

Hexatungstate subunit as building block in the hydrothermal synthesis of organic–inorganic hybrid materials: synthesis, structure and optical properties of $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ ($\text{bpy} = 4,4'$ -bipyridine)

Lijuan Zhang,^{a,*} Yongge Wei,^b Chongchen Wang,^a Hongyou Guo,^a and Ping Wang^{a,*}

^aDepartment of Applied Chemistry, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Chaoyang, Beijing 100029, China

^bState Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received 26 March 2004; received in revised form 25 May 2004; accepted 27 May 2004

Available online 20 July 2004

Abstract

A hydrothermal reaction of WO_3 , CoCl_2 and 4,4'-bipyridine, yields a novel organic–inorganic hybrid compound, $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$, at 170°C. X-ray single crystal structure determination reveals a two-dimensional covalent structure belonging to monoclinic crystal system, space group $C2/c$, with cell parameters $a = 19.971(4) \text{ \AA}$, $b = 11.523(2) \text{ \AA}$, $c = 16.138(3) \text{ \AA}$, $\beta = 96.49(3)^\circ$, $V = 3690.0 \text{ \AA}^3$ and $Z = 2$. The hexatungstate, $[\text{W}_6\text{O}_{19}]^{2-}$, acts as a building block in bidentate fashion to bridge the Co(II) centers in the crystal structure. The title compound is found to have an optical energy gap of 2.2 eV from UV–Vis–NIR reflectance spectra.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Organic–inorganic hybrid material; Hexatungstate; 4,4'-bipyridine; Hydrothermal synthesis; Crystal structure

1. Introduction

Early transition metal oxide anion clusters (polyoxometalates or POMs) are a rapidly growing class of compounds. POMs have been of great interest because of their so-called ‘Value-adding properties’ and conventional applications in photochemical response, conductivity, catalysis and medicine [1–3] and studied as molecular models to mimic the chemical reactivity of solid metal oxide surface [4–5]. Virtually, all molecular properties that impact the utility of the class of compounds can be altered by many methods that are now rational and defensible.

POMs are found to be extremely versatile inorganic building blocks for constructions of organic–inorganic hybrid materials with novel structures and unusual properties [6–9]. The use of the well-defined metal oxide clusters for the construction of materials with more or less predictable connectivity in the crystalline state is

attractive, since secondary metal-ligand bridges should provide linkages sufficiently strong to connect the clusters into kinetically stable crystal architectures.

Up to date, all reported the hybrid materials of POMs can be chemically formulated as $M_xL_y(X_mO_n)_z$ where M is cationic metal center called template species, L polydentate organic ligand and (X_mO_n) anionic polyoxometalate, called building block. Organic ligand L and anionic polyoxometalate (X_mO_n) also play the role of structure-directing effect for the constructions of such hybrid materials.

The organic–inorganic hybrid materials can be considered to be constructed with inorganic metal M polyoxometalate $[M_x(X_mO_n)_z]$, linked by L , the organic ligands; or with cationic coordination complex, $[M_xL_y]$, connected by (X_mO_n) , the ionic polyoxometalates. $M_xL_y(X_mO_n)_z$ compounds possess diverse structures, covalent framework of which can be zero-, one-, two- or three-dimensional.

In the $M_xL_y(X_mO_n)_z$ compounds reported, most of the (X_mO_n) anionic clusters are (Mo_mO_n) and (V_mO_n) , and the (Nb_mO_n) and (W_mO_n) clusters are rare [10].

*Corresponding author. Fax: +86-10-6443-4898.

E-mail addresses: dazlj@mail.buct.edu.cn (L. Zhang), wangping@mail.buct.edu.cn (P. Wang).

The (W_mO_n) polyoxotungstate and secondary [M_xL_y] metal-ligand subunit to produce organic–inorganic hybrid materials remains largely unexplored. Although [TTF]₃[W₆O₁₉], [TMTSF][W₆O₁₉]·2DMF, [BEDT TTF]₂W₆O₁₉ and (Tph-TTF)₂W₆O₁₉ have been synthesized and characterized [11,12], where the [W₆O₁₉]²⁻ acts as a discrete cluster and are only modified by the organic ligands on its surface, there no extended covalent network is formed in these compounds. In this paper, a novel inorganic/organic hybrid compound, Co₂(bpy)₆(W₆O₁₉)₂, with two-dimensional covalent framework, which was hydrothermally synthesized and structurally characterized, will be reported.

2. Experimental

2.1. Preparation

All commercially available chemicals and solvents are of reagent grade and used as received without further purification.

A mixture of CoCl₂·6H₂O (0.0476 g, 0.20 mmol), WO₃ (0.0928 g, 0.4 mmol), NH₄VO₃ (0.0468 g, 0.4 mmol), 4,4'-bipyridine (0.0769 g, 0.4 mmol) and H₂O (13 mL, 0.722 mol) in a mole ratio of 1:2:2:2:3610 in 25 mL polytetrafluoroethylene-lined stainless steel reaction container was heated for 3 days at 170°C and then cooled down to room temperature. The reaction system, pH ≈ 5.5, contains orange block-like crystals in yield ca. 81% based on WO₃. Elemental analysis for the product was performed by Elementar Vario EL-III. Anal. (%) Calc. for C₆₀H₄₈Co₂N₁₂O₃₈W₁₂: N 4.34, C 18.00, H 1.20. Found: N 4.67, C 20.27, H 1.91.

2.2. Infrared spectroscopy

Infrared (IR) spectra, in the region (400–4000 cm⁻¹), were recorded on a computer-controlled Nicolet-210 Fourier Transform infrared spectrophotometer. Experiment was performed on finely ground solid sample. 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).

2.3. Crystal structure determination

A single crystal (0.3 × 0.2 × 0.05 mm³) was selected for X-ray diffraction measurement. Intensity data was collected using Bruker Smart APEX-CCD diffractometer at 293(2) K, graphite-monochromated MoK α radiation ($\lambda = 0.71073$). The total reflections of 15,647 were measured, of which, 6887 reflections were unique

with $R_{\text{int}} = 0.0744$ and 5978 reflections were observed having $I \geq 2\sigma(I)$. The final unit cell parameters were obtained by global refinement of the positions of all collected reflections. An absorption correction was applied by the correction of symmetry-equivalent reflections using the ABCOR program [13]. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares on F^2 using the SHELX-97 program package [14]. The H atoms were placed at their calculated positions on the relevant atoms. The drawings were produced with XP and SCHAKAL92 [15]. The crystal data, atomic coordinates and selected bond lengths and angles are listed in Tables 1–3, respectively.

2.4. Diffuse reflectance spectra

To investigate the band-gap energy, diffuse reflectance spectra of the solid sample were measured by UV-3100 recording spectrophotometer with an integrating sphere of 60 mm in diameter over the range 200–2600 nm at room temperature. Barium sulfate (BaSO₄) was used as the standard with 100% reflectance [16].

Table 1
Crystal data and structure refinement for Co₂(bpy)₆(W₆O₁₉)₂

Empirical formula	C ₆₀ H ₄₈ Co ₂ N ₁₂ O ₃₈ W ₁₂
Formula weight	3869.16
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 19.971(4)$ Å, $\alpha = 90^\circ$ $b = 11.523(2)$ Å, $\beta = 96.49(3)^\circ$ $c = 16.138(3)$ Å, $\gamma = 90^\circ$
Volume	3690.0(13) Å ³
Z	2
Density (calculated)	3.482 Mg/m ³
Absorption coefficient	19.155 mm ⁻¹
$F(000)$	3476
Crystal size	0.30 × 0.20 × 0.05 mm ³
θ range for data collection	2.04–31.50°
Index ranges	$-29 \leq h \leq 28$, $-14 \leq k \leq 16$, $-23 \leq l \leq 15$
Reflections collected	15647
Independent reflections	5978 [$R_{\text{int}} = 0.0744$]
Completeness to $\theta = 31.50^\circ$	97.4%
Absorption correction	Empirical
Max. and min. transmission	0.4476 and 0.0690
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5978/0/279
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0656$, $wR2 = 0.1703$
R indices (all data)	$R1 = 0.0701$, $wR2 = 0.1740$
Largest diff. peak and hole	7.128 and -4.381 e. Å ⁻³

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
W(1)	3398(1)	2573(1)	1022(1)	11(1)
W(2)	1901(1)	3746(1)	743(1)	22(1)
W(3)	2932(1)	4053(1)	−651(1)	21(1)
Co(1)	5000	2736(1)	2500	4(1)
O(1)	2500	2500	0	4(2)
O(2)	3716(3)	1543(6)	265(5)	11(1)
O(3)	4061(4)	2682(7)	1801(5)	14(1)
O(4)	2736(3)	3570(6)	1467(4)	8(1)
O(5)	2866(3)	1325(6)	1406(4)	7(1)
O(6)	3585(3)	3847(6)	340(4)	10(1)
O(7)	2360(3)	4755(6)	77(4)	8(1)
O(8)	1653(3)	2249(6)	1112(4)	8(1)
O(9)	1487(4)	4628(7)	1312(5)	18(2)
O(10)	3240(4)	5159(7)	−1139(5)	15(1)
N(1)	5000	4643(9)	2500	7(2)
N(2)	5485(4)	2755(7)	1366(5)	9(1)
N(3)	5000	10824(10)	2500	12(2)
N(4)	7201(6)	2702(13)	−2179(7)	31(3)
C(1)	5455(5)	5252(8)	2135(6)	11(2)
C(2)	5463(5)	6455(8)	2103(6)	12(2)
C(3)	5000	7089(11)	2500	10(2)
C(4)	5000	8386(11)	2500	10(2)
C(5)	4968(7)	9007(9)	1756(7)	20(2)
C(6)	4937(6)	10215(9)	1789(7)	17(2)
C(7)	5243(5)	3322(9)	678(6)	10(2)
C(8)	5564(5)	3384(9)	−36(6)	13(2)
C(9)	6140(5)	2729(8)	−79(6)	8(2)
C(10)	6394(5)	2085(9)	630(6)	12(2)
C(11)	6060(5)	2121(9)	1335(6)	12(2)
C(12)	7021(6)	3689(13)	−1902(7)	25(3)
C(13)	6662(6)	3736(10)	−1225(6)	16(2)
C(14)	6509(5)	2712(9)	−826(6)	11(2)
C(15)	6713(7)	1654(11)	−1143(6)	22(2)
C(16)	7050(7)	1653(14)	−1832(7)	30(3)

 U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

3. Results and discussions

3.1. Synthesis

Hydrothermal reaction was adopted to prepare the title compound from the mixture of CoCl_2 , WO_3 , NH_4VO_3 , 4,4'-bipyridine and H_2O in a mole ratio of 1:2:2:2:3610 at 170°C , with pH ca. 5.5. The orange title compound does not contain V atom as confirmed by elemental analysis. While a black crystal was formed in the synthesis reaction, which was proved to be a known $\text{Co}(\text{bpy})\text{V}_2\text{O}_6$. In the synthesis reaction, it seems as if NH_4VO_3 would not play any part in assembly of the title compound. To investigate the role of the NH_4VO_3 , we tried to synthesize the title compound directly from CoCl_2 , WO_3 and 4,4'-bipyridine under the same conditions, no desired crystal was found. The title compound, therefore, cannot be formed in the synthesis reactions without NH_4VO_3 .

Table 3

Selected bond lengths (\AA) and angles (deg) for $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$

W(1)–O(3)	1.724(8)
W(1)–O(1)	2.2963(8)
W(2)–O(1)	2.2921(6)
W(3)–O(1)	2.2920(6)
Co(1)–O(3)#2	2.077(8)
Co(1)–O(3)	2.077(8)
Co(1)–N(2)#2	2.165(8)
Co(1)–N(2)	2.165(8)
Co(1)–N(1)	2.198(11)
Co(1)–N(3)#3	2.203(12)
O(1)–W(3)#1	2.2920(6)
O(1)–W(2)#1	2.2921(6)
O(1)–W(1)#1	2.2963(8)
O(3)#2–Co(1)–O(3)	176.6(4)
O(3)#2–Co(1)–N(2)#2	90.2(3)
O(3)–Co(1)–N(2)#2	89.8(3)
O(3)–Co(1)–N(2)	90.2(3)
N(2)#2–Co(1)–N(2)	178.8(4)
O(3)–Co(1)–N(1)	91.7(2)
N(2)–Co(1)–N(1)	89.4(2)
O(3)–Co(1)–N(3)#3	88.3(2)
N(2)–Co(1)–N(3)#3	90.6(2)
N(1)–Co(1)–N(3)#3	180.000(1)
W(1)–O(3)–Co(1)	166.0(5)
C(1)–N(1)–Co(1)	121.6(5)
C(7)–N(2)–Co(1)	123.7(6)
C(11)–N(2)–Co(1)	118.9(7)
C(6)–N(3)–Co(1)#4	121.6(6)

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

Without adding NH_4VO_3 , We dissolved WO_3 by HCl and NaOH aqueous solutions, respectively, and controlled pH of the reaction systems range from 3 to 10, meanwhile kept other reaction conditions constant, however we did not achieve the title compound. It shows that NH_4VO_3 not only influences pH values of the system, but also activates the synthesis reaction of the title compound.

The mole ratio of the reactants changed in a large range, say 1:4:2:2:3610, under the same condition, the orange title and the black side compounds were also found. But it was not favourable for crystal growth and good yield of the title compound, compared with the mole ratio 1:2:2:2:3610.

We also failed to synthesize the title compound under the same conditions, except for reaction temperatures, 120°C , 140°C , 150°C , 160°C and 180°C or higher temperatures. It indicates that temperature is also a key factor to hydrothermally synthesize the title compound.

3.2. Description of the crystal structure

$\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ is a novel organic–inorganic hybrid compound, crystallizing in the monoclinic crystal

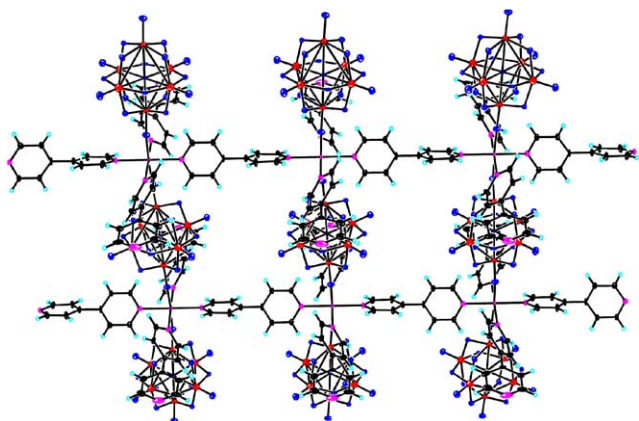


Fig. 1. Structure of the ${}^2_{\infty}[\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2]$ layer of the title compound.

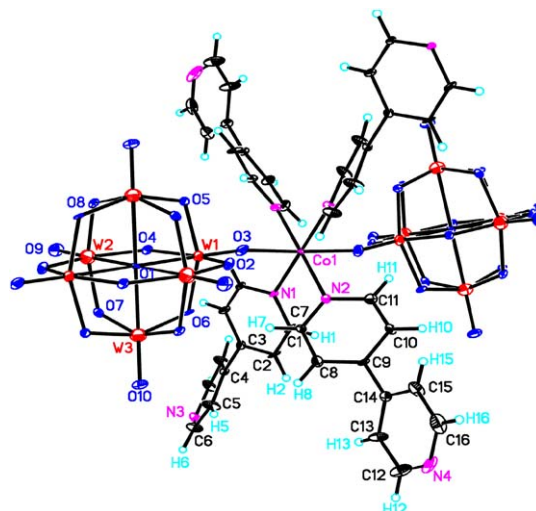


Fig. 2. ORTEP view of the $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ structure showing the atom labeling scheme (50% thermal ellipsoids).

system, space group $C2/c$. The crystal structure determination revealed it to be a novel layer-like structure. In the ${}^2_{\infty}[\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2]$ layer, as shown in Fig. 1, the Co(II) center is octahedrally coordinated by two oxygen atoms, O3 and O3^{#2}, at the axial direction, respectively from two $(\text{W}_6\text{O}_{19})^{2-}$ hexatungstates and four pyridyl nitrogen atoms, N1, N2, N3 and N2^{#2} in the equatorial plane, respectively from four 4,4'-bipyridine ligands (Fig. 2).

The Co-centered coordination octahedron is slightly distorted, with the bond lengths, 2.071(9) Å for Co–O bonds, and 2.163(9)–2.215(13) Å for Co–N bonds, and the bond angles approximate to 90° or 180°. The hexatungstate $(\text{W}_6\text{O}_{19})^{2-}$ basically keeps ‘superoctahedral’ Lindqvist-structure, which can be compared with the structure of previously reported isolated cluster anions in solid state [17].

The hexatungstate $(\text{W}_6\text{O}_{19})^{2-}$ coordinates to two Co(II) centers via its two centrally symmetric O3 atoms, respectively, to form an electrically neutral cobalt hexatungstate chain, ${}^1_{\infty}[\text{Co}(\text{W}_6\text{O}_{19})]$, along in the [101] direction, depicted in Fig. 3, where N atoms are from pyridyl groups of 4,4'-bipyridine ligands.

Of the four 4,4'-bipyridine ligands coordinating to each Co centre of the inorganic chain, two at para positions are terminal and other two coordinate act as N, N'-bidentate bridging ligands to coordinate with Co centers of the adjacent two ${}^1_{\infty}[\text{Co}(\text{W}_6\text{O}_{19})]$ chains, respectively, to construct an organic–inorganic covalent layer, ${}^2_{\infty}[\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2]$, paralleling to the (10 $\bar{1}$) plane.

The layers are packed by intermolecular forces to build up the whole crystal structure for the title compound, as drawn in Fig. 4.

The layered structure of $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ crystal is also described as coordination polymeric chains parallel to the *b*-axis direction, ${}^1_{\infty}[\text{Co}(\text{bpy})_3]^{2+}$ (Fig. 5), bridged

by O,O'-bidentate $(\text{W}_6\text{O}_{19})^{2-}$ ligands through the Co–O3 coordinated bonds.

$\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ is a novel organic–inorganic hybrid compound. The hexatungstate and 4,4'-bipyridine both are bidentate ligands to coordinate with the Co(II) centers to construct the extended two-dimensional covalent framework.

Here hexatungstate and 4,4'-bipyridine act as building blocks and Co(II) centers as node templates. However, according to our knowledge, in published organic–inorganic hybrid compounds, no polytungstate takes part in any extended structure [11,12,18–20]. For examples, in $(\text{TTF})_3(\text{W}_6\text{O}_{19})$ and $(\text{TMTSF})_3(\text{W}_6\text{O}_{19})$, the $(\text{W}_6\text{O}_{19})^{2-}$ was directly linked by the organic ligands to form the clusters [11]. The $(\text{W}_6\text{O}_{19})^{2-}$ unit is only chemically modified on the surface.

3.3. Optical energy gap

In order to explore the conductivity of the title 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 [21]. 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 [22]. 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 [23]. The F versus E plot for the title compound is shown in Fig. 6, where a steep absorption edge is displayed and the E_g can be assessed at 2.2 eV.

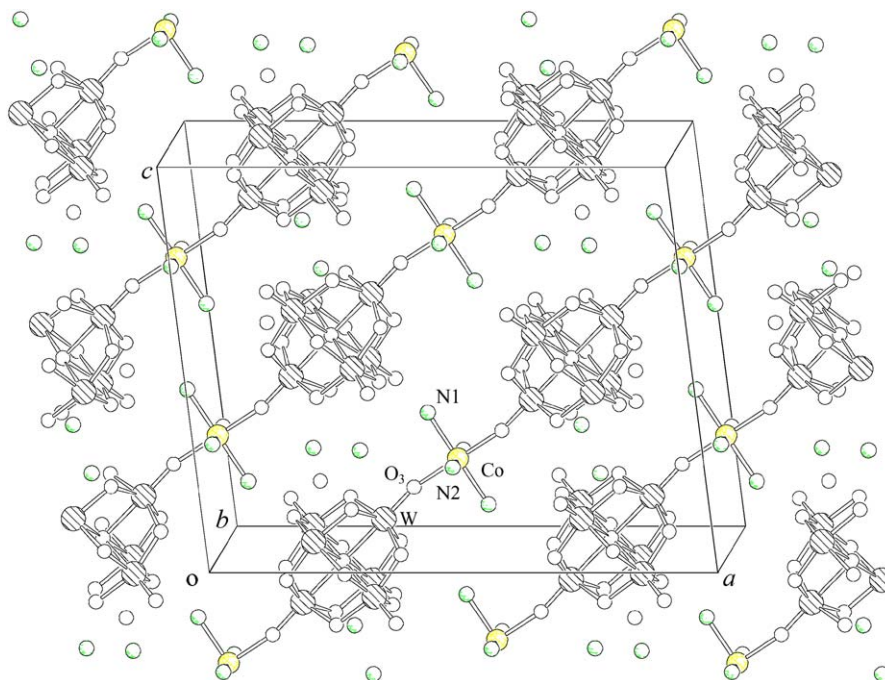


Fig. 3. $\frac{1}{\infty}[\text{Co}(\text{W}_6\text{O}_{19})]$ chains in the title compound.

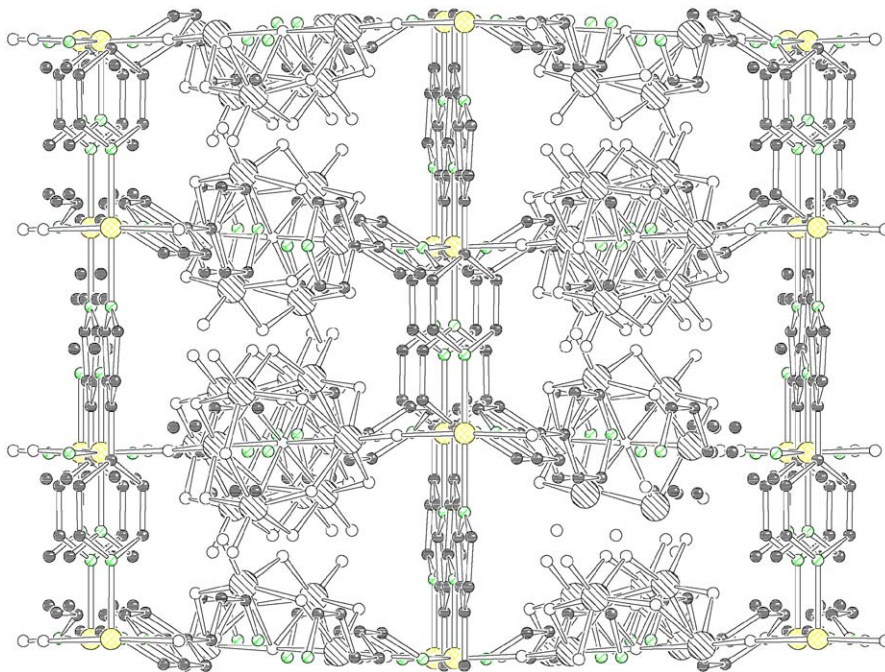


Fig. 4. A packing view along the c -axis direction with double shaded circles for Co, single shaded circles for W, partly pointed circles for N, open circles for O, and solid circles for C atoms.

4. Conclusions

A novel two-dimensional network organic–inorganic hybrid compound, $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$ has been synthe-

sized via a hydrothermal reaction of the mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, WO_3 , NH_4VO_3 , 4,4'-bpy, and H_2O in a mole ratio of 1:2:2:2:3610 at 170°C for 3 days and structurally characterized by single crystal X-ray

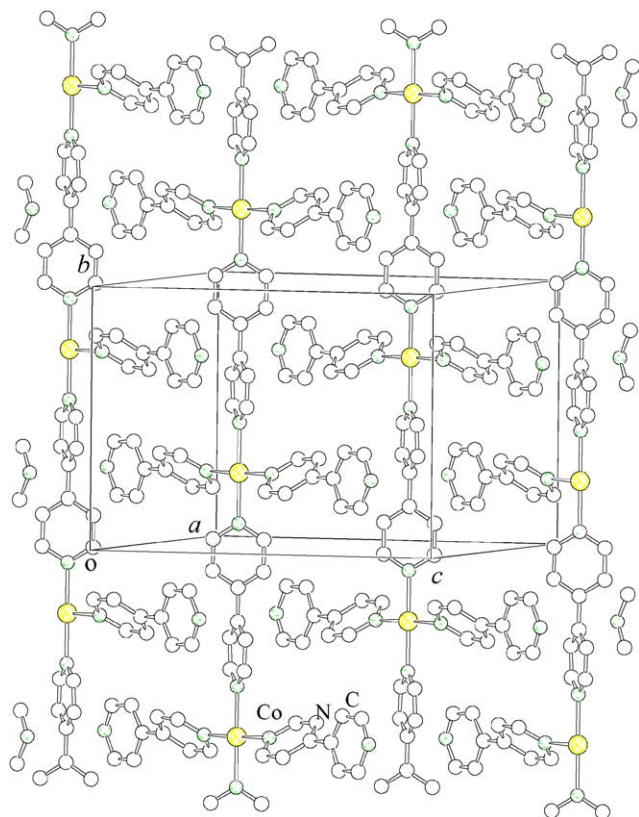


Fig. 5. $[\text{Co}(\text{bpy})_3]^{2+}$ coordination polymeric chains in $\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2$.

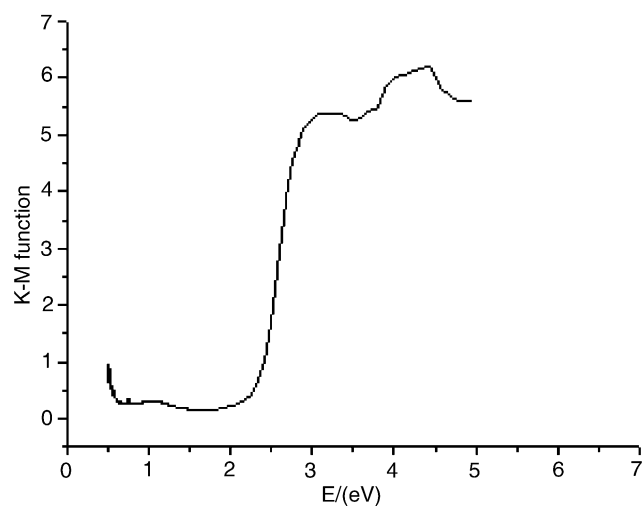


Fig. 6. Plot of K–M function versus energy $E(\text{eV})$ for the title compound.

diffraction. The hexatungstate, $[\text{W}_6\text{O}_{19}]^{2-}$, acts as a building block in a bidentate fashion to bridge the $\text{Co}(\text{II})$ centers in the crystal. The title compound is found to have an optical energy gap of 2.2 eV from its UV–Vis–NIR reflectance spectra.

References

- [1] D.E. Katsoulis, *Chem. Rev.* 98 (1998) 359.
- [2] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [3] J.T. Rhule, C.L. Hill, D.A. Judd, *Chem. Rev.* 98 (1998) 327.
- [4] T. Nagata, M. Pohl, H. Weiner, *Inorg. Chem.* 36 (1997) 1366.
- [5] K. Isobe, A. Yagasaki, *Acc. Chem. Res.* 26 (1993) 524.
- [6] R.S. Rarig Jr., L. Bewley, V. Golub, C.J. O'Connor, J. Zubieta, *Inorg. Chem. Commun.* 6 (2003) 539.
- [7] P.J. Hargman, D. Hargman, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* 34 (1999) 2638.
- [8] R.S. Rarig Jr, J. Zubieta, *Polyhedron* 22 (2003) 177.
- [9] P.J. Zapf, C.J. Warren, R.C. Haushalter, J. Zubieta, *Chem. Commun.* (1997) 1543.
- [10] P.J. Hargman, D. Hargman, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 2638.
- [11] S. Triki, L. Quahab, J.-F. Halet, et al., *J. Chem. Soc.* (1947) 358.
- [12] R. Bhattacharyya, S. Biswas, J. Armstrong, E.M. Hott, *Inorg. Chem.* 28 (1989) 4297.
- [13] T. Higashi, ABCOR, Empirical Absorption Correction based on Fourier Series Approximation, Rigaku Corporation, Tokyo, 1995.
- [14] G.M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.
- [15] E. Keller, SCHAKAL92: A Computer Program for Graphical Representation of Molecular and Crystallographic Models, University of Freiburg, Germany, 1992.
- [16] J. Li, Z. Chen, X. Wang, D.M. Proserpio, *J. Alloys Compds.* 28 (1997) 262.
- [17] A.J. Bridgeman, G. Cavigliasso, *Inorg. Chem.* 1761 (2002) 41.
- [18] R.N. Devi, E. Burkholder, J. Zubieta, *Inorg. Chim. Acta* 348 (2003) 150.
- [19] M. Vasylyev, R. Popovitz-Biro, L.J.W. Shimon, R. Neumann, *J. Mol. Struct.* 656 (2003) 27.
- [20] P. Zavalij, J. Guo, M.S. Whittingham, R.A. Jacobson, V. Pecharsky, C.K. Bucher, S. Hwu, *J. Solid State Chem.* 123 (1996) 83.
- [21] T.J. McCarthy, S.P. Ngeyi, J.-H. Liao, D.C. DeGroot, T. Hogan, C.R. Kannewurf, M.G. Kanatzidis, *Chem. Mater.* 5 (1993) 331.
- [22] J.I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1997, pp. 34–86.
- [23] G. Kortum, *Reflectance Spectroscopy*, Springer, New York, 1966, pp. 104–169.