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Syntheses, Structural Characterization, and Antibacterial Properties of a Hexanuclear Bimetallic Cluster Complex[1]

G. L. Zhang[a, b, *], L. Ran[a], X. Q. Luo[c, *], R. G. Hu[a], and J. Zeng[a]

[a]*College of Chemistry and Materials Engineering, GuiYang University, Guiyang, 550005 P.R. China*
[b]*GuiZhou Provincial High College Key and Special Laboratory for Pest Management and Resource, GuiYang University, Guiyang, 550005 P.R. China*
[c]*Institute of Resources Environment and Disaster, Guizhou normal College, Guiyang, 550018 P.R. China*
**e-mail: glzhang996@163.com; xuqiangluo@163.com*

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Abstract—A new bimetallic cluster complex with the formular $\{[Cu(Phen)_2]_2V_4O_{12}\} \cdot MeOH \cdot 5H_2O$ has been synthesized and structurally characterized by elemental analyses, IR spectrum, and single crystal X-ray diffraction. The heterobimetallic cluster complex is composed of a discrete $V_4O_{12}^{4-}$ cluster covalently attached to two $[Cu(Phen)_2]_2^{2+}$ fragments. The nonclassical hydrogen bonds and π–π stacking contribute to the formation of the three-dimensional supramolecular structure. Microdilution broth method indicated that the complex showed significant activity against *B. subtilis, S. aureus,* and *E. coli.*

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INTRODUCTION

In recent years, there has been extensive interest in organic-inorganic hybrid vanadium oxides for their structural diversity and potential applications in the fields of catalysis, electrical, conductivity, magnetism, biochemistry, medicine, photochemistry, and solid state devices [1–8]. The evolution of vanadium oxide is dependent upon the synthesis of new solids possessing unique structures and properties, although synthesis of these materials remains a challenge. Owing to the ability of vanadium to adopt a variety of coordinated geometries in various oxidation states [9–11], the influences of the second metal ions as well as the organic ligands on the structure could be significant [12, 13]. Therefore, novel structural types could be discovered by modifying the transition metal ions, the organic groups and the synthetic conditions, etc. [14, 15]. A variety of novel vanadium oxides templated or coordinated by transition metal complexes including discrete clusters, infinite chains and layer structures have been prepared by hydrothermal methods [16–19]. However, to the best of our knowledge, very few of this kind of complexes are synthesized in mild condition. Recently, we seek to incorporate the coordination complex structure into the vanadium oxide and expect to attain vanadium oxides with unique structures and properties by virtue of the synergistic interaction between complex and vanadium oxide subunit in mild condition.

In this paper we report the syntheses, crystal structure and antibacterial properties of a bimetallic cluster complex $[(CuL_2)V_4O_{12}] \cdot MeOH \cdot 5H_2O$ (**I**) (L = phenantrolene (Phen)). The structure is composed of a chair-like $[V_4O_{12}]^{4-}$ cluster covalently attached to two $(CuL_2)^{2+}$ fragments and extends into three-dimensional supramolecular arrays via π–π stacking interaction of Phen groups and hydrogen bonds.

EXPERIMENTAL

Materials and physical measurements. All reagents were purchased commercially and used without further purification. The C, H, and N microanalyses were performed on a PerkinElmer 240 elemental analyzer. IR spectra were recorded on a Nicolet-470 spectrometer using KBr pellets.

Synthesis of complex I. A mixture of $VOSO_4$ (0.0326 g, 0.2 mmol), $Cu(NO_3)_2 \cdot 6H_2O$ (0.0296 g, 0.1 mmol), 1,10-Phen (0.0396 g, 0.2 mmol), methanol (20 mL), and water (10 mL) was adjusted to pH 7.2 by the addition of $N(C_2H_5)_3$. It was then heated at 333 K for 4 h with continuously stirring. The oxidation-reduction reaction of $4VO^{2+} + O_2 + 12OH^- = V_4O_{12}^{4-} + 6H_2O$ occurred. After filtration of the slight amount of insoluble materials, the resulting blue solution was allowed to evaporate at room temperature. Blue crystals

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[1] The article is published in the original.

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

Parameter	Value
Formula weight	2732
Temperature, K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	14.342(3)
b, Å	14.632(3)
c, Å	16.111(3)
α, deg	102.51(3)
β, deg	107.57(3)
γ, deg	114.98(3)
V, Å^3	2680.1(18)
Z	2
ρ_{calcd}, g cm^{-3}	1.618
μ, mm^{-1}	2.588
$F(000)$	1435
θ Range, deg	1.5–25.2
Reflection collected	19769
Independent reflections (R_{int})	9562 (0.080)
Data/restraints/parameters	9562/0/720
Goodness-of-fit on F^2	0.99
Absorption correction	Empirical
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0862$, $wR_2 = 0.1991$
R indices (all data)	$R_1 = 0.1649$, $wR_2 = 0.2394$
Largest diff. peak and hole, e Å^{-3}	1.649 and –0.563

were obtained after two weeks. The yield was 20.4 mg (65%).

For $C_{49}H_{43}N_8O_{18}V_4Cu_2$			
anal. calcd., %:	C, 43.04;	H, 3.37;	N, 8.20.
Found, %:	C, 42.16;	H, 3.45;	N, 8.40.

X-ray crystallography. Diffraction data were collected on a Bruker APEX area-detector diffractometer, using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The crystal structure was solved by the heavy atom method followed by Fourier syntheses. Structure refinement was performed by full matrix least-squares procedures on F^2 using SHELXL-97 [20]. H atoms of water molecules were located in a difference Fourier map and included in structure-factor calculation with fixed positional and displacement parameters (0.08 Å^2); all other H atoms were placed in calculated positions with C–H = 0.97 Å (methylene) and 0.93 Å (Csp^2–H) and included in the final cycles of refinement in the riding mode with $U_{iso}(H) = 1.2U_{eq}$ and $1.5U_{eq}$ (methyl). Crystal data and relevant crystallographic details are given in Table 1. Selected bond lengths and angles listed in Table 2. The ORTEP view of the crystal is given in Fig. 1.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 900305; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2. Selected bond lengths (Å) and angles (deg) in structure **I***

Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	2.184(8)	Cu(1)–N(2)	2.006(8)
Cu(1)–N(3)	2.002(8)	Cu(1)–N(4)	2.082(8)
Cu(2)–N(5)	2.114(7)	Cu(2)–N(6)	1.995(7)
Cu(2)–N(7)	1.976(7)	Cu(2)–N(8)	2.153(8)
Cu(1)–O(1)	1.914(6)	Cu(2)–O(7)	1.923(6)
V(1)–O(1)	1.658(7)	V(1)–O(2)	1.770(6)
V(1)–O(3)	1.610(7)	V(1)–O(4)	1.762(6)
V(2)–O(2)	1.790(6)	V(2)–O(5)	1.622(7)
V(2)–O(6)	1.624(8)	V(2)–O(4)^{i}	1.792(6)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Cu(1)N(2)	80.1(3)	N(1)Cu(1)N(3)	95.7(3)
N(1)Cu(1)N(4)	94.8(3)	N(2)Cu(1)N(3)	72.9(3)
N(2)Cu(1)N(4)	93.9(3)	N(3)Cu(1)N(4)	80.7(3)
N(1)Cu(1)O(1)	116.6(3)	N(2)Cu(1)O(1)	94.6(3)
N(3)Cu(1)O(1)	92.4(3)	N(4)Cu(1)O(1)	148.4(3)
N(5)Cu(2)N(6)	81.2(3)	N(5)Cu(2)N(7)	94.0(3)
N(6)Cu(2)N(7)	172.6(3)	N(7)Cu(2)N(8)	80.2(3)
N(5)Cu(2)O(7)	129.6(3)	N(6)Cu(2)O(7)	91.1(3)
N(7)Cu(2)O(7)	96.4(3)	N(8)Cu(2)O(7)	129.1(3)
O(1)V(1)O(2)	110.3(3)	O(1)V(1)O(3)	108.9(4)
O(1)V(1)O(4)	108.3(4)	O(2)V(1)O(3)	109.7(4)
O(2)V(1)O(4)	110.3(3)	O(3)V(1)O(4)	109.4(4)
O(2)V(2)O(5)	109.2(4)	O(2)V(2)O(6)	108.9(4)
O(2)V(2)O(4)^{i}	111.8(3)	O(5)V(2)O(6)	108.2(4)
O(5)V(2)O(4)^{i}	111.0(4)	O(6)V(2)O(4)^{i}	107.7(4)
O(7)V(3)O(8)	108.1(4)	O(7)V(3)O(9)	109.1(3)
O(7)V(3)O(10)	112.5(3)	O(8)V(3)O(9)	108.6(4)
O8V(3)O(10)	110.4(3)	O(9)V(3)O(10)	108.1(3)
O8V(4)O(11)	110.9(4)	O(8)V(4)O(12)	109.1(4)
O(1)(1)V(4)O(12)	107.9(4)	O(11)V(4)O(10)^{ii}	109.2(4)
O(12)V(4)O(10)^{ii}	110.0(4)		

* Symmetry codes: ^{i} $-x + 2, -y, -z + 2$; ^{ii} $-x + 2, -y + 1, -z + 1$.

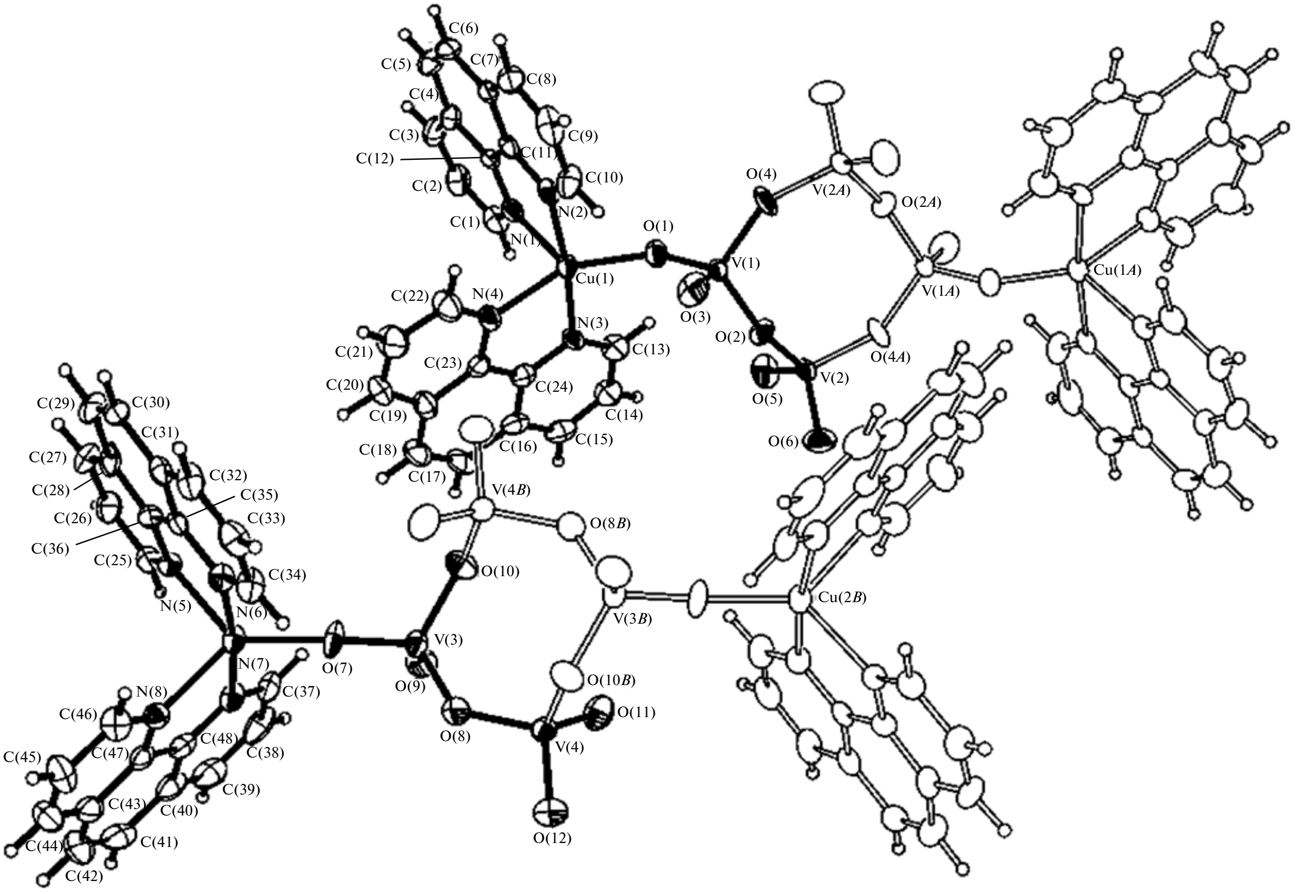

Fig. 1. ORTEP drawing of the compound with 30% probability displacement ellipsoids, solvent molecules have been omitted for clarity (symmetry codes: (*A*) $-x + 2, -y, -z + 2$; (*B*) $-x + 2, -y + 1, -z + 1$).

The antibacterial assay. The used bacteria were *E. coli, B. subtilis*, *S. aureus*, and *B. pvocvaneum*. The antibacterial activities were determined qualitatively using the paper disc method. A lawn of microorganisms was prepared by pipetting and evenly spreading 100 μL of inoculum (adjusted turbidmetrically to 10^5–10^6 CFU/mL (CFU = colony forming units)) onto nutrient agar set in Petri dishes. Paper discs of 6 mm diameter were impregnated with the stock solution of the complexes (5 mg/mL DMSO solution) and dried under sterile conditions. The dried discs were then placed on the previously inoculated agar surface. The plates were inverted and incubated at 37 ± 2°C. After 24 h the inhibition circle were seen.

In order to understand quantitatively the magnitude of the antibacterial activities, complex **I** was evaluated for its MIC (minimum inhibitory concentrations) by the microdilution broth method. Complex solution (2 mg/mL) was added to broth for different concentrations (range from 5 to 100 μg/mL). Suspensions of the bacterial strains, with an optical density of McFarland 0.5 (10^7–10^8 CFU), were made in isotonic sodium chloride solution. Samples measuring 25 μL of each bacterial suspension were added to the serial dilution of the test substances. The inoculated test tubes were incubated at 37 ± 2°C under aerobic conditions. After 72 h the turbidity was evaluated. The MIC is defined as the lowest antimicrobial concentration of the test compounds which completely inhibits bacterial growth. The experiments were repeated three times.

RESULTS AND DISCUSSION

Complex **I** is sparingly soluble in water, ethanol, CCl_4, $CHCl_3$ and benzene; but soluble in DMF and DMSO to give stable solutions at room temperature. In the solid state the compound is fairly stable in air, thus facilitating physical measurements. The compound was further characterized by the following IR spectrum and crystal structure.

In the spectrum of the compound, the strong bands at 802, 850 and 919 cm^{-1} are due to the terminal V–O stretching. The 644 and 723 cm^{-1} are attributed to symmetrical V–O stretching. Band at 1428, 1519, 1569, and 1616 cm^{-1} are the characteristic ones of 1,10-Phen. The broad band at 3424 cm^{-1} is assigned to the stretching of C–H.

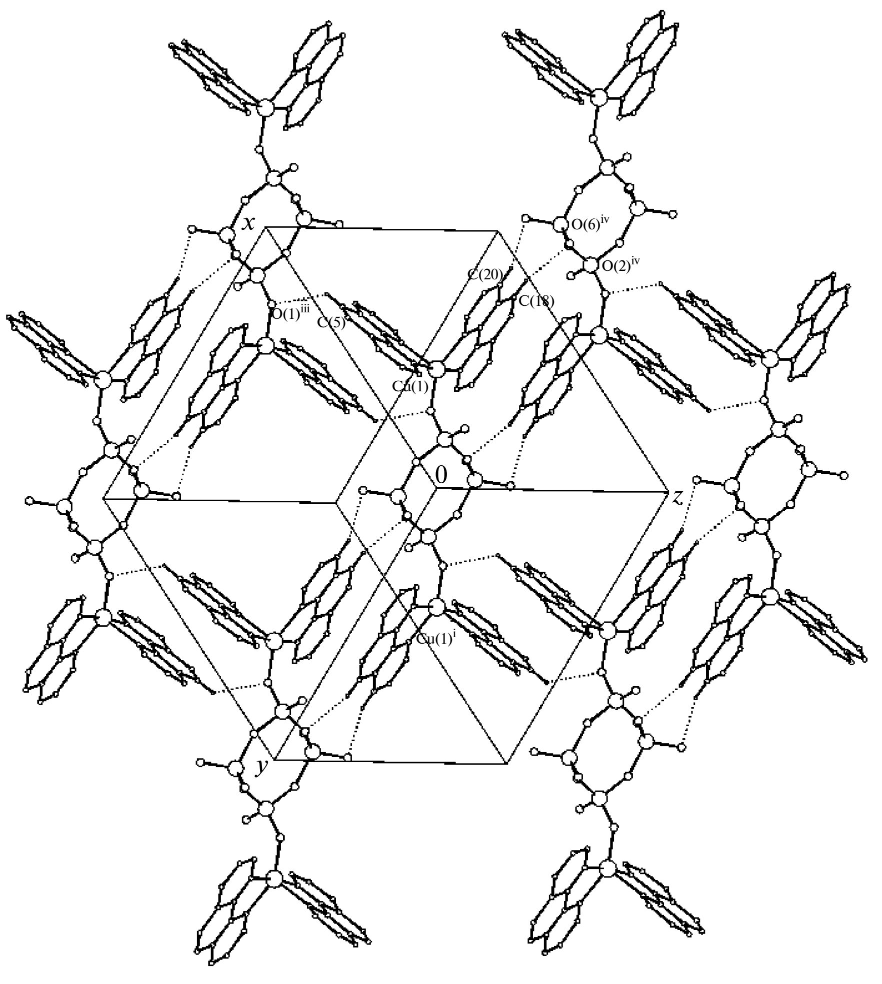

Fig. 2. The hydrogen-bonding and π–π stacking beteen Phen rings (symmetry codes: ^{i} $-x + 2, -y, -z + 2$; ^{iii} $1 - x, -y, 2 - z$; ^{iv} $2 - x, 1 - y, 2 - z$.

The asymmetric unit of complex contains two different inversion centers of half $(CuL_2)_2V_4O_{12}$, five solvent water molecules and one methanol molecule. The structure of $[\{Cu(Phen)_2\}_2V_4O_{12}]$ features a discrete hexanuclear heterometallic cluster built up from a $V_4O_{12}^{4-}$ cluster and two $(CuL_2)_2^{2+}$ fragments (Fig. 1). The $V_4O_{12}^{4-}$ cluster has a cyclic eight-membered core formed by corner sharing of four distorted VO_4 tetrahedra, and two VO_4 tetrahedron contains one terminal and three bridging O atoms which are linked to one Cu atom and two V atoms, respectively. The other two VO_4 tetrahedron contain two terminal and two bridging O atoms which are linked to two V atoms. The V–O bond distance are in the range 1.610(7)–1.624(8) for O_t atoms, 1.658(7)–1.770(6) for O_b. The VOV bond angles alternate 110.3(3)°–111.8(3)° within the $\{V_4O_4\}$ ring, which are similar to those in $(ZnL_2)_2V_4O_{12}]$ and $(MnL_2)_2V_4O_{12} \cdot H_2O$. Valence sum calculations indicate that all V are pentavalent [21]. This oxidation state is consistent with the overall charge balance of the compound. The $V_4O_{12}^{4-}$ ring acts as a bidentate ligand to each of two $(CuL_2)_2^{2+}$ units. Each $(CuL_2)_2^{2+}$ moiety bonds to two oxygen atoms from two alternate VO_4 tetrahedra. Thus, each Cu center displays a distorted trigonal bipyramid environment. It coordinates four N atoms from two 1,10-Phen ligands and one terminal oxygen atom of adjacent vanadium atoms on the $V_4O_{12}^{4-}$ ring. N(1)–N(4)–O(1) and N(5)–N(8)–O(7) define the equatorial plan, the maximum deviation of copper ions from the least-squares plane N(1)–N(4)–O(1)–Cu(1) and N(5)–N(8)–O(7)–Cu(2) are 0.032(3) and 0.019(3) Å, respectively. The axial coordination sites are occupied by two nitrogen atoms (N(2), N(3) or N(6), N(7)) with Cu–N average bond distances of 1.985 Å while in equatorial plan the average bond distances of Cu–N is 2.133(8) Å.

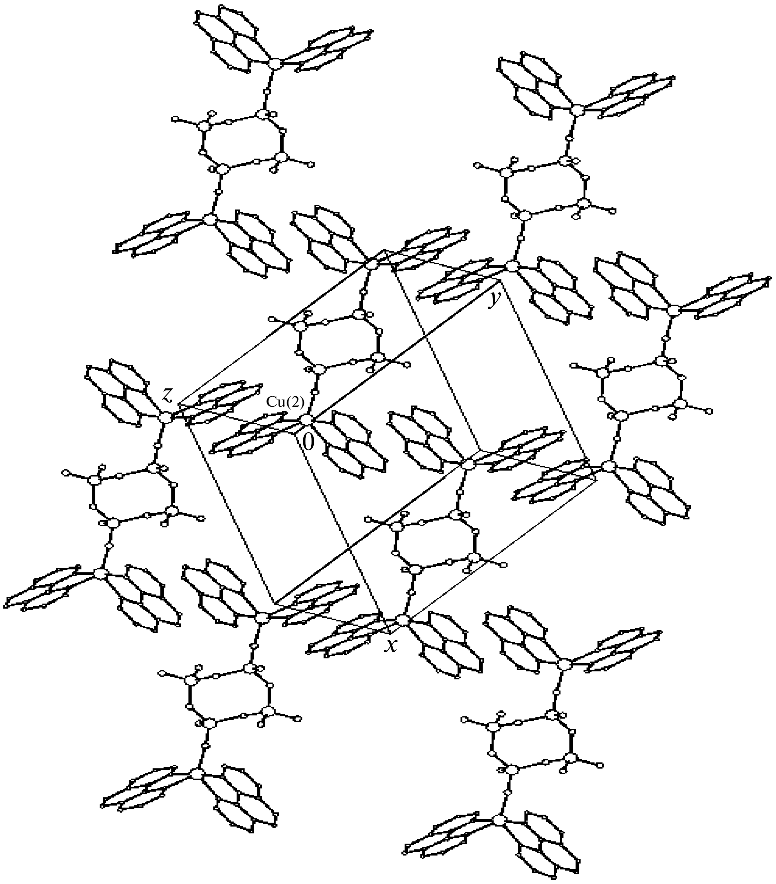

Fig. 3. π–π Stacking beteen Phen rings.

Table 3. Geometric parameters of hydrogen bonds for structure **I***

Contact D–H···A	Distance, Å		Angle DHA, deg
	H···A	D···A	
C(2)–H(2)···O(11)^{iv}	2.45	3.286(12)	150
C(5)–H(5)···O(1)^{iii}	2.57	3.261(16)	131
C(6)–H(6)···O(9)^{v}	2.46	3.338(15)	158
C(10)–H(10)···O(3)	2.55	3.376(17)	148
C(18)–H(18)···O(2)^{iv}	2.54	3.451(15)	166
C(20)–H(20)···O(6)^{iv}	2.59	3.428(17)	150
C(27)–H(27)···O(11)^{vii}	2.41	3.332(16)	170
C(30)–H(30)···O(5)^{viii}	2.36	3.262(13)	162
C(32)–H(32)···O(6)^{viii}	2.40	3.322(14)	173
C(33)–H(33)···O(14)	2.56	3.36(3)	144
C(44)–H(44)···O(8)^{vi}	2.58	3.441(18)	154

* Symmetry codes: ^{iii} 1 – x, –y, 2 – z; ^{iv} 2 – x, 1 – y, 2 – z; ^{v} x – 1, y – 1, z; ^{vi} 2 – x, 2 – y, 1 – z; ^{vii} x – 1, y, z; ^{viii} x – 1, y, z – 1.

It is noteworthy that π–π stacking (Figs. 2 and 3) interaction between intermolecular Phen groups and nonclassical hydreogen bonds C(18)–H(18)···O(2)^{iv}, C(20)–H(20)···O(6)^{iv} (^{iv} 2 – x, 1 – y, 2 – z) (Table 3) plays a significant role in stabilization of the structure. The close contact distance between adjacent Phen groups is 3.466 Å. Therefore, the discrete hexanuclear heterometallic cluster are extended into interesting three-dimensional supermolecular arrays via π–π staking interactions of Phen groups and nonclassical hydreogen bonds.

The paper disc method was used at preliminary antibacterial screening. The complex shows activity against *E. coli, B. subtilis,* and *S. aureus* (inhibition zones less than 15 mm) and inactivity against *B. pvocvaneum*. Microdilution broth method indicated that the complex showed significant activity against *B. subtilis, S. aureus,* and *E. coli* with MIC 13, 25, and 6.5 μg cm^{-3}, respectively. Its potential as an antibacterial agent may be confirmed after further pharmacological studies.

We have reported a new vanadium oxide incorporating copper–ligand complex. The successful isolation of this compound shows that we can synthesize this kind of inorganic-organic hybrid materials in mild condition. Further investigations are underway to determine whether the Phen can be exchanged for other nitrogen donor chelating ligand in similar systems and expecting to synthesize vanadium oxides with new structures and properties.

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