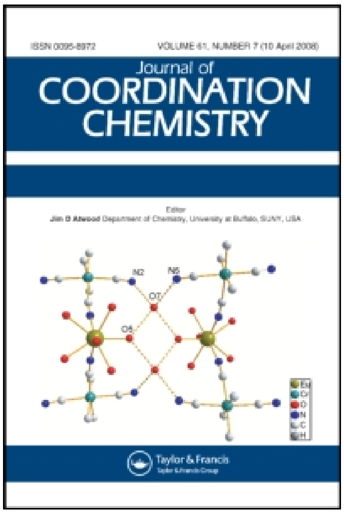

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A one-dimensional organic–inorganic hybrid constructed by saturated Keggin polyoxoanions and $[\mathrm{Cu^{I}(4,4'\text{-}bipy)}]_n^{n+}$ chains

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A one-dimensional (1-D) organic–inorganic hybrid compound $\{(H_3O)[\mathrm{Cu^{I}(4,4'\text{-}bipy)}]_3[SiW_{12}O_{40}]\}\cdot 1.5H_2O$ (**1**) has been synthesized from hydrothermal reaction of Keggin polyoxometalate, cupric nitrate and 4,4′-bipyridine (4,4′-bipy). Single crystal X-ray diffraction shows 1-D zigzag chains built up of saturated Keggin polyoxoanions and infinite $[\mathrm{Cu^{I}(4,4'\text{-}bipy)}]_n^{n+}$ units. Zipper-like arrangement of adjacent zigzag chains by hydrogen-bonding interactions leads to a 2-D layer and π–π interactions of 4,4′-bipy ligands from adjacent layers further result in the 3-D structure of **1**. All Cu atoms in **1** are three-coordinated with "T-type" geometries, indicating they are univalent in the resultant compound. This result has further been confirmed by the absence of signal in the EPR spectrum of **1**.

Keywords: Organic–inorganic hybrid; Hydrothermal synthesis; Saturated Keggin; Transition metal complexes

1. Introduction

Polyoxometalates (POMs) are discrete anionic metal-oxygen clusters with many potential applications due to their electronic versatility and structural diversity [1–3]. Modulating the properties of POM building blocks by organic units or secondary metal coordination complexes to obtain functionalized organic–inorganic hybrid materials is a focus. A number of hybrid materials based on POMs have been reported [4–15], and our group reported several organic–inorganic hybrid compounds based on $[MnV_{13}O_{38}]^{7-}$ [16], $[V_7^{IV}V_9^{IV}O_{38}Cl]^{4-}$ [17], $[M(OH)_7Mo_6O_{17}]^{2-}$ (M = Al, Cr) [18], and $[Ln(PW_{11}O_{39})_2]^{11-}$ [19]. Our current interest lies in surface modification of the saturated Keggin framework with transition metal complexes. As the surface charge density of the POM increases and the surface oxygen atoms are activated by reducing the metal centers or by replacing metal center(s) with high oxidation state by other lower-valence metal(s), the coordination ability of the polyoxoanions improve [20]. Compounds based on lacunary [6, 21] or capped [22] Keggin-type POMs have been reported. However, compounds of saturated Keggin units modified by transition metal coordination

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complexes are relatively rare, due to low charge density. We investigated the reaction of saturated Keggin polyoxometalate, cupric nitrate, and 4,4′-bipyridine (4,4′-bipy) under hydrothermal conditions and isolated a hybrid compound $\{(H_3O)[Cu^I(4,4'\text{-bipy})]_3[SiW_{12}O_{40}]\} \cdot 1.5H_2O$ (**1**), which consists of 1-D zigzag chains built up of saturated Keggin polyoxoanions and infinite $[Cu^I(4,4'\text{-bipy})]_n^{n+}$ units. A striking feature of the structure is that the $[SiW_{12}O_{40}]^{4-}$ polyoxoanion in **1** is supported by three parallel infinite $[Cu^I(4,4'\text{-bipy})]_n^{n+}$ polymeric chains in a single W_3O_{13}. It is rare that the transition metal complexes are supported in the same W_3O_{13} triplet [23, 24]. Herein, we report the synthesis and structure of the compound.

2. Experimental

2.1. *Materials and general methods*

The $H_4SiW_{12}O_{40} \cdot xH_2O$ was synthesized according to the procedure described in the literature [25] and characterized by IR. All other chemicals were obtained from commercial sources and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer; Si, Cu, and W were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermal gravimetric (TG) analysis was performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ C\,min^{-1}$. EPR spectrum was recorded on a JESFE3AX spectrometer at room temperature. Photoluminescence was measured on a Hitachi F-4500 fluorescence spectrophotometer. There was no fluorescence observed for **1**.

2.2. *Syntheses*

$\{(H_3O)[Cu^I(4,4'\text{-bipy})]_3[SiW_{12}O_{40}]\} \cdot 1.5H_2O$ (**1**): A mixture of $H_4SiW_{12}O_{40} \cdot xH_2O$ (608 mg, 0.20 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (144 mg, 0.60 mmol), oxalic acid dihydrate (25 mg, 0.20 mmol), 4,4′-bipyridine (60 mg, 0.40 mmol), ethanol (2 mL), and H_2O (8 mL) adjusted by 1 mol L^{-1} NaOH to around pH 3.5 was sealed in a 16 mL Teflon-lined stainless steel reactor and heated at 160°C for 5 days, followed by slow cooling to room temperature at a rate of $10^\circ C\,h^{-1}$. Compound **1** was obtained as yellow prismatic crystals (Yield: *ca.* 41% based on W). Anal. Calcd for $C_{30}H_{30}Cu_3N_6O_{42.5}SiW_{12}$(%): C, 10.07; H, 0.85; N, 2.35; Si, 0.78; Cu, 5.33; W, 61.63. Found: C, 9.98; H, 0.86; N, 2.32; Si, 0.76; Cu, 5.30; W, 61.59.

2.3. *X-ray crystallography*

Crystal data for **1** were collected at 298 K on a Rigaku R-AXIS RAPID IP diffractometer (graphite monochromated Mo Kα radiation: $\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Absorption correction was applied. The structure was solved by the

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

	1
Formula	$C_{30}H_{30}Cu_{3}N_{6}\ O42_{.5}SiW_{12}$
fw	3579.42
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimension (Å, °)	
a	12.974
b	13.674
c	17.935
α	88.71
β	87.49
γ	75.69
V (Å^3)	3079.9
Z	2
Dc (mg m^{-3})	3.860
Abs. coeff. (mm^{-1})	23.437
Reflns. collected	27300
Independent reflns	12450
θ range (deg)	3.05–26.37
GOF on F^2	1.015
R_1 $[I > 2\sigma(I)]$[a]	0.0559
wR_2 (all data)[b]	0.1421

Notes: [a] $R1 = \sum \| F_o | - | F_c \| / \sum | F_o |$.
[b] $wR2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all nonhydrogen atoms. Hydrogen atoms for bipy were fixed in ideal positions. There were some disordered lattice waters, which showed many peaks of low electron density in the difference Fourier maps. The SQUEEZE subroutine of PLATON software [26] was applied to create new reflection data where contributions from the disordered lattice waters were removed from the original data but were included in the structure factor calculations. The number of lattice waters was determined by elemental analyses, TG and calculations of electron count inside the frameworks with SQUEEZE [27]. X-ray data for **1** are listed in table 1.

3. Results and discussion

3.1. *Synthesis*

When a mixture of $H_4SiW_{12}O_{40} \cdot xH_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, oxalic acid dihydrate, and 4,4′-bipyridine in a mixture of ethanol and H_2O reacts under hydrothermal conditions, suitable crystals for X-ray diffraction of **1** were obtained. In the hydrothermal process, many factors affect formation of the final products such as starting materials, pH values, reaction time, and temperature [28]. Parallel experiments showed that the pH value and starting materials of the reaction system were crucial for formation of **1**. Compound **1** was only obtained in pH range 3.0–4.0. All Cu atoms in the resultant compound are reduced to univalent. Similar reduction of Cu(II) to Cu(I) was observed in POMs bridged by copper complexes [29]. In the reaction of **1**, reductant may be oxalic acid because **1** cannot be obtained without it. In comparison, a similar compound, $\{[Cu(4,4'\text{-bipy})]_3[HSiMo_{12}O_{40}]\} \cdot 1.5H_2O$, has been reported to be synthesized by using triethylamine as reductant [24]. Oxalic acid is a good reductant, which could keep the intact frameworks of presynthesized saturated Keggin POMs from decomposing and reassembling into a new cluster under hydrothermal conditions.

3.2. *Structural descriptions*

Single-crystal X-ray diffraction reveals that the asymmetric unit of **1** consists of $[SiW_{12}O_{40}]^{4-}$, three $[Cu^I(4,4'\text{-bipy})]^+$ moieties, and 2.5 water molecules (figure 1). Further studies reveal that **1** consists of 1-D zigzag chains built up of $[SiW_{12}O_{40}]^{4-}$ polyanions and infinite $[Cu^I(4,4'\text{-bipy})]_n^{n+}$ units (figure 2). There are three crystallographically independent Cu^I atoms in **1**. Each is coordinated by two nitrogens from two 4,4′-bipyridine ligands with Cu^I–N bond lengths of 1.88(0)–1.92(7) Å (Cu1–N),

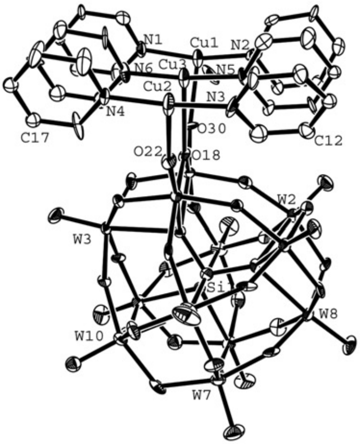

Figure 1. ORTEP view of the asymmetric unit of **1** with thermal ellipsoids at 50% level; hydrogen atoms and water molecules are omitted for clarity.

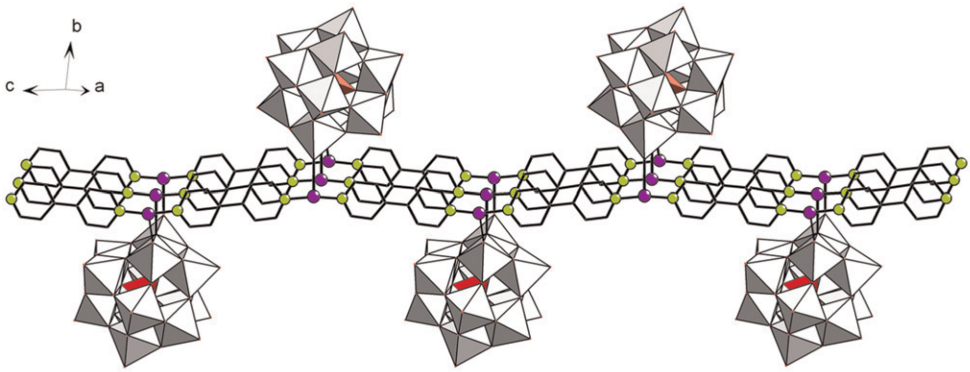

Figure 2. View of the 1-D chain of **1**. The hydrogen atoms and crystal water molecules are omitted for clarity. W: gray; Cu: purple; O: red; N: light green (color online).

1.90(3)–1.90(5) Å (Cu2–N), and 1.86(7)–1.87(6) Å (Cu3–N) and one oxygen from $[SiW_{12}O_{40}]^{4-}$ with Cu^I–O bond lengths of 2.29 Å (Cu1–O30), 2.44 Å (Cu2–O22), and 2.58 Å (Cu3–O18) to finish its "T-type" coordination geometry. The 4,4′-bipy groups are bidentate bridging adjacent copper centers into infinite polymeric chains. The bond lengths and angles in the $[SiW_{12}O_{40}]^{4-}$ polyoxoanion are in the usual range [30]. Selected bond lengths and angles for **1** are presented in table S1 (Supplementary Material).

A striking feature of the structure is that the $[SiW_{12}O_{40}]^{4-}$ poloxoyanion in **1** is supported by three parallel infinite $[Cu^I(4,4'\text{-bipy})]_n^{n+}$ polymeric chains though O30, O18, and O22 of a W_3O_{13} triplet (W3, W4, and W9). Along parallel $[Cu^I(4,4'\text{-bipy})]_n^{n+}$ polymer chains, the neighboring $[SiW_{12}O_{40}]^{4-}$ anions project toward two sides. Zipper-like arrangement of adjacent zigzag chains by hydrogen-bonding interactions (table 2) leads to a 2-D layer (figure 3) and π–π interactions of 4,4′-bipy ligands from adjacent layers (the distances between the least-square planes [31] of the bipy ligands are about 3.29 Å) further result in the 3-D structure of **1**. Bond-valence calculations [32] indicate that in **1** all oxygens are in their usual range from 1.63 to 2.07, tungstens are +6 and all coppers are +1. There is no signal in the EPR spectrum of **1**.

3.3. *Spectroscopic properties*

The infrared spectrum of **1** exhibits characteristic peaks of Keggin anions at low wavenumber. Peaks at 779, 877, 964, and 918 cm^{-1} in **1** are attributed to W–Oe/c–W and W–Ot and Si–Oa vibrations. All the peaks shift slightly to lower wavenumbers, compared to the typical *a*-Keggin type heteropolyoxoanion $[a\text{-}SiW_{12}O_{40}]^{4-}$ [25]. This may be due to interaction between SiW_{12} and copper-organonitrogen coordination polymer. Characteristic bands from 1413 to 1607 cm^{-1} are from 4,4′-bipy presented in figure S1 of Supplementary Material.

3.4. *Thermogravimetric analyses*

The TG analysis was performed with N_2 atmosphere for **1**. The TG curve of **1** exhibits two weight loss stages in the range 15–569°C in figure S2 of Supplementary Material.

Table 2. Geometrical parameters of hydrogen bonds (Å, °) in **1**.[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
C(4)–H(4)···O(18)	0.93	2.56	3.26	133
C(5)–H(5)···O(11)	0.93	2.44	3.13	130
C(5)–H(5)···O(14)	0.93	2.55	3.44	161
C(6)–H(6)···O(11)	0.93	2.40	3.06	128
C(9)–H(9)···O(29)	0.93	2.37	3.23	154
C(15)–H(15)···O(10)	0.93	2.43	3.14	133
C(15)–H(15)···O(13)	0.93	2.45	3.32	156
C(16)–H(16)···O(8)	0.93	2.48	3.39	169
C(16)–H(16)···O(10)	0.93	2.56	3.21	128
C(20)–H(20)···O(16)	0.93	2.36	3.26	162
C(21)–H(21)···O(36)	0.93	2.43	3.13	132
C(29)–H(29)···O(7)	0.93	2.57	3.47	165
C(30)–H(30)···O(40)	0.93	2.39	3.15	139

Note: [a]D = Donor, A = Acceptor.

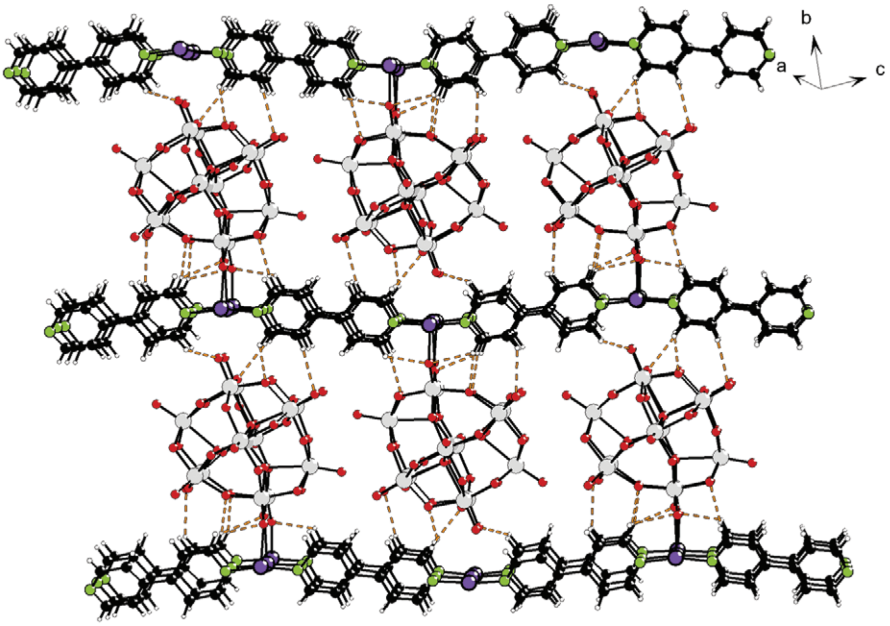

Figure 3. The 2-D framework of **1** formed by zipper-like arrangement of adjacent zigzag chains by hydrogen-bonding interactions.

The first loss of 1.28% at 15–248°C corresponds to release of all water molecules (Calcd 1.26%). The second weight loss of 13.13% in the range 248–569°C agrees with the release of coordinated 4,4′-bipy molecules (Calcd 13.09%). The total loss of 14.41% is in agreement with the calculated value of 14.35%.

4. Conclusion

We have synthesized an organic–inorganic hybrid compound using pre-synthesized Keggin POM as precursor. Compound **1** consists of 1-D zigzag chains built up of saturated Keggin polyoxoanions and infinite $[\mathrm{Cu^I}(4,4'\text{-bipy})]_n^{n+}$ units. Zipper-like arrangement of adjacent zigzag chains by hydrogen-bonding interactions leads to a 2-D layer and π–π interactions of 4,4′-bipy ligands from adjacent layers further result in the 3-D structure of **1**. The presence of Cu(I) in **1** is due to reduction of Cu(II) under hydrothermal conditions. The isolation of the title compound shows the POM family may be extended through modification of the POM clusters.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, with deposition number CCDC 653945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(Fax: +44 1223 336 033, E-mail: deposit@ccdc.cam.ac.uk; or on the web: http://www.ccdc.cam.ac.uk). Supplementary material associated with the article can be found in the online version.

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References

[1] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin (1983).
[2] M.T. Pope, A. Müller. *Angew. Chem., Int. Ed. Engl.*, **30**, 34 (1991).
[3] A. Corma. *Chem. Rev.*, **95**, 559 (1995).
[4] P.Q. Zheng, Y.P. Ren, L.S. Long, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **44**, 1190 (2005).
[5] H.Y. An, E.B. Wang, D.R. Xiao, Y.G. Li, Z.M. Su, L. Xu. *Angew. Chem., Int. Ed.*, **44**, 1 (2005).
[6] C.M. Wang, S.T. Zheng, G.Y. Yang. *Inorg. Chem.*, **46**, 616 (2007).
[7] Z.G. Han, Y.L. Zhao, J. Peng, H.Y. Ma, Q. Liu, E.B. Wang, N.H. Hu, H.Q. Jia. *Eur. J. Inorg. Chem.*, 264 (2005).
[8] J.P. Wang, X.Y. Duan, X.D. Du, J.Y. Niu. *Cryst. Growth Des.*, **6**, 2266 (2006).
[9] A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse. *Chem. Eur. J.*, **9**, 2914 (2003).
[10] S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacôte, S. Thorimbert, M. Malacria. *J. Am. Chem. Soc.*, **127**, 6788 (2005).
[11] V. Shivaiah, S.K. Das. *Inorg. Chem.*, **44**, 8846 (2005).
[12] D. Hagrman, P.J. Hagrman, J. Zubieta. *Angew. Chem., Int. Ed.*, **38**, 3165 (1999).
[13] H. Abbas, C. Streb, A.L. Pickering, A.R. Neil, D.L. Long, L. Cronin. *Cryst. Growth Des.*, **8**, 635 (2008).
[14] J.W. Zhao, J. Zhang, S.T. Zheng, G.Y. Yang. *Chem. Commun.*, 570 (2008).
[15] H.H. Yu, X.B. Cui, J.W. Cui, L. Kong, W.J. Duan, J.Q. Xu, T.G. Wang. *J. Chem. Soc., Dalton Trans.*, 195 (2008).
[16] D.H. Li, S.X. Liu, C.Y. Sun, L.H. Xie, E.B. Wang, N.H. Hu, H.Q. Jia. *Inorg. Chem. Commun.*, **8**, 433 (2005).
[17] S.X. Liu, L.H. Xie, B. Gao, C.D. Zhang, C.Y. Sun, D.H. Li, Z.M. Su. *Chem. Commun.*, 5023 (2005).
[18] R.G. Cao, S.X. Liu, L.H. Xie, Y.B. Pan, J.F. Cao, Y.H. Ren, L. Xu. *Inorg Chem.*, **46**, 3541 (2007).
[19] J.F. Cao, S.X. Liu, R.G. Cao, L.H. Xie, Y.H. Ren, C.Y. Gao, L. Xu. *J. Chem. Soc., Dalton Trans.*, 115 (2008).
[20] P. Gouzerh, A. Proust. *Chem. Rev.*, **98**, 77 (1998).
[21] S. Reinoso, P. Vitoria, J.M. Gutiérrez-Zorrilla, L. Lezama, L.S. Felices, J.I. Beitia. *Inorg. Chem.*, **4**, 9731 (2005).
[22] C.M. Liu, J.L. Luo, D.Q. Zhang, N.L. Wang, Z.J. Chen, D.B. Zhu. *Eur. J. Inorg. Chem.*, 4774 (2004).
[23] L.S. Felices, P. Vitoria, J.M. Gutiérrez-Zorrilla, L. Lezama, S. Reinoso. *Inorg. Chem.*, **44**, 9731 (2005).
[24] J.Q. Sha, J. Peng, H.S. Liu, J. Chen, B.X. Dong, A.X. Tian, Z.M. Su. *Eur. J. Inorg. Chem.*, 1268 (2007).
[25] R.D. Claude, F. Michel, F. Raymonde, T. Rene. *Inorg. Chem.*, **22**, 207 (1983).
[26] A.L. Spek. *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands (1998).
[27] A.L. Spek. *J. Appl. Crystallogr.*, **36**, 7 (2003).
[28] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem., Int. Ed.*, **38**, 2638 (1999).
[29] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang. *Inorg. Chem.*, **41**, 5636 (2002).
[30] P.M. Smith, PhD thesis, Georgetown University, 1971 P.M. Smith Diss. Abs. **B32**, 5136 (1972).
[31] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[32] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B: Struct. Sci.*, **41**, 244 (1985).