1)–Cu(1)–O(4)^a	106.3(1)	O(4)–P(1)–O(6)	107.3(1)
N(2)–Cu(1)–O(4)^a	96.6(1)	O(3)–P(1)–O(6)	111.5(2)
O(2)–V(1)–O(3)^b	97.6(2)	O(4)–P(1)–O(5)	110.4(2)
O(2)–V(1)–O(2)^b	153.8(1)	O(3)–P(1)–O(5)	106.6(2)
O(3)^b–V(1)–O(2)^b	87.7(1)	O(6)–P(1)–O(5)	108.6(2)
O(2)–V(1)–O(3)	86.4(1)	V(1)–O(2)–Cu(1)	132.9(2)
O(3)^b–V(1)–O(3)	156.4(1)	P(1)–O(3)–V(1)	133.5(2)
O(2)^b–V(1)–O(3)	79.3(1)	P(1)–O(4)–Cu(1)	123.2(1)
O(2)–V(1)–O(1)	85.4(2)	Cu(1)–O(4)–Cu(1)^a	99.9(1)
O(3)^b–V(1)–O(1)	85.2(1)	P(1)–O(5)–V(2)	133.2(2)
O(2)^b–V(1)–O(1)	69.4(2)	P(1)–O(6)–V(2)^c	136.1(2)

Compound 2

	Bond distances		Bond distances
V(2)–O(2)	1.620(3)	V(1)–N(1)	2.281(4)
V(2)–O(3)	1.658(3)	P(1)–O(5)	1.521(3)
V(2)–O(1)	1.787(1)	P(1)–O(6)	1.530(3)
V(2)–O(8)^a	1.838(3)	P(1)–O(8)	1.574(3)
V(1)–O(4)	1.612(4)	P(1)–O(7)	1.588(4)
V(1)–O(5)	1.982(3)	O(1)–V(2)^c	1.787(1)
V(1)–O(6)^b	1.994(3)	O(6)–V(1)^b	1.994(3)
V(1)–O(3)	2.075(3)	O(8)–V(2)^d	1.838(3)
V(1)–N(2)	2.141(4)		

	Bond angles		Bond angles
O(2)–V(2)–O(3)	108.5(2)	O(4)–V(1)–N(1)	164.9(2)
O(2)–V(2)–O(1)	109.8(1)	O(5)–V(1)–N(1)	85.7(1)
O(3)–V(2)–O(1)	110.0(1)	O(6)^b–V(1)–N(1)	88.2(1)
O(2)–V(2)–O(8)^a	108.4(2)	O(3)–V(1)–N(1)	80.2(1)
O(3)–V(2)–O(8)^a	109.4(2)	N(2)–V(1)–N(1)	72.7(1)
O(1)–V(2)–O(8)^a	110.8(1)	O(5)–P(1)–O(6)	117.3(2)
O(4)–V(1)–O(5)	100.1(2)	O(5)–P(1)–O(8)	110.3(2)
O(4)–V(1)–O(6)^b	105.8(2)	O(6)–P(1)–O(8)	108.9(2)
O(5)–V(1)–O(6)^b	88.6(1)	O(5)–P(1)–O(7)	104.0(2)
O(4)–V(1)–O(3)	94.0(2)	O(6)–P(1)–O(7)	109.2(2)
O(5)–V(1)–O(3)	165.8(1)	O(8)–P(1)–O(7)	106.7(2)
O(6)^b–V(1)–O(3)	89.0(1)	V(2)^c–O(1)–V(2)	180.0(1)
O(4)–V(1)–N(2)	93.6(2)	V(2)–O(3)–V(1)	144.2(2)
O(5)–V(1)–N(2)	86.0(1)	P(1)–O(5)–V(1)	139.3(2)
O(6)^b–V(1)–N(2)	160.5(1)	P(1)–O(6)–V(1)^b	133.6(2)
O(3)–V(1)–N(2)	91.7(1)	P(1)–O(8)–V(2)^d	144.6(2)

Symmetry codes:
Compound 1: $^a-x, -y, -z+2$; $^b-x+1, -y, -z+2$; $^c-x, -y-1, -z+2$.
Compound 2: $^ax+1, y, z$; $^b-x, -y+2, -z+1$; $^c-x+1, -y+1, -z+1$; $^dx-1, y, z$.

3. Results and discussion

3.1. Description of crystal structures

There are one copper, one phosphorus, and two vanadium atoms in the asymmetric unit in **1**, as shown in Fig. 1. The Cu(1) is square-pyramidally coordinated by two nitrogen atoms [Cu–N, 2.008(3) and 2.027(3) Å] from a phen ligand and three oxygen atoms [Cu–O, 1.957(3), 1.975(2) and 2.305(2) Å]. The crystallographic site of V(1) is close to an inversion center and the distance V(1)–V(1) is too short. Thus, it is necessary to have half occupation at V(1) site. The V(1) site adopts a square-pyramidal geometry formed by four oxygen atoms and one water molecule. The V(1)–O distances are in the range of 1.647(3)–2.388(5) Å. The O(1) atom comes from water molecule and also has half occupation of site. The V(2) site features a tetrahedron, being coordinated by two terminal oxygen atoms (V–O, 1.612(3) and 1.617(3) Å) and two oxygen atoms from phosphate groups (V–O, 1.861(3) and 1.871(3) Å). Bond valence sum calculation [20,21] confirmed that V(1) and V(2) are tetravalent and pentavalent, respectively.

The structure of **1** consists of $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chains that are bridged by 4-MRs of $\{(VO_2)(PO_4)\}_2$ via oxygen-sharing into a two-dimensional network (Fig. 2(a)). The $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chain (Fig. 2(b)) is formed by edge-sharing or corner-sharing of polyhedra in the sequence of $CuN_2O_3 \rightarrow CuN_2O_3 \rightarrow VO_5 \rightarrow CuN_2O_3$. In other words, the $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chain can also be viewed as constructed from oxygen-sharing of dimeric $[Cu_2(phen)_2O_4]$ units and VO_5 square pyramids. Two copper atoms in a dimeric $[Cu_2(phen)_2O_4]$ units are related by an inversion center and each is bounded to

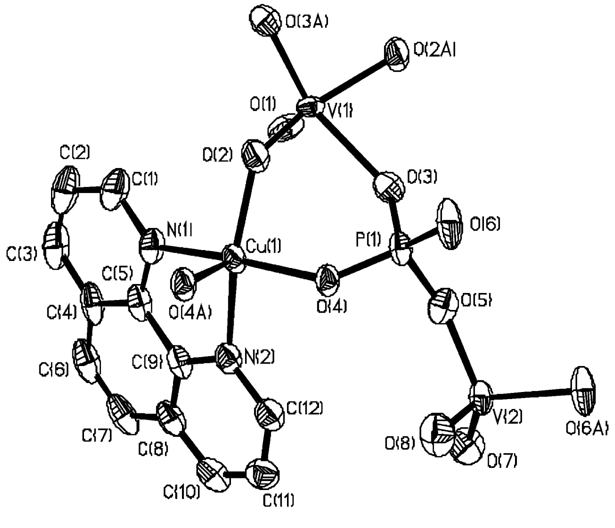


Fig. 1. Perspective view of the coordination environments of the metal atoms in **1** showing the atom-labeling scheme and 35% thermal ellipsoids.

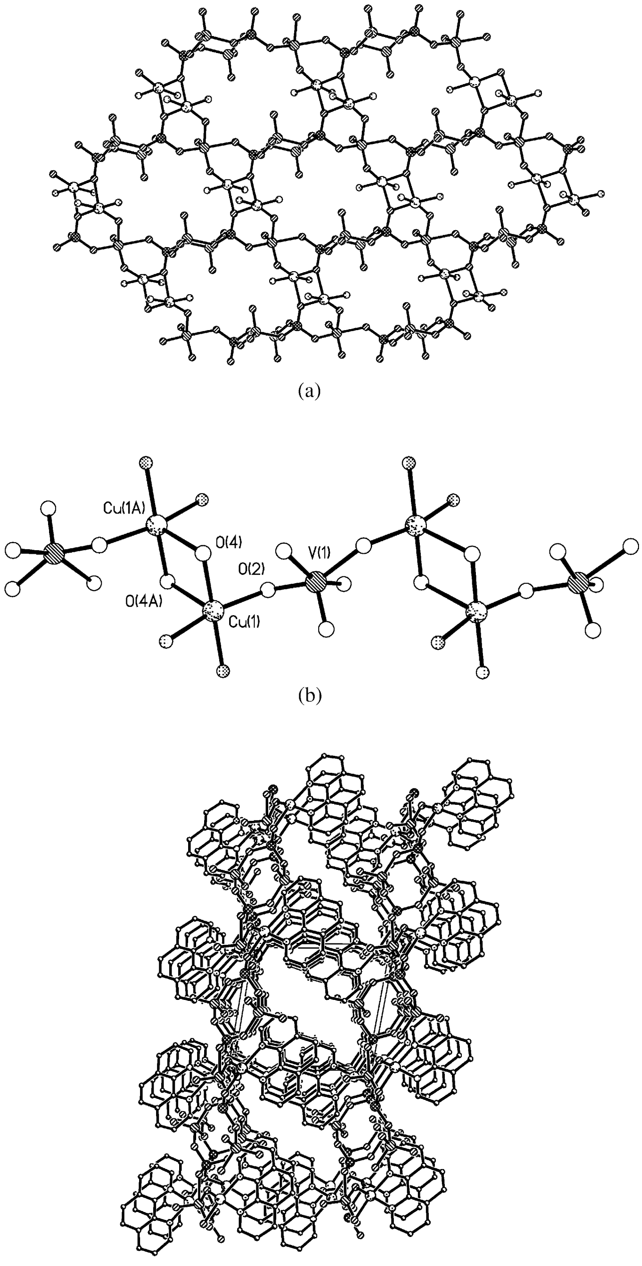
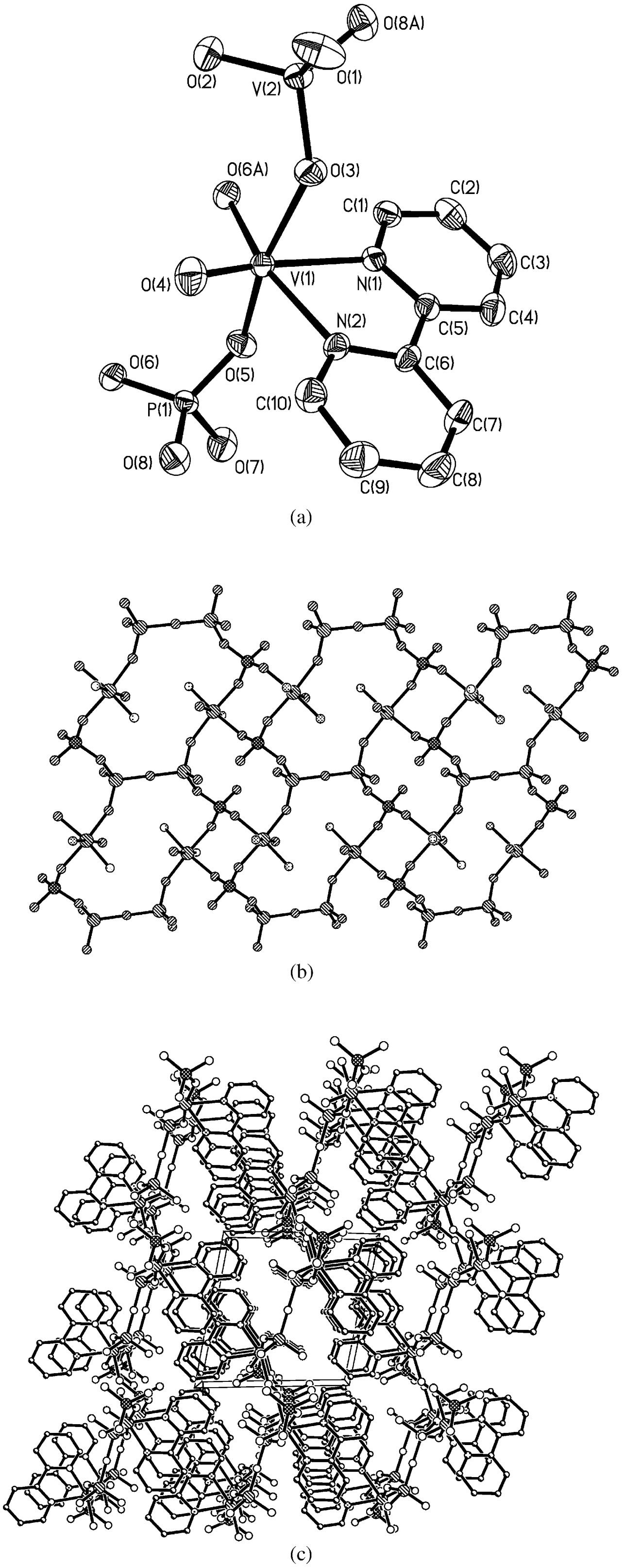


Fig. 2. Perspective views of **1**. (a) The two-dimensional layer viewed along the *c*-axis. (b) The $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chain. For clarity, the carbon atoms of phen are omitted. (c) The packing array of two-dimensional layers viewed along the *a*-axis, showing the interlayer stacking of phen groups.

the other via two oxygen atoms. The intra-dimeric Cu···Cu distance is 3.28 Å and Cu–O–Cu bond angle is 99.9(1)°. The $\{(VO_2)(PO_4)\}_2$ 4-MR is composed of alternative corner-sharing VO_4 and PO_4 tetrahedra. The consequence of the $\{(VO_2)(PO_4)\}_2$ 4-MRs bridging $[\{Cu(phen)\}_2V^{IV}O_6(H_2O)]_\infty$ chains gives rise to $\{Cu_2V_4P_4O_{10}\}$ 10-MRs. Oxygen atoms from one PO_4 tetrahedron bond to the copper and vanadium atoms to form $\{CuVPO_3\}$ 3-MRs.

It is noteworthy that compound **1** is isostructural to compound $[\{Cu(phen)\}_2(V^VO_2)_3(OH)(PO_4)_2]$ (**1′**) in which all vanadium atoms are pentavalent [22]. The square-pyramidal site of vanadium consists of two V = O double bonds [V–O distances 1.602(6) and 1.618(4)] and three V–O single bond [V–O distances 1.825(4), 1.957(4) and 2.148(4) Å] in **1′** but one V = O double bonds [V–O distance 1.647(3) Å] and four V–O single bond [V–O distances 1.832(3), 1.954(3), 2.147(3), 2.388(5) Å] in **1**. Compound **1′** can be viewed as the fully oxidized form of compound **1**. Therefore, compounds **1** and **1′** represent a relatively rare example among all V(V) and V(V)/V(IV) mixed valence analogs in the solid state.

Compared with **1** and other known solid-state coordination complexes of oxovanadium phosphate, the organic 2,2′-bpy ligands in **2** are directly coordinated to vanadium atoms which is relatively uncommon but not unprecedented [23]. The asymmetric unit of **2** consists of 23 non-hydrogen atoms, as shown in Fig. 3(a). The O(1) atom lies on an inversion center. The V(1) site consists of a distorted octahedral center coordinated by two nitrogen atoms [V–N, 2.141(4) and 2.281(4) Å] of a 2,2′-bpy, a terminal oxo [V–O, 1.612(4) Å] and three bridging oxygen atoms connected to VO_4 and PO_4 tetrahedra. The V(2) site consists of a tetrahedral center coordinated by one terminal oxo [V–O, 1.620(3) Å] and three bridging atoms [V–O, 1.658(3), 1.787(1) and 1.838(3) Å] connected to adjacent VN_2O_4, VO_4 and PO_4 polyhedra. One of the four oxygen atoms of PO_4 is pendant and three are connected to one VO_4 tetrahedron and two VN_2O_4 octahedra by corner-sharing connection. In **2**, the corner-sharing connection of VN_2O_4, VO_4, and PO_4 polyhedra results in a chain and the adjacent two chains are linked by V(1)–O–P(1) into a ribbon. The adjacent ribbons are further linked by V(2)–O–V(2) into a two-dimensional layer. The connection gives rise to $\{V_6P_2O_8\}$ 8-MRs, $\{V_4P_2O_6\}$ 6-MRs and $\{V_2P_2O_4\}$ 4-MRs in **2**, as is shown in Fig. 3(b). It should be noted that the structure of **2** shows topological relevance to complex $[V_3O_7(phen)]$ [13], which contains only $\{V_8O_8\}$ 8-MRs and $\{V_4O_4\}$ 4-MRs. The preparation of **2** demonstrates that the replacement of vanadium(V) atoms with cheap phosphorus(V) atoms can generate a relevant topological structure. In $[V_3O_7(phen)]$, adjacent chains are linked together by sharing corners of the VN_2O_4 octahedron and VO_4 tetrahedron [V(1)–O–V(2)] and two VO_4 tetrahedra [V(2)–O–V(2)]. In contrast, adjacent chains in **2** are linked together uniquely by sharing corners of the VN_2O_4 octahedron and PO_4 tetrahedron [V(1)–O–P(1)]. Bond valence sum calculation [20,21] confirmed V(2) site being tetravalent and the pendant O(7) atom of phosphate being protonated. The IR spectrum of **2** shows a strong and broad band at 3418 nm, indicating existence of hydrogen bonded O–H



(a)

(b)

(c)

Fig. 3. Perspective views of **2**. (a) The coordination environments of vanadium and phosphorus atoms in **2** showing the atom-labeling scheme and 35% thermal ellipsoids. (b) The two-dimensional layer viewed along the *c*-axis. (c) The packing array of two-dimensional layers viewed along the *b*-axis direction, showing the interlayer stacking of 2,2′-bpy groups.

groups in **2**. The direct V–N bonds as well as organic 2,2′-bpy ligands in **2** are somewhat reminiscent of the recent reported oxovanadium phosphate $[(V^{IV}O)_3(PO_4)_2(2,2'\text{-bpy})(H_2O)]$ **2′** [23]. However, the structures of **2** and **2′** are quite different. **2′** has a one-dimensional tubular chain-like structure in which all vanadium sites are tetravalent and show octahedral geometry; in contrast, **2** has a two-dimensional layered structure in which vanadium sites are V(IV/V) mixed valent and show octahedral or tetrahedral geometries. In a different expressing way, the two-dimensional layer of **2** is formed by corner sharing of $\{V_2P_2O_4\}$ 4-MRs and $[V_2O_7]$ groups.

In addition, it should be noted that interlayer phen in 1 and 2,2′-bpy in **2** are stacked in a parallel and displaced fashion with the interplanar separations of ca. 3.3 and 3.4 Å, respectively (Figs. 2(c) and 3(c)), similar to $[Zn(phen)Zn(VO)(PO_4)_2]$, indicating there are very strong $\pi-\pi$ stacking interactions [16]. Therefore, the two-dimensional layers of **1** and **2** are further extended into three-dimensional supramolecular arrays via aromatic $\pi-\pi$ stacking interactions between adjacent aromatic rings.

3.2. Magnetic properties

The variable-temperature (2–300 K) magnetic susceptibilities of **1** have been measured on a crystalline sample in a field of 1 T. A plot of $\chi_m T$ vs. T is shown in Fig. 4, where χ_m is the molar magnetic susceptibility. The $\chi_m T$ value at 300 K is $1.08\,cm^3\,K\,mol^{-1}$ and the corresponding effective magnetic moments is 2.94 B.M., which is close to the spin-only value of two Cu^{II} ions and one V^{IV} ion (3.00 B.M.). The $\chi_m T$ value decreases smoothly with decreasing temperature, obeying the Curie–Weiss law with a negative Weiss constant, and reaches the minimum of $0.92\,cm^3\,K\,mol^{-1}$ at 85 K. Upon further decrease in temperature, the $\chi_m T$ value increases to reach a maximum of $0.99\,cm^3\,K\,mol^{-1}$ at 14 K before decreasing again. It is apparent that compound **1** shows antiferromagnetic interactions in the high-temperature region which is dominated by a residual orbital contribution and ferromagnetic interactions in low-temperature region. Taking the structure of **1** into consideration, there are two super-exchange pathways in the $[\{Cu(phen)\}_2V^{IV}(OH)_2O_5]_\infty$ chain: the $Cu^{II}\cdots Cu^{II}$ exchange via bis-oxo bridges and $Cu^{II}\cdots V^{IV}$ exchange via one oxygen bridge. The Cu···Cu distance is 3.28 Å and Cu–O–Cu bond angle is 99.9(1)°. The $Cu^{II}\cdots V^{IV}$ distance is 3.31 Å and the Cu–O–V bond angle is 132.9(2)°. It is well-known that a bis-oxo bridge tends to transmit antiferromagnetic coupling [24]. Thus, the ferromagnetic properties of **1** at low temperature may be the result of $Cu^{II}\cdots V^{IV}$ ferromagnetic interactions. In addition, the existence of very week $Cu^{II}\cdots Cu^{II}$

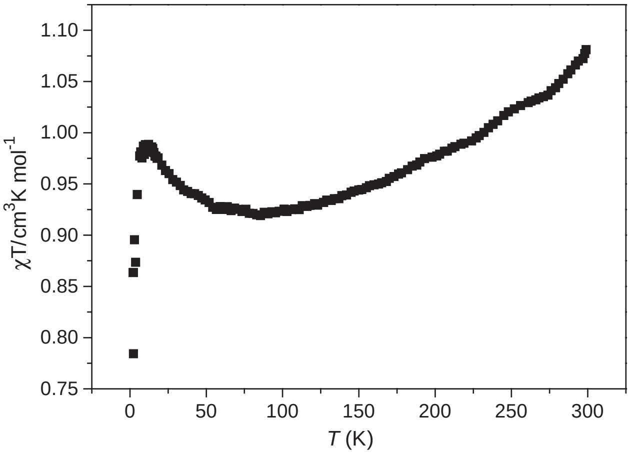


Fig. 4. The temperature dependence of $\chi_m T$ for **1**.

magnetic interactions in **1** leads to a non-magnetic ground state.

4. Conclusions

Two new layered solid-state coordination complexes of oxovanadium phosphate were synthesized and structurally characterized. Compound **1** with alternating ferro- and antiferromagnetic interactions is structurally analogous to $[\{Cu(phen)\}_2(V^VO_2)_3(OH)(PO_4)_2]$ **1′** but the oxidization states of vanadium sites in **1** and **1′** are different which is responsible for the magnetic properties of **1**. Compounds **1′** and **1** represent a relatively rare example of all V(V) and V(V)/V(IV) mixed valence analogue in the solid state. The vanadium atoms in **2** are directly coordinated to organic 2,2′-bpy ligand which is also relatively uncommon. Compound **2** shows topological relevance to $[V_3O_7(phen)]$ and its preparation demonstrates that the replacement of vanadium(V) atoms with cheap phosphorus(V) atoms can generate a topologically relevant structure.

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