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Hydrothermal Synthesis, Structure and Optical Properties of Organic-Inorganic Hybrid Material Containing Divanadium Hexatungstate as Subunit

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A hydrothermal reaction of NH_4VO_3, WO_3, $CoCl_2$ and 4,4'-bipyridine yields a novel organic-inorganic hybrid compound, $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ (bpy= 4,4'-bipyridine) ($C_{30}H_{26}N_6CoO_{19}V_2W_4$, M_r = 1670.78), which was characterized by elemental analysis, IR, single-crystal X-ray diffraction analysis and UV-Vis-NIR diffuse reflectance spectrum. It crystallizes in monoclinic, space group C2/c with a = 20.187(2) Å, b = 11.6596(13) Å, c = 16.3043(17) Å, β = 96.472(2)º, V = 3813.2(7) $Å^3$, Z = 4, D_c = 2.910 Mg/m^3, μ = 12.998 mm^{-1} and F(000) = 3076. The final R = 0.0556 and wR = 0.1523 for 3343 observed reflections with $I > 2\sigma(I)$. In the crystal, each Co(II) is six-coordinated by two oxygen atoms from two $[V_2W_4O_{19}]^{4-}$ and two nitrogen atoms from two bidentate bpy ligands and two nitrogen atoms from two protonated and terminal bpy ligands. The $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ (bpy= 4,4'-bipyridine) is found to have an optical energy gap of 2.3 eV from UV-Vis-NIR diffuse reflectance spectrum.

Key Words: Polyoxometalate, 4,4'-Bipyridine, Cobalt, Divanadium hexatungstate, Crystal structure.

INTRODUCTION

The polyoxometalates have been of great interest because of their value-adding properties and conventional applications in photochemical response, conductivity, catalysis and medicine[1-3]. Polyoxometalates are found to be extremely versatile inorganic building blocks for construction of inorganic-organic hybrid materials with novel structures and unusual properties[4-6].

Organic-inorganic hybrid compounds containing polyoxotungstate subunits remain largely unexplored[4], although $[TTF]_3[W_6O_{19}]$, $[TMTSF][W_6O_{19}]\cdot 2DMF$, $[BEDtTTF]_2$-$[W_6O_{19}]$, $(Tph\text{-}TTF)_2[W_6O_{19}]$, $[(n\text{-}C_4H_9)_4N]_3[VW_5O_{19}]$ and $[(n\text{-}C_4H_9)_4N]_3H[V_2W_4O_{19}]$ have been synthesized and characterized[7-9], in which the polyoxotungstate subunit only acts as a discrete cluster and modified by organic ligands on its surface, not inorganic ligand to link the metal centers. In this article, we report a novel organic-inorganic compound constructed by Co(II), $(V_2W_4O_{19})^{4-}$, bidentate bpy ligands and protonated bpy, where positional disorder with respect to the vanadium atoms is observed.

EXPERIMENTAL

All commercially available chemicals are reagent grade and used as received without further purification. Elemental analysis of $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ was performed by Elementar Vario EL-III. Infrared (IR) spectra, in the region (4000-400 cm^{-1}), were recorded on Perkin-Elmer spectrum 100 Fourier transform infrared spectrophotometer. UV-Vis-NIR diffuse reflectance spectra of the solid sample were measured by UV-3100 recording spectrophotometer, Barium sulfate was used as the standard with 100 % reflectance[10].

Synthesis: Yellow block-like $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ was obtained from hydrothermal reaction of the mixture of $CoCl_2·6H_2O$ (0.0480 g, 0.20 mmol), WO_3 (0.0928 g, 0.40 mmol), NH_4VO_3 (0.0468 g, 0.4 mmol), 4,4'-bipyridine (0.0769 g, 0.4 mmol) and distilled water (13 mL, 0.722 mol) in a mole ratio of 1:2:2:3610 in 25 mL polytetrafluoroethylene-lined stainless steel reaction container at 150 ºC for 72 h. Anal. calcd. (%) for $C_{30}H_{26}N_6CoO_{19}V_2W_4$: N 5.04, C 21.60, H 1.56. Found: N 5.12, C 22.64, H 1.59. IR (KBr)/cm^{-1}: 3458(w), 3086(w), 3058(m), 1638(w), 1600(m), 1548(w), 1514(w), 1484.60(m), 1413(m), 1328(w), 1295(w), 1220(w), 1200(w), 1099(w), 1072(w), 1010(m), 952(s), 929(s), 876(m), 786(s), 628(m), 576(s), 526(m), 439(s).

Crystal structure determination: A yellow single crystal (0.36 mm × 0.34 mm × 0.23 mm) was carefully selected under microscope and was mounted on a glass fiber capillary for intensity data collection on a Bruker CCD area detector diffractometer with a graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) from a generator operating at 50 kV and 30 mA. The intensity data were collected in the range of $2.02° \leq \theta \leq 25.01°$ using φ-ω mode at 298(2) K. Total reflections of 9054 were collected, of which 3343 reflections with $R_{int} = 0.0820$ were unique in the ranges of $-23 \leq h \leq 24$, $-12 \leq k \leq 13$, $-19 \leq l \leq 15$. Empirical absorption corrections were performed with the SADABS program. The structure has been solved by direct methods (SHELXS-97)[11] and refined by full-matrix-least squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97)[11]. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. The final full-matrix least-squares refinements including 304 parameters for 3343 reflections with $I>2\sigma(I)$ gave R1 = 0.0556, wR2 = 0.1523 $\{w = 1/[\sigma^2(F_0^2) + (0.0816(F_0^2 + 2F_c^2)/3)^2 + 0.09\ (F_0^2 + 2F_c^2)/3]\}$, $(\Delta\rho)_{max} = 2.819$ e.Å^{-3}, $(\Delta\rho)_{min} = -3.051$ e.Å^{-3}. All structural calculations were carried out using the SHELX-97 program package[11].

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters, the selected bond lengths and bond angles, anisotropic displacement parameters and hydrogen coordinates are listed in Tables 1-4, respectively. Ortep view of the $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ structure and structure of the ${}^2_\infty[Co(V_2W_4O_{19})(bpy)(Hbpy)_2]$ layer of the present compound are illustrated in Figs. 1 and 2, respectively.

TABLE-1
ATOMIC COORDINATES (×10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (×10^3 Å^2)

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
W(1)	3398(1)	7427(1)	1022(1)	21(1)	O(9)	1763(5)	10151(9)	1137(6)	20(2)
W(2)	1901(10)	6253(18)	743(12)	11(6)	O(10)	1485(5)	5380(9)	1315(6)	20(2)
W(3)	2068(9)	9053(17)	650(12)	10(6)	C(1)	6059(7)	7866(14)	1333(9)	20(3)
V(1)	1900(40)	6250(80)	740(50)	10(30)	C(2)	6395(8)	7894(15)	635(9)	22(3)
V(2)	2070(40)	9050(70)	650(50)	10(30)	C(3)	6141(8)	7265(14)	-72(10)	23(3)
Co(1)	5000	7273(2)	2500	12(1)	C(4)	5561(8)	6635(14)	-35(9)	23(3)
N(1)	5493(6)	7263(11)	1367(8)	18(3)	C(5)	5244(7)	6663(14)	684(9)	19(3)
N(2)	7200(7)	7362(13)	-2181(9)	32(4)	C(6)	7022(8)	6340(17)	-1897(10)	29(4)
N(3)	5000	5379(15)	2500	17(4)	C(7)	6661(8)	6288(16)	-1220(10)	26(4)
N(4)	5000	9193(15)	2500	19(4)	C(8)	6511(8)	7308(15)	-816(10)	24(4)
O(1)	2500	7500	0	14(3)	C(9)	6710(8)	8323(16)	-1161(10)	27(4)
O(2)	2738(5)	6429(9)	1459(6)	16(2)	C(10)	7052(8)	8334(17)	-1830(10)	31(4)
O(3)	2862(5)	8686(9)	1398(6)	15(2)	C(11)	5449(7)	4747(13)	2141(9)	19(3)
O(4)	1662(5)	7732(9)	1117(6)	15(2)	C(12)	5458(7)	3544(14)	2091(9)	20(3)
O(5)	3577(5)	6184(9)	322(6)	18(2)	C(13)	5000	2909(19)	2500	17(4)
O(6)	3713(5)	8445(9)	252(6)	18(2)	C(14)	5072(8)	9799(13)	3218(9)	21(3)
O(7)	2368(5)	5238(9)	65(6)	17(2)	C(15)	5039(8)	10995(14)	3246(10)	23(3)
O(8)	4075(5)	7324(9)	1789(6)	19(2)	C(16)	5000	11629(19)	2500	20(5)

U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

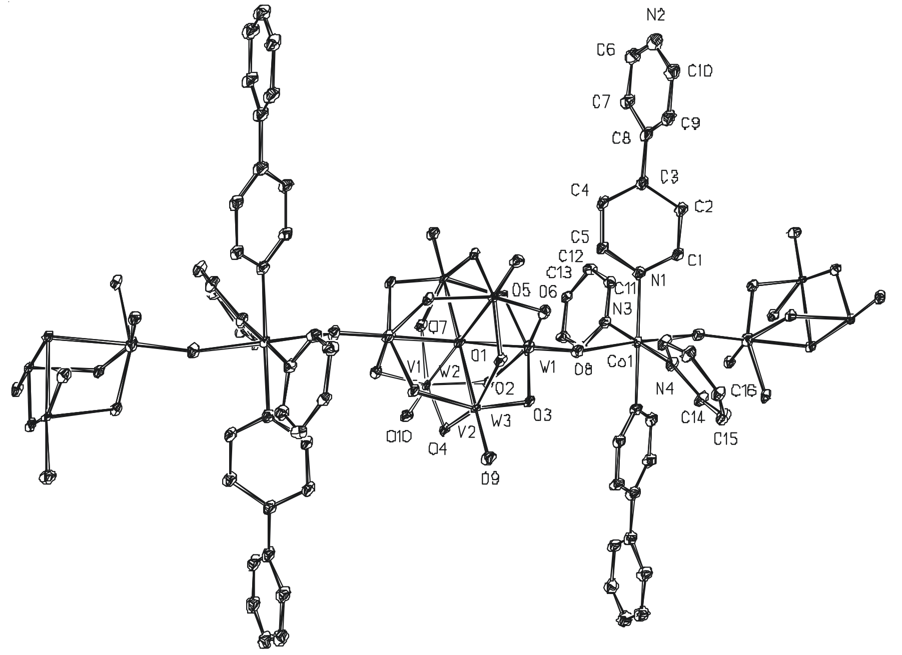

Fig. 1. Ortep view of the $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ structure with atomic labelling of one asymmetric unit, and the position occupancy factor ratio of W2/V1 and W3/V2 are 0.50/0.50 and 0.50/0.50, respectively

TABLE-2
SELECTED BOND LENGTH (Å) AND ANGLES (°)

W(1)-O(8)	1.749(10)	O(8)-W(1)-O(6)	103.0(5)	O(10)-V(1)-O(4)	102(4)
W(1)-O(6)	1.888(10)	O(8)-W(1)-O(5)	101.0(5)	O(10)-V(1)-O(7)	105(5)
W(1)-O(5)	1.905(10)	O(6)-W(1)-O(5)	88.8(4)	O(4)-V(1)-O(7)	153(5)
W(1)-O(3)	1.962(10)	O(8)-W(1)-O(3)	104.0(4)	O(10)-V(1)-O(2)	101(4)
W(1)-O(2)	1.963(10)	O(6)-W(1)-O(3)	88.7(4)	O(4)-V(1)-O(2)	87(3)
W(1)-O(1)	2.3210(6)	O(5)-W(1)-O(3)	154.8(4)	O(7)-V(1)-O(2)	88(3)
W(2)-O(10)	1.67(2)	O(8)-W(1)-O(2)	101.9(4)	O(10)-V(1)-O(6)#1	105(4)
W(2)-O(4)	1.91(2)	O(6)-W(1)-O(2)	155.1(4)	O(4)-V(1)-O(6)#1	87(4)
W(2)-O(7)	1.94(2)	O(5)-W(1)-O(2)	87.0(4)	O(7)-V(1)-O(6)#1	87(3)
W(2)-O(2)	1.95(2)	O(3)-W(1)-O(2)	84.8(4)	O(2)-V(1)-O(6)#1	154(5)
W(2)-O(6)#1	1.96(2)	O(8)-W(1)-O(1)	178.1(3)	O(10)-V(1)-O(1)	178(5)
W(2)-O(1)	2.32(2)	O(6)-W(1)-O(1)	78.1(3)	O(4)-V(1)-O(1)	76(3)
W(3)-O(9)	1.66(2)	O(5)-W(1)-O(1)	77.5(3)	O(7)-V(1)-O(1)	77(3)
W(3)-O(7)#1	1.91(2)	O(3)-W(1)-O(1)	77.5(3)	O(2)-V(1)-O(1)	77(3)
W(3)-O(4)	1.94(2)	O(2)-W(1)-O(1)	77.0(3)	O(6)#1-V(1)-O(1)	77(3)
W(3)-O(3)	1.95(2)	O(10)-W(2)-O(4)	102.2(11)	O(9)-V(2)-O(7)#1	104(4)
W(3)-O(5)#1	1.95(2)	O(10)-W(2)-O(7)	104.7(12)	O(9)-V(2)-O(4)	103(4)
W(3)-O(1)	2.318(19)	O(4)-W(2)-O(7)	153.1(12)	O(7)#1-V(2)-O(4)	153(5)
V(1)-O(10)	1.67(8)	O(10)-W(2)-O(2)	100.7(11)	O(9)-V(2)-O(3)	101(4)
V(1)-O(4)	1.91(9)	O(4)-W(2)-O(2)	87.0(9)	O(7)#1-V(2)-O(3)	88(3)
V(1)-O(7)	1.94(9)	O(7)-W(2)-O(2)	87.8(9)	O(4)-V(2)-O(3)	86(3)
V(1)-O(2)	1.95(8)	O(10)-W(2)-O(6)#1	105.2(11)	O(9)-V(2)-O(5)#1	104(4)
V(1)-O(6)#1	1.96(8)	O(4)-W(2)-O(6)#1	86.8(9)	O(7)#1-V(2)-O(5)#1	87(3)
V(1)-O(1)	2.32(8)	O(7)-W(2)-O(6)#1	86.6(9)	O(4)-V(2)-O(5)#1	86(3)
V(2)-O(9)	1.66(8)	O(2)-W(2)-O(6)#1	154.1(12)	O(3)-V(2)-O(5)#1	154(5)
V(2)-O(7)#1	1.91(8)	O(10)-W(2)-O(1)	177.6(12)	O(9)-V(2)-O(1)	179(5)
V(2)-O(4)	1.94(8)	O(4)-W(2)-O(1)	76.5(8)	O(7)#1-V(2)-O(1)	77(3)
V(2)-O(3)	1.95(8)	O(7)-W(2)-O(1)	76.6(7)	O(4)-V(2)-O(1)	76(3)
V(2)-O(5)#1	1.95(8)	O(2)-W(2)-O(1)	77.3(7)	O(3)-V(2)-O(1)	78(3)
V(2)-O(1)	2.32(8)	O(6)#1-W(2)-O(1)	76.9(7)	O(5)#1-V(2)-O(1)	77(3)
Co(1)-O(8)	2.085(10)	O(9)-W(3)-O(7)#1	103.8(11)	O(8)-Co(1)-O(8)#2	176.8(6)
Co(1)-O(8)#2	2.085(10)	O(9)-W(3)-O(4)	103.2(11)	O(8)-Co(1)-N(1)	89.7(4)
Co(1)-N(1)	2.195(12)	O(7)#1-W(3)-O(4)	153.1(12)	O(8)#2-Co(1)-N(1)	90.3(4)
Co(1)-N(1)#2	2.195(12)	O(9)-W(3)-O(3)	101.2(10)	O(8)-Co(1)-N(1)#2	90.3(4)
Co(1)-N(3)	2.208(18)	O(7)#1-W(3)-O(3)	88.5(9)	O(8)#2-Co(1)-N(1)#2	89.7(4)
Co(1)-N(4)	2.238(18)	O(4)-W(3)-O(3)	86.2(9)	N(1)-Co(1)-N(1)#2	179.4(7)
		O(9)-W(3)-O(5)#1	104.3(11)	O(8)-Co(1)-N(3)	91.6(3)
		O(7)#1-W(3)-O(5)#1	87.4(9)	O(8)#2-Co(1)-N(3)	91.6(3)
		O(4)-W(3)-O(5)#1	86.1(9)	N(1)-Co(1)-N(3)	89.7(3)
		O(3)-W(3)-O(5)#1	154.4(12)	N(1)#2-Co(1)-N(3)	89.7(3)
		O(9)-W(3)-O(1)	178.7(12)	O(8)-Co(1)-N(4)	88.4(3)
		O(7)#1-W(3)-O(1)	77.2(7)	O(8)#2-Co(1)-N(4)	88.4(3)
		O(4)-W(3)-O(1)	75.9(7)	N(1)-Co(1)-N(4)	90.3(3)
		O(3)-W(3)-O(1)	77.8(7)	N(1)#2-Co(1)-N(4)	90.3(3)
		O(5)#1-W(3)-O(1)	76.6(7)	N(3)-Co(1)-N(4)	180.000(4)

Symmetry transformations used to generate equivalent atoms: #1: -x+1/2,-y+3/2,-z; #2 -x+1,y,-z+1/2; #3 x,y-1,z; #4 x,y+1,z

TABLE-3
ANISOTROPIC DISPLACEMENT PARAMETERS (×10^3 Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	22(1)	27(1)	13(1)	-1(1)	-4(1)	1(1)
W(2)	15(13)	14(15)	4(14)	1(11)	0(11)	-4(11)
W(3)	13(13)	12(15)	5(14)	-3(10)	-1(11)	2(11)
V(1)	10(60)	10(60)	0(60)	0(50)	0(50)	0(50)
V(2)	10(60)	10(60)	0(60)	0(40)	0(50)	0(40)
Co(1)	14(1)	14(1)	7(1)	0	-2(1)	0
N(1)	21(6)	20(7)	12(6)	1(5)	1(5)	-2(5)
N(2)	32(8)	44(10)	18(8)	1(6)	-3(6)	-4(7)
N(3)	20(9)	18(10)	12(9)	0	1(7)	0
N(4)	24(9)	17(10)	14(9)	0	-2(7)	0
O(1)	17(7)	18(8)	8(7)	-1(5)	-1(6)	-1(5)
O(2)	19(5)	18(6)	10(5)	0(4)	-2(4)	0(4)
O(3)	18(5)	18(6)	9(5)	-3(4)	-2(4)	0(4)
O(4)	18(5)	19(6)	8(5)	-1(4)	-3(4)	-1(4)
O(5)	20(5)	21(6)	11(5)	-3(4)	-2(4)	0(4)
O(6)	20(5)	20(6)	13(5)	0(4)	-3(4)	1(4)
O(7)	21(5)	17(6)	12(5)	-1(4)	-1(4)	-1(4)
O(8)	21(5)	21(6)	14(6)	-2(4)	-1(4)	1(4)
O(9)	24(5)	21(6)	14(5)	-2(4)	-3(4)	6(4)
O(10)	26(5)	22(6)	14(5)	-2(4)	4(4)	-4(5)
C(1)	25(8)	23(8)	12(7)	-3(6)	0(6)	-4(7)
C(2)	27(8)	27(9)	12(8)	0(6)	0(6)	-6(7)
C(3)	27(8)	28(9)	13(8)	0(6)	-1(7)	-4(7)
C(4)	27(8)	28(9)	12(8)	-3(6)	-3(6)	-4(7)
C(5)	22(8)	22(8)	12(7)	-2(6)	-2(6)	-2(6)
C(6)	31(9)	38(11)	17(9)	1(7)	-3(7)	0(8)
C(7)	31(9)	33(10)	14(8)	2(7)	-1(7)	-3(7)
C(8)	27(9)	30(10)	13(8)	0(7)	-2(7)	-4(7)
C(9)	32(9)	34(10)	14(8)	0(7)	-3(7)	-7(7)
C(10)	33(9)	39(11)	18(9)	1(8)	-1(7)	-7(8)
C(11)	22(8)	20(8)	15(8)	0(6)	1(6)	-2(6)
C(12)	24(8)	20(9)	18(8)	0(6)	5(6)	2(6)
C(13)	22(11)	18(11)	12(10)	0	0(8)	0
C(14)	29(8)	20(9)	14(8)	1(6)	-4(6)	1(6)
C(15)	31(9)	20(9)	17(8)	-1(6)	-2(7)	-3(7)
C(16)	26(11)	17(12)	17(11)	0	-2(9)	0

TABLE-4
HYDROGEN COORDINATES (×10^4) AND ISOTROPIC
DISPLACEMENT PARAMETERS (×10^3 Å^2)

	x	y	z	U(eq)		x	y	z	U(eq)
H(2)	7417	7385	-2605	38	H(7)	6520	5584	-1035	31
H(1)	6232	8280	1796	24	H(9)	6605	9017	-925	33
H(2A)	6784	8323	633	27	H(10)	7183	9028	-2042	37
H(4)	5385	6198	-484	27	H(11)	5780	5143	1906	23
H(5)	4848	6258	697	23	H(12)	5762	3173	1793	25
H(6)	7139	5668	-2152	35	H(14)	5146	9398	3713	25
					H(15)	5043	11372	3749	28

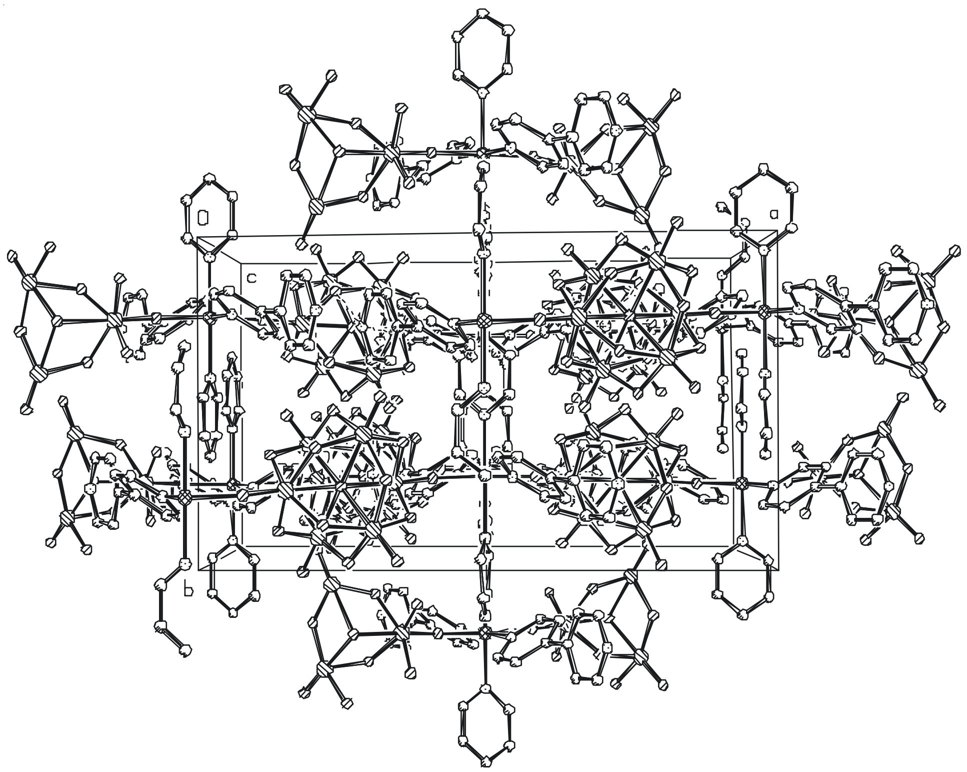

Fig. 2. Structure of [$Co(V_2W_4O_{19})(bpy)(Hbpy)_2$]

Crystal structure: The $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ compound crystallizes in monoclinic system with space group symmetry of C2/c. Positional disorder with respect to the vanadium atoms is present in the structure, which is common for the substituted heteropoly anions[9,12]. The X-ray data can be explained assuming random orientation of vanadium atoms in the tungstate framework. The stoichiometry of substituted heteropoly anions in the crystal structures can only be inferred from the relative site occupancies and this kind of analysis is intrinsically associated with large errors. The structure of the present compound was refined to relatively W:V occupancies of 2:1, which indicates two vanadium atoms could be present in the crystal, in well agreement with the stoichiometry of $[V_2W_4O_{19}]^{4-}$. In detail, the position occupancy factor ratio of W2/V1 and W3/V2 are 0.50/0.50 and 0.50/0.50, respectively.

In the structure, the Co(II) center is octahedrally coordinated by two oxygen atoms, O8 and O8B (symmetry code (B): -x+1, y, -z+1/2), at the axial direction, respectively from two divanadium hexatungstates $(V_2W_4O_{19})^{4-}$ and four pyridyl nitrogen atoms, N1, N1B, N3 and N4 in the equatorial plane, respectively from four 4,4'-bipyridine ligands, as shown in Fig. 1. The Cobalt-centered coordination octahedron is slightly distorted, with the bond lengths, 2.085 Å for Co-O bond, 2.195-2.238 Å for Co-N bonds and the bond angles approximate to 90º or 180º.

Of the four 4,4'-bipyridine ligands coordinating to Co(II) centers, two at *para* positions are terminal and the nitrogen atom attached on the other end of pyridyl ring was protonated to balance the charge of the compound. While the other two act as N,N'-bidentate bridging ligands to link cobalt centers of the adjancent two 1-D $[Co(V_2W_4O_{19})]^{2-}$ anion chains, to build a 2-D organic-inorganic covalent layer $[Co(V_2W_4O_{19})]$ (bpy)$(Hbpy)_2$, as drawn in Fig. 2. The layers are packed by intermolecular forces to build up the whole crystal structure for the present compound.

The inorganic building blocks of divanadium hexatungstate $[V_2W_4O_{19}]^{4-}$ are coordinated to two Co centers *via* its two centrically symmetric O8 atoms respectively (Fig. 1). And $[V_2W_4O_{19}]^{4-}$ basically keeps 'superoctahedral' Lindqvist-structure just like $[W_6O_{19}]^{2-}$, which is also reported in literature[9].

The $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ compound is a novel organic-inorganic hybrid compound, in which both the divanadium hexatungstate $[V_2W_4O_{19}]^{4-}$ and 4,4'-bipyridine act as bidenate ligand to coordinate with the Co(II) centers to build the extended 2-D covalent framework. Up to now, $[V_2W_4O_{19}]^{4-}$ unit is often chemically modified on the surface[9], quiet different from acting as building blocks together with 4,4'-bipyridine ligands in the construction of the 2-D network of the present compound described in this paper.

Optical energy gap: In order to explore the conductivity of the present compound, the measurement of diffuse reflectivity for a powder sample was used to obtain its band gap E_g, which agrees rather well with that obtained by absorption measurement from a single crystal[13]. The band gap E_g was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function F against energy E[14]. Kubelka-Munk function, $F = (1-R)^2/2R$, was converted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at a given wavelength[15]. The F *versus* E plot for the present compound is shown in Fig. 3, where a steep absorption edge is displayed and the E_g can be assessed at 2.3 eV.

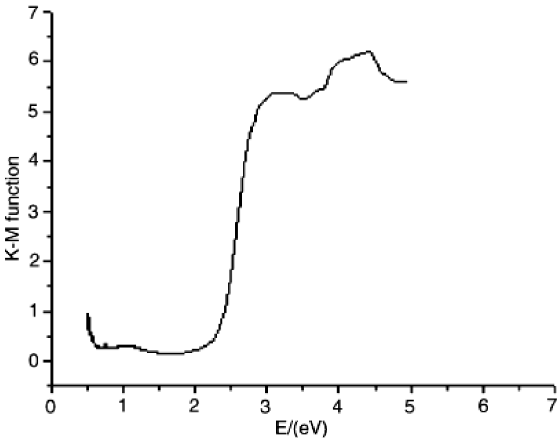

Fig. 3. Plot of K-M function *vs.* energy E(eV) for the $Co(V_2W_4O_{19})(bpy)(Hbpy)_2$ compound

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