# Hydrothermal Synthesis, Crystal Structure and Optical Properties of A 2-D Organic-Inorganic Compound $Mn(V_2W_4O_{19})(bpy)(Hbpy)_2$ (bpy = 4,4'-Bipyridine)

CHONG-CHEN WANG

*School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, No. 1, Zhanlanguan Road, Xicheng District, Beijing-100044, P.R. China*
*E-mail: chongchenwang@126.com*

A hydrothermal reaction of $NH_4VO_3$, $WO_3$, $MnCl_2$ and 4,4'-bipyridine yields a novel organic-inorganic hybrid compound, $Mn(V_2W_4O_{19})$ $(bpy)(Hbpy)_2$ (bpy = 4,4'-bipyridine) ($C_{30}H_{26}N_6MnO_{19}V_2W_4$, $M_r$ = 1666.79), 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 = 19.931(2) Å, b = 11.4920(12) Å, c = 16.0917(19) Å, $\beta$ = 96.432(2)°, V = 3662.6(7) Å$^3$, Z = 4, $D_c$ = 3.023 Mg/m$^3$, $\mu$ = 13.424 mm$^{-1}$ and F(000) = 3068. The final R = 0.0630 and wR = 0.1679 for 3234 observed reflections with I>2σ(I). In the crystal, each Mn(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 title compound is found to have an optical energy gap of 2.1 eV from UV-Vis-NIR diffuse reflectance spectrum.

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

## INTRODUCTION

Polyoxometalates (POMs) are a rapidly growing class compound, due to their so-called 'value-adding properties' like diverse chemistry and favourable structural and electronic properties[1-3]. As species of extremely versatile inorganic building blocks, POMs are found to participate the construction of the organic-inorganic hybrid materials with novel structures and unusual properties[4-6].

Organic-inorganic hybrid compounds containing polyoxotungstate subunits remain largely unexplored[4], although $[TTF]_3[W_6O_{19}]$, $[TMTSF][W_6O_{19}]·2DMF$, $[BEDtTTF]_2[W_6O_{19}]$, $(Tph-TTF)_2[W_6O_{19}]$, $[(n-C_4H_9)_4N]_3[VW_5O_{19}]$ and $[(n-C_4H_9)_4N]_3H[V_2W_4O_{19}]$ 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 Mn(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 for the present compound 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 ($BaSO_4$) was used as the standard with 100 % reflectance[10].

**Synthesis:** Yellow block-like $Mn(V_2W_4O_{19})(bpy)(Hbpy)_2$ was obtained from hydrothermal reaction of the mixture of $MnCl_2 \cdot 4H_2O$ (0.0395 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 $C_{30}H_{26}N_6MnO_{19}V_2W_4$: N 5.04, C 21.60, H 1.56. Found: N 5.12, C 22.64, H 1.59. IR (KBr, $\nu_{max}$, cm$^{-1}$): 3454 (w), 3082 (w), 3061 (m), 1642 (w), 1604 (m), 1550 (w), 1514 (w), 1487 (m), 1420 (m), 1323 (w), 1293 (w), 1225 (w), 1202 (w), 1104 (w), 1079 (w), 1015 (m), 955 (s), 932 (s), 879 (m), 784 (s), 635 (m), 577 (s), 527 (m), 460 (s).

**Crystal structure determination:** A yellow single crystal (0.40 mm × 0.39 mm × 0.21 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$\alpha$ radiation ($\lambda = 0.71073$ Å) from a generator operating at 50 kV and 30 mA. The intensity data were collected in the range of $2.05º \leq \theta \leq 25.01º$ using $\phi$-$\omega$ mode at 298(2) K. Total reflections of 8793 were collected, of which 3233 reflections with $R_{int} = 0.0929$ were unique in the ranges of $-23 \leq h \leq 21$, $-13 \leq k \leq 12$, $-18 \leq l \leq 19$. 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 3233 reflections with I>2$\sigma$(I) gave R1 = 0.0630, wR2 = 0.1679 {w = 1/[$\sigma^2(F_0^2)$ + (0.0816 $(F_o^2 + 2F_c^2)/3)^2$ + 0.09 $(F_0^2 + 2F_c^2)/3$]}, $(\Delta\rho)_{max} = 3.249$ e.Å$^{-3}$, $(\Delta\rho)_{min} = -3.506$ 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 $Mn(V_2W_4O_{19})(bpy)(Hbpy)_2$ structure and structure of the $^2_\infty[Mn(V_2W_4O_{19})(bpy)(Hbpy)_2]$ layer of the present compound are illustrated in Figs. 1 and 2, respectively.

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

| Atom | x | y | z | U (eq) | Atom | x | y | z | U (eq) |
|------|---|---|---|--------|------|---|---|---|--------|
| W(1) | 3397(1) | 7428(1) | 1021(1) | 17(1) | O(9) | 1756(5) | 10166(10) | 1130(7) | 16(2) |
| W(2) | 1902(10) | 6254(19) | 744(12) | 9(6) | O(10) | 1481(6) | 5370(10) | 1309(7) | 18(3) |
| W(3) | 2068(10) | 9053(19) | 649(12) | 8(6) | C(1) | 6058(8) | 7877(15) | 1338(10) | 16(3) |
| V(1) | 1900(40) | 6250(80) | 740(50) | 10(30) | C(2) | 6389(9) | 7915(16) | 621(9) | 18(4) |
| V(2) | 2070(40) | 9050(80) | 650(50) | 10(30) | C(3) | 6135(9) | 7271(15) | -76(10) | 18(4) |
| Mn(1) | 5000 | 7274(3) | 2500 | 3(1) | C(4) | 5567(8) | 6634(16) | -35(10) | 19(4) |
| N(1) | 5487(7) | 7263(12) | 1356(8) | 14(3) | C(5) | 5242(8) | 6666(15) | 672(9) | 14(3) |
| N(2) | 7196(8) | 7353(14) | -2187(10) | 27(4) | C(6) | 7025(9) | 6323(18) | -1896(11) | 24(4) |
| N(3) | 5000 | 5364(16) | 2500 | 12(4) | C(7) | 6659(9) | 6282(17) | -1229(10) | 22(4) |
| N(4) | 5000 | 9189(17) | 2500 | 14(4) | C(8) | 6507(9) | 7293(16) | -829(10) | 19(4) |
| O(1) | 2500 | 7500 | 0 | 11(3) | C(9) | 6712(9) | 8313(17) | -1145(10) | 23(4) |
| O(2) | 2740(5) | 6437(10) | 1461(6) | 13(2) | C(10) | 7050(9) | 8355(18) | -1838(11) | 26(4) |
| O(3) | 2868(5) | 8680(10) | 1399(6) | 13(2) | C(11) | 5456(8) | 4732(14) | 2135(9) | 13(3) |
| O(4) | 1655(5) | 7735(10) | 1107(7) | 13(2) | C(12) | 5459(8) | 3536(14) | 2090(10) | 15(3) |
| O(5) | 3573(5) | 6176(10) | 315(6) | 13(2) | C(13) | 5000 | 2920(20) | 2500 | 14(5) |
| O(6) | 3717(5) | 8465(10) | 254(6) | 13(2) | C(14) | 5064(8) | 9798(14) | 3213(10) | 16(3) |
| O(7) | 2367(5) | 5234(10) | 60(6) | 14(2) | C(15) | 5041(9) | 10988(15) | 3241(10) | 19(4) |
| O(8) | 4072(6) | 7327(10) | 1808(7) | 15(2) | C(16) | 5000 | 11630(20) | 2500 | 16(5) |

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

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

| | | | | | |
|---|---|---|---|---|---|
| W(1)-O(8) | 1.745(11) | O(2)-W(1)-O(1) | 77.1(3) | O(4)-W(3)-O(3) | 86.8(10) |
| W(1)-O(6) | 1.879(10) | O(8)-W(1)-W(2)#1 | 136.4(5) | O(5)#1-W(3)-O(3) | 154.5(13) |
| W(1)-O(5) | 1.890(11) | O(6)-W(1)-W(2)#1 | 33.2(5) | O(9)-W(3)-O(1) | 179.3(13) |
| W(1)-O(3) | 1.923(11) | O(5)-W(1)-W(2)#1 | 81.7(5) | O(7)#1-W(3)-O(1) | 77.3(8) |
| W(1)-O(2) | 1.929(11) | O(3)-W(1)-W(2)#1 | 82.7(5) | O(4)-W(3)-O(1) | 76.0(8) |
| W(1)-O(1) | 2.2906(7) | O(2)-W(1)-W(2)#1 | 122.4(5) | O(5)#1-W(3)-O(1) | 76.9(8) |
| W(1)-W(2)#1 | 3.22(2) | O(1)-W(1)-W(2)#1 | 45.3(4) | O(3)-W(3)-O(1) | 77.6(8) |
| W(1)-W(3)#1 | 3.23(2) | O(8)-W(1)-W(3)#1 | 134.1(5) | W(2)#1-W(3)-W(2) | 90.0(7) |
| W(2)-O(10) | 1.65(2) | O(6)-W(1)-W(3)#1 | 82.8(5) | W(1)#1-W(3)-W(2) | 59.6(5) |
| W(2)-O(4) | 1.88(3) | O(5)-W(1)-W(3)#1 | 32.2(5) | O(10)-V(1)-O(4) | 103(4) |
| W(2)-O(7) | 1.92(2) | O(3)-W(1)-W(3)#1 | 122.8(5) | O(10)-V(1)-O(7) | 104(5) |
| W(2)-O(2) | 1.93(2) | O(2)-W(1)-W(3)#1 | 81.4(5) | O(4)-V(1)-O(7) | 153(5) |
| W(2)-O(6)#1 | 1.94(2) | O(1)-W(1)-W(3)#1 | 45.1(4) | O(10)-V(1)-O(2) | 101(4) |
| W(2)-O(1) | 2.29(2) | W(2)#1-W(1)-W(3)#1 | 60.4(6) | O(4)-V(1)-O(2) | 87(4) |
| W(2)-W(1)#1 | 3.22(2) | O(10)-W(2)-O(4) | 102.6(12) | O(7)-V(1)-O(2) | 88(4) |
| W(2)-W(3)#1 | 3.23(3) | O(10)-W(2)-O(7) | 104.4(13) | O(10)-V(1)-O(6)#1 | 104(4) |
| W(2)-W(3) | 3.24(3) | O(4)-W(2)-O(7) | 153.0(13) | O(4)-V(1)-O(6)#1 | 87(4) |
| W(3)-O(9) | 1.65(2) | O(10)-W(2)-O(2) | 101.4(11) | O(7)-V(1)-O(6)#1 | 86(3) |
| W(3)-O(7)#1 | 1.88(2) | O(4)-W(2)-O(2) | 87.4(10) | O(2)-V(1)-O(6)#1 | 155(5) |
| W(3)-O(4) | 1.91(2) | O(7)-W(2)-O(2) | 88.2(10) | O(10)-V(1)-O(1) | 178(5) |
| W(3)-O(5)#1 | 1.92(2) | O(10)-W(2)-O(6)#1 | 104.0(11) | O(4)-V(1)-O(1) | 76(3) |
| W(3)-O(3) | 1.94(2) | O(4)-W(2)-O(6)#1 | 86.7(10) | O(7)-V(1)-O(1) | 77(3) |
| W(3)-O(1) | 2.29(2) | O(7)-W(2)-O(6)#1 | 86.0(9) | O(2)-V(1)-O(1) | 77(3) |
| W(3)-W(2)#1 | 3.23(3) | O(2)-W(2)-O(6)#1 | 154.6(13) | O(6)#1-V(1)-O(1) | 77(3) |
| W(3)-W(1)#1 | 3.23(2) | O(10)-W(2)-O(1) | 178.2(13) | O(9)-V(2)-O(7)#1 | 03(5) |

| V(1)-O(10) | 1.65(9) | O(4)-W(2)-O(1) | 76.5(8) | O(9)-V(2)-O(4) | 03(4) |
|---|---|---|---|---|---|
| V(1)-O(4) | 1.88(9) | O(7)-W(2)-O(1) | 76.6(7) | O(7)#1-V(2)-O(4) | 53(5) |
| V(1)-O(7) | 1.92(9) | O(2)-W(2)-O(1) | 77.1(8) | O(9)-V(2)-O(5)#1 | 04(4) |
| V(1)-O(2) | 1.93(8) | O(6)#1-W(2)-O(1) | 77.5(7) | O(7)#1-V(2)-O(5)#1 | 8(3) |
| V(1)-O(6)#1 | 1.94(8) | O(10)-W(2)-W(1)#1 | 136.1(11) | O(4)-V(2)-O(5)#1 | 6(4) |
| V(1)-O(1) | 2.29(9) | O(4)-W(2)-W(1)#1 | 79.6(8) | O(9)-V(2)-O(3) | 102(4) |
| V(2)-O(9) | 1.65(9) | O(7)-W(2)-W(1)#1 | 80.5(7) | O(7)#1-V(2)-O(3) | 88(4) |
| V(2)-O(7)#1 | 1.88(9) | O(2)-W(2)-W(1)#1 | 122.5(9) | O(4)-V(2)-O(3) | 87(4) |
| V(2)-O(4) | 1.91(9) | O(6)#1-W(2)-W(1)#1 | 32.1(5) | O(5)#1-V(2)-O(3) | 154(5) |
| V(2)-O(5)#1 | 1.92(8) | O(1)-W(2)-W(1)#1 | 45.4(4) | O(9)-V(2)-O(1) | 179(5) |
| V(2)-O(3) | 1.94(8) | O(10)-W(2)-W(3)#1 | 135.8(12) | O(7)#1-V(2)-O(1) | 77(3) |
| V(2)-O(1) | 2.29(9) | O(4)-W(2)-W(3)#1 | 121.6(10) | O(4)-V(2)-O(1) | 76(3) |
| Mn(1)-O(8) | 2.050(11) | O(7)-W(2)-W(3)#1 | 31.5(6) | O(5)#1-V(2)-O(1) | 77(3) |
| Mn(1)-O(8)#2 | 2.050(11) | O(2)-W(2)-W(3)#1 | 81.4(8) | O(3)-V(2)-O(1) | 78(3) |
| Mn(1)-N(1)#2 | 2.175(13) | O(6)#1-W(2)-W(3)#1 | 80.7(8) | O(8)-Mn(1)-O(8)#2 | 176.6(6) |
| Mn(1)-N(1) | 2.175(13) | O(1)-W(2)-W(3)#1 | 45.1(5) | O(8)-Mn(1)-N(1)#2 | 89.9(5) |
| Mn(1)-N(3) | 2.195(19) | W(1)#1-W(2)-W(3)#1 | 60.4(5) | O(8)#2-Mn(1)-N(1)#2 | 90.1(5) |
| Mn(1)-N(4) | 2.20(2) | O(10)-W(2)-W(3) | 134.2(12) | O(8)-Mn(1)-N(1) | 0.1(5) |
| O(8)-W(1)-O(6) | 103.2(5) | O(4)-W(2)-W(3) | 31.6(6) | O(8)#2-Mn(1)-N(1) | 89.9(5) |
| O(8)-W(1)-O(5) | 101.9(5) | O(7)-W(2)-W(3) | 121.5(10) | N(1)#2-Mn(1)-N(1) | 179.3(7) |
| O(6)-W(1)-O(5) | 89.3(5) | O(2)-W(2)-W(3) | 80.4(8) | O(8)-Mn(1)-N(3) | 91.7(3) |
| O(8)-W(1)-O(3) | 103.1(5) | O(6)#1-W(2)-W(3) | 81.6(8) | O(8)#2-Mn(1)-N(3) | 91.7(3) |
| O(6)-W(1)-O(3) | 88.4(5) | O(1)-W(2)-W(3) | 44.9(5) | N(1)#2-Mn(1)-N(3) | 89.7(4) |
| O(5)-W(1)-O(3) | 154.8(5) | W(1)#1-W(2)-W(3) | 60.0(5) | N(1)-Mn(1)-N(3) | 89.7(4) |
| O(8)-W(1)-O(2) | 101.2(5) | W(3)#1-W(2)-W(3) | 90.0(7) | O(8)-Mn(1)-N(4) | 88.3(3) |
| O(6)-W(1)-O(2) | 155.6(5) | O(9)-W(3)-O(7)#1 | 103.3(12) | O(8)#2-Mn(1)-N(4) | 88.3(3) |
| O(5)-W(1)-O(2) | 87.2(5) | O(9)-W(3)-O(4) | 103.5(12) | N(1)#2-Mn(1)-N(4) | 90.3(4) |
| O(3)-W(1)-O(2) | 84.6(5) | O(7)#1-W(3)-O(4) | 153.3(13) | N(1)-Mn(1)-N(4) | 90.3(4) |
| O(8)-W(1)-O(1) | 178.1(4) | O(9)-W(3)-O(5)#1 | 103.5(11) | N(3)-Mn(1)-N(4) | 180.000(4) |
| O(6)-W(1)-O(1) | 78.5(3) | O(7)#1-W(3)-O(5)#1 | 87.6(9) | C(5)-N(1)-C(1) | 118.9(13) |
| O(5)-W(1)-O(1) | 77.2(3) | O(4)-W(3)-O(5)#1 | 85.7(10) | C(5)-N(1)-Mn(1) | 122.8(10) |
| O(3)-W(1)-O(1) | 77.7(3) | O(9)-W(3)-O(3) | 101.9(11) | C(1)-N(1)-Mn(1) | 118.4(10) |
| | | O(7)#1-W(3)-O(3) | 88.1(10) | | |

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 ($\times 10^3$ Å$^2$)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| W(1) | 16(1) | 26(1) | 9(1) | -1(1) | -3(1) | 1(1) |
| W(2) | 10(14) | 14(16) | 3(13) | 1(11) | 1(11) | -4(11) |
| W(3) | 9(14) | 12(15) | 3(13) | -2(11) | 0(11) | 2(11) |
| V(1) | 10(60) | 10(70) | 0(60) | 0(50) | 0(50) | 0(50) |
| V(2) | 10(60) | 10(70) | 0(60) | 0(50) | 0(50) | 0(50) |
| Mn(1) | 3(1) | 4(2) | 1(1) | 0 | 0(1) | 0 |
| N(1) | 15(7) | 18(7) | 7(6) | 1(5) | -1(5) | -3(6) |
| N(2) | 24(9) | 39(11) | 16(8) | 0(7) | 1(7) | -2(7) |
| N(3) | 12(9) | 15(10) | 8(9) | 0 | 0(7) | 0 |
| N(4) | 15(10) | 16(11) | 10(9) | 0 | -2(8) | 0 |
| O(1) | 13(8) | 15(9) | 7(8) | 0(6) | 1(6) | -1(6) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O(2) | 13(6) | 19(6) | 7(5) | 2(4) | -1(4) | -2(5) |
| O(3) | 13(6) | 19(6) | 6(5) | 1(4) | -2(4) | 2(5) |
| O(4) | 12(6) | 19(6) | 7(5) | 0(4) | -3(4) | 0(5) |
| O(5) | 13(6) | 19(6) | 5(5) | -2(4) | 0(4) | -2(4) |
| O(6) | 15(6) | 18(6) | 7(5) | 2(4) | -1(4) | -2(5) |
| O(7) | 15(6) | 18(6) | 8(5) | 0(4) | 0(4) | -1(5) |
| O(8) | 14(6) | 21(7) | 10(6) | 1(4) | -2(5) | 0(5) |
| O(9) | 15(6) | 20(6) | 11(5) | 0(5) | -5(5) | 5(5) |
| O(10) | 19(6) | 22(7) | 14(6) | 0(5) | 0(5) | -8(5) |
| C(1) | 18(9) | 21(9) | 8(7) | -2(7) | 1(7) | -2(7) |
| C(2) | 20(9) | 26(10) | 8(7) | -1(7) | 0(7) | -4(7) |
| C(3) | 20(9) | 25(10) | 9(8) | 0(7) | 0(7) | -3(7) |
| C(4) | 20(9) | 26(10) | 10(8) | -2(7) | 0(7) | -3(7) |
| C(5) | 15(8) | 19(9) | 8(7) | -1(6) | 0(6) | -3(7) |
| C(6) | 23(10) | 35(11) | 14(8) | -1(8) | 0(7) | 1(8) |
| C(7) | 23(9) | 31(11) | 11(8) | 0(7) | 0(7) | -1(8) |
| C(8) | 21(9) | 27(10) | 10(8) | -1(7) | 0(7) | -3(7) |
| C(9) | 25(10) | 32(11) | 12(8) | -2(8) | -1(7) | -4(8) |
| C(10) | 26(10) | 36(12) | 15(9) | 2(8) | 0(8) | -6(8) |
| C(11) | 13(8) | 17(9) | 9(7) | 1(6) | 0(6) | -1(6) |
| C(12) | 13(8) | 17(9) | 15(8) | 0(7) | 1(7) | 3(7) |
| C(13) | 14(11) | 15(12) | 11(11) | 0 | -3(9) | 0 |
| C(14) | 21(9) | 17(9) | 9(8) | -1(7) | -5(7) | -2(7) |
| C(15) | 22(9) | 19(10) | 13(8) | -4(7) | -4(7) | -4(7) |
| C(16) | 17(12) | 19(13) | 12(11) | 0 | -5(9) | 0 |

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

| | x | y | z | U(eq) | | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| H(2) | 7411 | 7371 | -2622 | 32 | H(9) | 6619 | 9005 | -882 | 28 |
| H(1) | 6236 | 8284 | 1812 | 19 | H(10) | 7173 | 9062 | -2057 | 31 |
| H(2A) | 6776 | 8366 | 608 | 22 | H(11) | 5792 | 5133 | 1897 | 16 |
| H(4) | 5398 | 6175 | -487 | 22 | H(12) | 5764 | 3151 | 1789 | 18 |
| H(5) | 4838 | 6262 | 678 | 17 | H(14) | 5127 | 9393 | 3716 | 19 |
| H(6) | 7154 | 5639 | -2144 | 29 | H(15) | 5053 | 11367 | 3753 | 22 |
| H(7) | 6512 | 5570 | -1043 | 26 | | | | | |

**Crystal structure:** The compound Mn(V$_2$W$_4$O$_{19}$)(bpy)(Hbpy)$_2$ 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 the 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 crystal structure, the Mn(II) center is octahedrally coordinated by two oxygen atoms, O8 and O8$^{\#2}$ (#2: -x+1, y, -z+1/2), at the axial direction, respectively from two divanadium hexatungstates $[V_2W_4O_{19}]^{4-}$ and 4 pyridyl nitrogen atoms, N1$^{\#2}$ (#2: -x+1, y, -z+1/2), N1, N3, N4, in equatorial plane, respectively from four 4,4'-bipyridine ligands, as shown in Fig. 1. The Mn-centered coordination octahedron is slightly distorted, with bonds length 2.050(11) Å for Ni-O and 2.175(13)- 2.20(2) Å for Ni-N bonds and the related bond angles approximate to 90º and 180º.
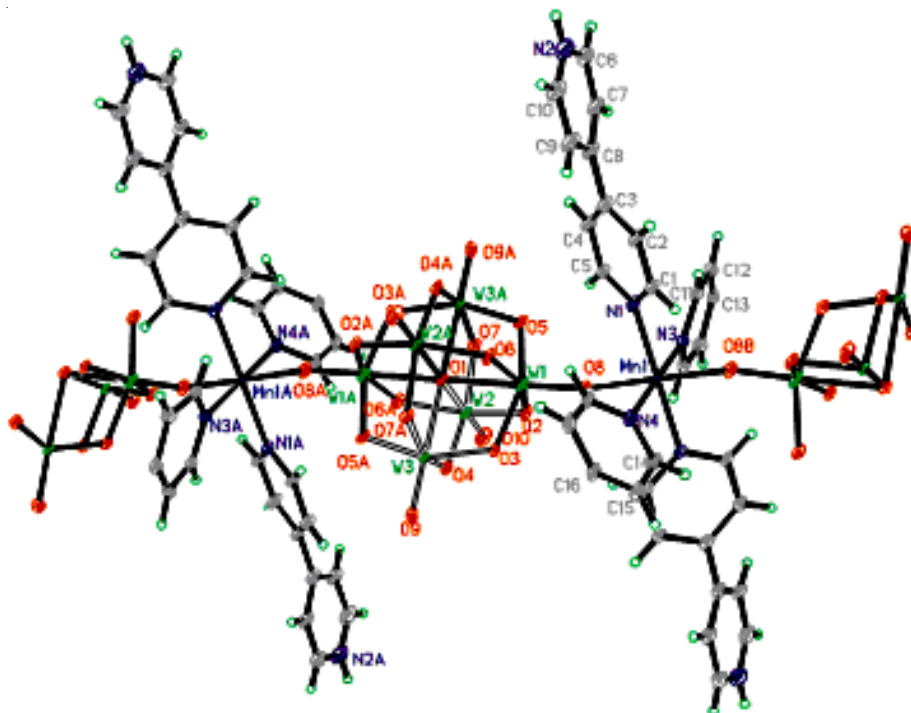


Fig. 1.   Ortep view of the Mn(V$_2$W$_4$O$_{19}$)(bpy)(Hbpy)$_2$ structure with atomic labelling of one asymmetric unit, and the position occupancy factor ratio of W2/V1 and W3/V2 are 0.50/0.50 and 0.50/0.50, respectively

As illustrated in Fig. 1, of the four 4,4'-bipyridine ligands coordinating to Mn(II) centres, two at *para* positions are terminal and the nitrogen atom in the another 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 Mn centres of the adjacent two 1-D $[Mn(V_2W_4O_{19})]^{2-}$ anion chains, to build a 2-D organic-inorganic covalent
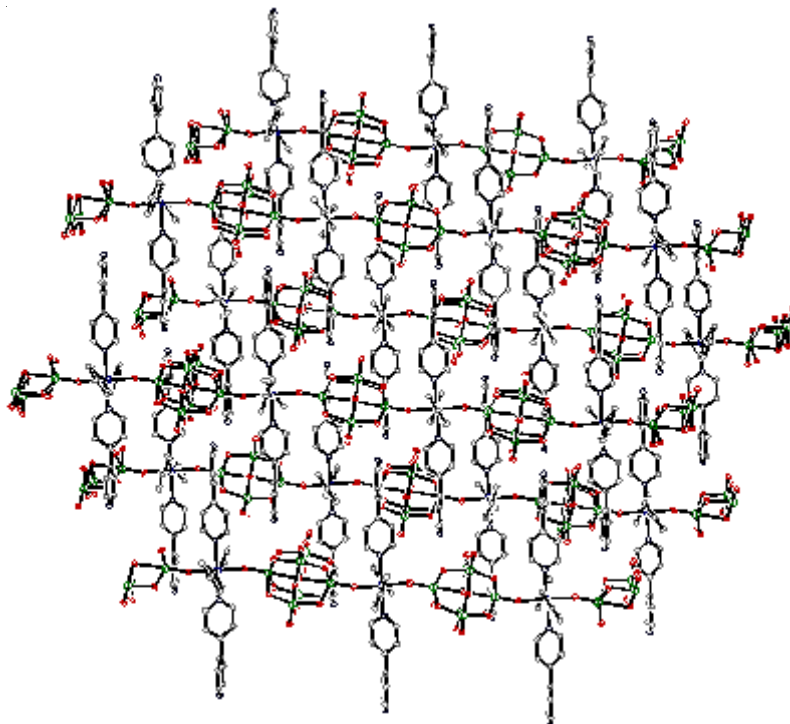
Fig. 2. Structure of the [Mn(V$_2$W$_4$O$_{19}$)(bpy)(Hbpy)$_2$] layer

layer Mn(V$_2$W$_4$O$_{19}$)(bpy)(Hbpy)$_2$, as drawn in Fig. 3. The layers are packed by intermolecular forces to build up the whole crystal structure for the title compound.

The inorganic building blocks of divanadium hexatungstate [V$_2$W$_4$O$_{19}$]$^{4-}$ are coordinated to two Mn centers *via* its two centrically symmetric O8 atoms, respectively (Fig. 1). And [V$_2$W$_4$O$_{19}$]$^{4-}$ basically keeps 'superoctahedral' Lindqvist-structure just like [W$_6$O$_{19}$]$^{2-}$, which is also reported by previous workers[9].

The present compound is a novel organic-inorganic hybrid compound, in which both the divanadium hexatungstate [V$_2$W$_4$O$_{19}$]$^{4-}$ and 4,4'-bipyridine act as bidenate ligand to coordinate with the Mn(II) centers to build the extended 2-D covalent framework. Up to now, [V$_2$W$_4$O$_{19}$]$^{4-}$ 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 title compound described in present paper.

**Optical energy gap:** In order to explore the conductivity of Mn(V$_2$W$_4$O$_{19}$)(bpy)(Hbpy)$_2$, the measurement of diffuse reflectivity for a powder sample was used to obtain its band gap E$_g$; which agrees 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 title compound is shown in Fig. 3, where a steep absorption edge is displayed and the $E_g$ can be assessed at 2.1 eV.
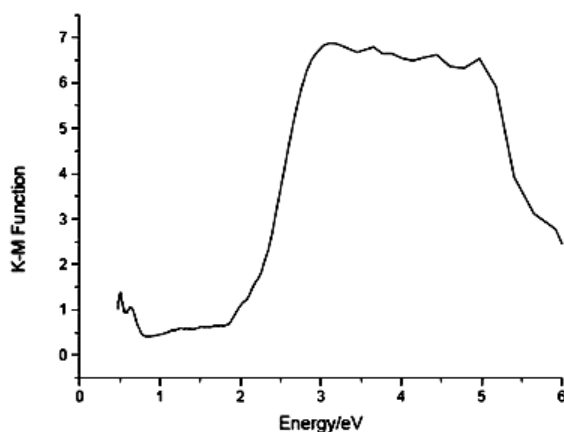


Fig. 3. Plot of K-M function *versus* energy E(eV) of the present compound

## ACKNOWLEDGEMENTS

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