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Synthesis, Crystal Structure, and Magnetic Property of an Organic–Inorganic Hybrid Silicotungstate With Supporting Dinuclear Copper Complexes

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A new organic–inorganic hybrid silicotungstate $[\text{Cu}_2(\text{phen})_2\text{Cl}(\text{H}_2\text{O})(\text{OH})]_2[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 8 \text{H}_2\text{O}$ (1) (phen = 1,10-phenanthroline) with supporting dinuclear copper complexes has been hydrothermally synthesized and structurally characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. The molecular unit of 1 consists of two pendant coordination cations $[\text{Cu}_2(\text{phen})_2\text{Cl}(\text{H}_2\text{O})(\text{OH})]^{2+}$ and one saturated Keggin-type silicotungstate polyoxoanion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ and eight lattice water molecules. The most intriguing feature is that each bi-copper cation $[\text{Cu}_2(\text{phen})_2(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{OH})]^{2+}$ is constructed from two $[\text{Cu}(\text{phen})]^{2+}$ cations linked by one $\mu_2\text{-Cl}$ and one hydroxyl bridges. Magnetic measurements indicate that 1 demonstrates the ferromagnetic exchange interactions within Cu^{II} centers.

Keywords: polyoxometalate, binuclear copper complex, silicotungstate

Introduction

The extensive interest in the design and synthesis of inorganic–organic hybrid materials are thanks to their intriguing structural features and surprising compositional variability as well as their charming theoretical and practical applications in such fields as catalysis, absorption, electric, optic, and magnetism.^[1–3] Among them, polyoxometalate (POM)-based organic–inorganic hybrids have attracted considerable attention in past several decades. Such typical examples include $[\text{Ni}(\text{phen})_3][\text{PMo}_9^{\text{VI}}\text{Mo}_3^{\text{V}}\text{O}_{40}\{\text{Ni}(\text{phen})\}_2]$ (phen = phenanthroline),^[4] $[4,4'\text{-H}_2\text{bpy}][\text{Cu}(4,4'\text{-bpy})_2][\text{HPCuMo}_{11}\text{O}_{39}]$,^[5] $[\text{Ni}(4,4'\text{-Hbpy})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_2][\text{SiW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$,^[6] $\{[\text{Cu}(4,4'\text{-bpy})]_3[\text{HSiMo}_{12}\text{O}_{40}]\} \cdot 1.5 \text{H}_2\text{O}$,^[7] $\{[\text{Cu}(4,4'\text{-bpy})]_4[\text{SiW}_{12}\text{O}_{40}]\} \cdot 3\text{H}_2\text{O}$,^[7] $[\text{Ag}(4,4'\text{-bpy})(\text{OH})][\text{Ag}(4,4'\text{-bpy})_2][\text{PAgW}_{12}\text{O}_{40}] \cdot 3.5\text{H}_2\text{O}$,^[8] $\text{K}_5[\text{Cu}(\text{ac})(\text{pmdien})][\text{SiW}_{11}\text{CuO}_{39}] \cdot 12\text{H}_2\text{O}$ (ac = acetate, pmdien = N, N, N', N'', N''-pentamethyldiethylenetriamine),^[9] $\text{K}_{14}\{[\text{Cu}_2(2,2'\text{-bpy})_2(\mu\text{-ox})]\} \{[\text{SiW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})]\}_2 \cdot [\text{SiW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})] \cdot \sim 55\text{H}_2\text{O}$ (ox = oxalate),^[10] $\text{K}_4\{[\text{SiW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})]\} \{[\text{Cu}_2(\text{ac})_2(\text{phen})_2(\text{H}_2\text{O})]\} \cdot 14\text{H}_2\text{O}$,^[11]

and $\{[\text{Cu}(\text{deta})(\text{H}_2\text{O})_2][\text{Cu}(\text{Deta})(\text{H}_2\text{O})][\alpha\text{-XCuW}_{11}\text{O}_{39}]\} \cdot 5\text{H}_2\text{O}$ (deta = diethylenetriamine).^[12] Currently, with the aim of preparing novel POM-based organic–inorganic hybrids with interesting structures and properties, we are exploiting the reactions of lacunary POM precursors with transition-metal (TM)/lanthanide (Ln) cations in the presence of organic components under hydrothermal conditions and have obtained a class of novel inorganic–organic hybrid polyoxotungstates (POTs) such as a CdSO_4 -like 3-D framework $[\text{Cu}(\text{en})_2]_3[\alpha\text{-AsW}_{11}\text{NaO}_{39}] \cdot 2\text{H}_2\text{O}$ ^[13]; three multi-nickel substituted arsenotungstates $[\text{enH}_2]_2[\text{Ni}(\text{H}_2\text{O})_4]_2[\text{Ni}(\text{en})_2]_2[\text{Ni}(\text{en})]_2\{[\alpha\text{-AsW}_6\text{O}_{26}]\text{Ni}_6(\text{OH})_2(\text{H}_2\text{O})_3(\text{en})(\text{B}\text{-}\alpha\text{-AsW}_9\text{O}_{34})\}_2[\text{W}_4\text{O}_{16}][\text{Ni}_3(\text{H}_2\text{O})_2(\text{en})]_2 \cdot 16\text{H}_2\text{O}$,^[14] $[\text{Ni}(\text{H}_2\text{O})(\text{en})_2]_2[\text{Ni}(\text{H}_2\text{O})_3(\text{en})][\text{Ni}(\text{H}_2\text{O})(\text{en})]\{[\alpha\text{-AsW}_6\text{O}_{26}]\text{Ni}_6(\text{OH})_2(\text{en})_{2.5}(\text{B}\text{-}\alpha\text{-AsW}_9\text{O}_{34})\}_2\text{H}_4[\text{W}_4\text{O}_{16}][\text{Ni}_4(\text{H}_2\text{O})_2(\text{en})_2]_2 \cdot 13\text{H}_2\text{O}$,^[14] and $[\text{Na}(\text{H}_2\text{O})_3]_2[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{Ni}(\text{H}_2\text{O})_5]\{[\text{Ni}_3(\text{dap})(\text{H}_2\text{O})_2]_2(\text{H}_2\text{W}_4\text{O}_{16})\}\{(\alpha\text{-H}_2\text{AsW}_6\text{O}_{26})[\text{Ni}_6(\text{OH})_2(\text{H}_2\text{O})(\text{dap})_2]_2(\text{B}\text{-}\alpha\text{-HAsW}_9\text{O}_{34})\}_2 \cdot 7\text{H}_2\text{O}$ (dap = 1,2-diaminopropane)^[15]; a dimer $[\text{enH}_2]_4\{[\text{Cu}(\text{en})_2][(\text{A}\text{-}\beta\text{-H}_2\text{AsW}_9\text{O}_{34})\text{Cu}(\text{en})_2]_2\} \cdot 8\text{H}_2\text{O}$ containing $[\text{A}\text{-}\beta\text{-AsW}_9\text{O}_{34}]^{9-}$ fragments^[16]; and two hexa-Cu sandwiched arsenotungstates $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2[\text{Cu}(\text{en})_2][\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})_2(\text{B}\text{-}\alpha\text{-AsW}_9\text{O}_{34})]_2 \cdot \text{en} \cdot 9\text{H}_2\text{O}$ and $[\text{Cu}(\text{dap})_2]_3[\text{Cu}_6(\text{dap})_2(\text{H}_2\text{O})_2(\text{B}\text{-}\alpha\text{-AsW}_9\text{O}_{34})]_2 \cdot 4\text{H}_2\text{O}$ ^[17]; a series of POM-based Cu–Ln heterometallic derivatives $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_4[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{H}_2\text{O})_4]_{0.5}\{[\text{Cu}(\text{en})_2]_2[\text{H}_2\text{Ce}^{\text{IV}}(\alpha\text{-AsW}_{11}\text{O}_{39})_2]_2\} \cdot 10\text{H}_2\text{O}$ [18], $\text{Na}_3[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2]_{1.5}[\text{H}_3\text{Ln}(\alpha\text{-AsW}_{11}\text{O}_{39})_2] \cdot x\text{H}_2\text{O}$ [Ln = Pr^{III} , x = 5; Ln = Nd^{III} , x = 4.5; Ln = Sm^{III} , x = 5.5; Ln = Eu^{III} , x = 4; Ln = Tb^{III} , x = 4],^[18] $[\text{Cu}(\text{en})_2]_2\text{H}_6[\text{Ce}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 8\text{H}_2\text{O}$,^[19] $[\text{Cu}(\text{dap})_2(\text{H}_2\text{O})]_2\{[\text{Cu}(\text{dap})_2]_2[\alpha\text{-H}_2\text{SiW}_{11}\text{O}_{39}\text{Ln}(\text{H}_2\text{O})_3]_2\} \cdot x \text{H}_2\text{O}$

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[Ln = Ce^{III}, $x = 9$; Ln = Pr^{III}, $x = 10$, Ln = Nd^{III}, $x = 10$, Ln = Sm^{III}, $x = 10$, Ln = Eu^{III}, $x = 10$, Ln = Gd^{III}, $x = 9$, Ln = Tb^{III}, $x = 8$, Ln = Dy^{III}, $x = 8$, Ln = Er^{III}, $x = 9$],^[20] NaH[Cu(dap)₂(H₂O)] [Cu(dap)₂]_{4.5}[Ln(α-SiW₁₁O₃₉)₂]₇·7H₂O (Ln = Sm^{III}, Dy^{III}, Gd^{III}),^[21] and [Cu(dap)₂(H₂O)]₂{Cu(dap)₂[α-H₂SiW₁₁O₃₉Y(H₂O)₂]₂}₂·10H₂O.^[22] As a part of our continuous work, an organic–inorganic hybrid silicotungstate [Cu₂(phen)₂Cl(H₂O)(OH)]₂[α-SiW₁₂O₄₀]₄·8H₂O (**1**) (phen = 1,10-phenanthroline) with binuclear copper complex cations has been hydrothermally synthesized and structurally characterized by elemental analyses, IR spectroscopy, inductively coupled plasma atomic emission spectrometry (ICP–AES) analyses, and single-crystal X-ray diffraction. The magnetic properties of **1** have been measured.

Experimental

Materials and Physical Measurements

The precursor Na₁₀[α-SiW₉O₃₄]₂·18H₂O was synthesized according to Hervé and Tezé^[23] and confirmed by IR spectra. Other chemical reagents were used as purchased without further purification. Elemental analyses (C, H, and N) were conducted on a Perkin Elmer 2400–II CHNS/O elemental analyzer. IR spectra were obtained from a solid sample palletized with KBr on Nicolet FT–IR 360 spectrometer in the range of 4000–400 cm^{−1}. ICP–AES analyses were performed on a Perkin Elmer Optima 2000 ICP–AES spectrometer. Magnetic susceptibility measurements were carried out with a Quantum Design MPMS–XL–7 magnetometer in the temperature range of 2–300 K. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables.

Synthesis of [Cu₂(phen)₂Cl(H₂O)(OH)]₂[α-SiW₁₂O₄₀]₄·8H₂O (**1**)

Na₁₀[α-SiW₉O₃₄]₂·18H₂O (0.150 g, 0.0539 mmol), CuCl₂·2H₂O (0.190 g, 1.114 mmol), SmCl₃ (0.050 g, 0.195 mmol), 1,10-phen (0.030 g, 0.151 mmol), and 2,3-pyrazine dicarboxylic acid (0.030 g, 0.178 mmol) were dissolved in H₂O (10 mL, 556 mmol), and then ethylalcohol (5 mL, 85.9 mmol) was added under stirring. The resulting mixture was stirred for 4.0 h, sealed in 25 mL Teflon-lined stainless steel autoclave, kept for 5 days at 120°C, and cooled to room temperature. Blue prismatic crystals were obtained by filtration, washed with distilled water and dried in air at ambient temperature. Yield: ca. 31% based on Na₁₀[α-SiW₉O₃₄]₂·18H₂O. Elemental Anal. Calcd. (%) for C₄₈H₄₂Cl₂Cu₄N₈O₄₆SiW₁₂ (**1**): C 14.31, H 1.05, N 2.78, Si 0.70, Cl 1.76, Cu 6.31, W 54.79. Found: C 14.45, H 1.16, N 2.69, Si 0.84, Cl 1.65, Cu 6.48, W 54.87. Obviously, there are no Sm element and 2,3-pyrazine dicarboxylic acid in the structure of **1** although SmCl₃ and 2,3-pyrazine dicarboxylic acid were used the starting materials. Thus, the parallel experiments were carried out: when SmCl₃ and 2,3-pyrazine dicarboxylic acid were removed from the reactants, **1** were not formed. These results suggest that SmCl₃ and 2,3-pyrazine dicarboxylic acid play a

synergistic action with other components in the formation of **1**, albeit their specific roles are not well understood in the reaction process. Similar phenomena have been previously reported.^[16,17]

X-Ray Crystallographic Determination

Intensity data for **1** were collected at 296(2) K on a Bruker APEX–II CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve their structures and to locate the heavy atoms using the SHELXTL–97 program package.^[24,25] The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Lorentz polarization and empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. No hydrogen atoms associated with the water molecules were located from the difference Fourier map. Crystal data and structure refinements for **1** are summarized in Table 1.

Results and Discussion

Structural Description of **1**

X-ray single-crystal structural analysis reveals that **1** belongs to the monoclinic space group $P2_1/c$. The asymmetrical structural unit of **1** consists of two supporting coordination cations [Cu₂(phen)₂Cl(H₂O)(OH)]²⁺ and one saturated Keggin-type silicotungstate polyoxoanion [α-SiW₁₂O₄₀]^{4−}

Table 1. Crystallographic data and structural refinements for **1**

	1
Formula	C ₄₈ H ₄₂ Cl ₂ Cu ₄ N ₈ O ₄₆ SiW ₁₂
M_r (g·mol ^{−1})	4033.47
T (K)	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.532(7)
b (Å)	23.730(15)
c (Å)	14.941(10)
β (°)	95.706(16)
V (Å ³)	3716(4)
Z	2
D_c (g cm ^{−3})	3.605
μ (mm ^{−1})	19.838
Limiting indices	$-11 \leq h \leq 12$ $-28 \leq k \leq 26$ $-17 \leq l \leq 14$
No. of reflections collected	30873
No. of independent reflections	21617
Data / restraints / parameters	6540 / 110 / 560
Goodness-of-fit on F^2	1.029
R_1, wR_2 [$I > 2\sigma(I)$]	0.0703, 0.2459
R_1, wR_2 [all data]	0.0868, 0.2552

and eight coordination water molecules (Figure 1a). Two symmetrical binuclear copper $[\text{Cu}_2(\text{phen})_2(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{OH})]^{2+}$ cations covalently link to the saturated Keggin-type polyoxoanion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ subunit by two Cu–O–W bridges. The most intriguing feature is that each binuclear copper cation $[\text{Cu}_2(\text{phen})_2(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{OH})]^{2+}$ is built by two $[\text{Cu}(\text{phen})]^{2+}$ cations bridged by one $\mu_2\text{-Cl}$ and one hydroxyl groups with a Cu1...Cu2 distance close to 3.047 Å, which provides a precondition for the magnetic coupling between two copper centers. The bond valence sum calculations (BVS)^[26] indicate that the BVS value of the O23 atom is 1.09, suggesting that it is monoprotonated. This result is in good agreement with the charge balance consideration. In **1**, there are two crystallographically independent Cu^{II} cations (Cu1 and Cu2), which occupy the usual sites with the site occupancy factor of 1. The Cu1 cation exhibits a five-coordinate square pyramid geometry, in which two nitrogen atoms from one phen ligand [Cu–N: 2.01(3)–2.02(2) Å] and one hydroxyl group [Cu–O: 1.88(2) Å] and one $\mu_2\text{-Cl}$ atom [Cu–

Cl: 2.321(8) Å] occupy the basal plane, and a water ligand stands on the apex [Cu–O: 2.311(19)], while the Cu2 cation also adopts the square pyramid configuration where two N atoms from a phen ligand [Cu–N: 1.99(2)–2.02(2) Å] and one hydroxyl group [Cu–O: 1.927(19) Å] and one $\mu_2\text{-Cl}$ atom [Cu–Cl: 2.321(8) Å] establish the basal plane and one terminal O atom from the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion [Cu–O: 2.55(2)] occupies the axial site. The $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion exhibits the well-known α -Keggin-type structure, in which a central SiO_4 tetrahedron is surrounded by 12 WO_6 octahedra, every three of which constitute a W_3O_{13} triad in an edge-sharing mode and four such triads are combined together in corner-sharing motif through the central SiO_4 tetrahedron constructing the α -Keggin-type structure. It should be noted that four oxygen atoms in the central SiO_4 tetrahedron are all disordered over two positions for each. Similar disordered phenomena have been reported in the previous studies.^[27,28] In the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion, the oxygen atoms can be classified into four types, O_a , $\text{O}_{b(c)}$, and O_t , according to their coordination numbers and types. O_a is bound to the central Si and three W atoms; $\text{O}_{b(c)}$ is shared by two W atoms (O_b is shared by two W atoms from different W_3O_{13} triads, while O_c is shared by two W atoms from one W_3O_{13} triad); O_t is the terminal oxygen atom combined with only one W atom. Accordingly, the W– O_a , W– $\text{O}_{b(c)}$ and W– O_t distances fall in the ranges of 2.24(4)–2.49(3) Å, 1.83(3)–2.09(3) Å, and 1.65(2)–1.68(2) Å, respectively. In addition, the packing alignments of **1** along *a* and *c* axis show the mode of –AAA– (Figure 1b).

Notably, although **1** and $\{[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot 8\text{H}_2\text{O}\}^{29}$ have some common similarities (for example, both contain a saturated $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion with two-supporting di-copper complex cations and were synthesized by means of $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]\cdot n\text{H}_2\text{O}$), four evident differences are observed between them: (a) the former was prepared by the conventional aqueous solution at room temperature, on the contrary, the latter was obtained under hydrothermal conditions at 120°C; (b) the former crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.532(7)$ Å, $b = 23.730(15)$ Å, $c = 14.941(10)$ Å, $\beta = 95.706(16)^\circ$, $V = 3716(4)$ Å³, however, the latter belongs to the monoclinic space group $P2_1/n$ with $a = 18.185(5)$ Å, $b = 13.081(5)$ Å, $c = 20.769(5)$ Å, $\beta = 97.933(5)^\circ$, $V = 4893(3)$ Å³; (c) two di-copper $[\text{Cu}_2(\text{phen})_2(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{OH})]^{2+}$ cations symmetrically links to the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion in the former while two di-copper $[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})]_2^{2+}$ cations asymmetrically coordinate to the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion in the latter; (d) the di-copper $[\text{Cu}_2(\text{phen})_2(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{OH})]^{2+}$ cation in **1** is built by two $[\text{Cu}(\text{phen})]^{2+}$ cations bridged by one $\mu_2\text{-Cl}$ and one hydroxyl groups whereas the di-copper $[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})]_2^{2+}$ cation is constructed from by two $[\text{Cu}(\text{phen})]^{2+}$ cations connected by two hydroxyl groups in the latter.

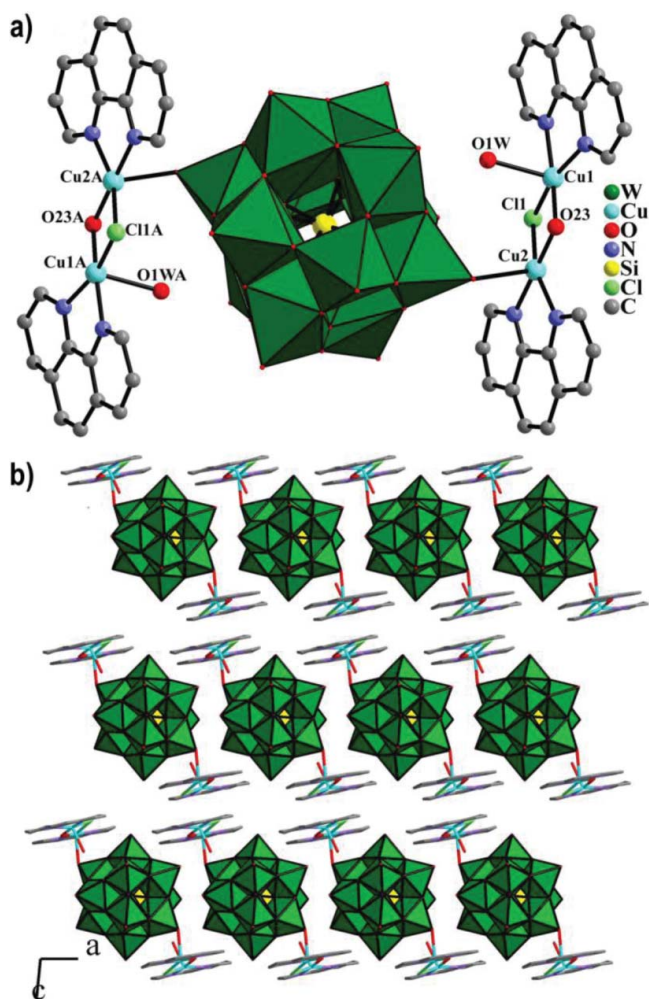


Fig. 1. (a) The molecular unit of **1** with the selected labeling scheme. Lattice water molecules and hydrogen atoms attached to carbon, nitrogen, and oxygen atoms are omitted for clarity. (b) The stacking of **1** showing the alignment mode of –AAA–. The atoms with the suffix A are generated by the symmetry operation. A: 1 $-x, -y, -z$.

IR Spectra

The IR spectrum of **1** has been recorded between 4000 and 400 cm^{-1} with a KBr pellet as shown in Figure 2. There are

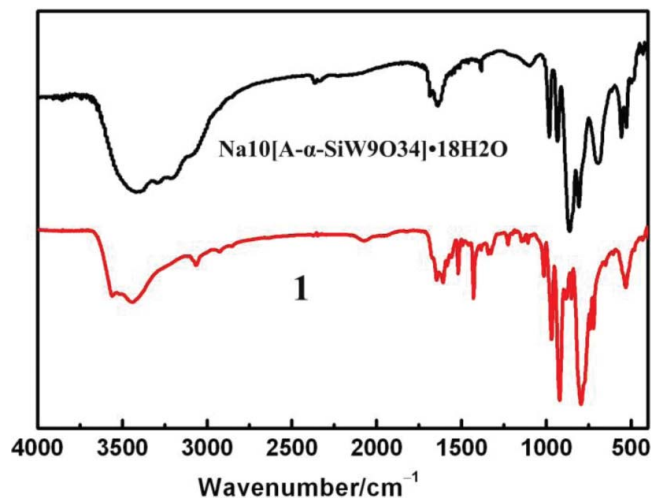


Fig. 2. IR spectra of **1** and $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}] \cdot 18\text{H}_2\text{O}$.

four groups of characteristic vibration absorption bands observed at 969, 919, 874, and 795 cm^{-1} , which are attributed to the $\nu(\text{W}-\text{O}_t)$, $\nu(\text{Si}-\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$, and $\nu(\text{W}-\text{O}_c)$ bonds, respectively, which are in agreement with the IR data of saturated Keggin-type silicotungstate.^[30] The IR spectrum of **1** is evidently different from that of $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}] \cdot 18\text{H}_2\text{O}$, which suggests the transformation of the trivacant $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-} \rightarrow$ the saturated $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$. The characteristic bands at 1515, 1223, and 1146 cm^{-1} are attributed to the vibrations of phen groups.^[29]

Magnetic Properties

Since binuclear copper cations exist in the molecular structure of **1**, the variable-temperature magnetic susceptibilities of **1** have been measured for the polycrystalline sample in the temperature range of 2–300 K at an applied field of 2000 Oe. The plots of χ_M , $\chi_M T$, and χ_M^{-1} versus T are shown in Figure 3. The temperature dependence of the χ_M shows a slow increase from 0.006 emu mol^{-1} at 300 K to 0.118 emu mol^{-1} at 25 K and then rapidly reaches 0.794 emu mol^{-1} at 2 K (Figure 3a). The $\chi_M T$ product at 300 K is 1.70 emu K mol^{-1} , being consistent with the theoretical value (1.50 emu K mol^{-1}) expected for four non-interacting Cu^{II} cations ($S = 1/2$) assuming $g = 2$ per formula unit. Upon cooling, the $\chi_M T$ product gradually increases to a maximum of 2.38 emu K mol^{-1} at 26 K, and then sharply decreases to 1.59 emu K mol^{-1} at 2 K. This behavior demonstrates dominant ferromagnetic interactions among magnetic centers.^[31] The sharp drop in the $\chi_M T$ value below apex temperature can be attributed to antiferromagnetic interactions or intermolecular interactions.^[32] The curve of χ_M^{-1} versus T in 300–160 K can be described using the Curie–Weiss law [$\chi = C / (T - \theta)$], C is the Curie constant, and θ is the Curie–Weiss temperature] affording the $C = 1.45 \text{ emu K mol}^{-1}$ (Figure 3b) and $\theta = 48.19 \text{ K}$, but the relation of χ_M^{-1} versus T between 160 and 2 K somewhat deviates from the Curie–Weiss law, which may be caused by the ferromagnetic coupling interactions

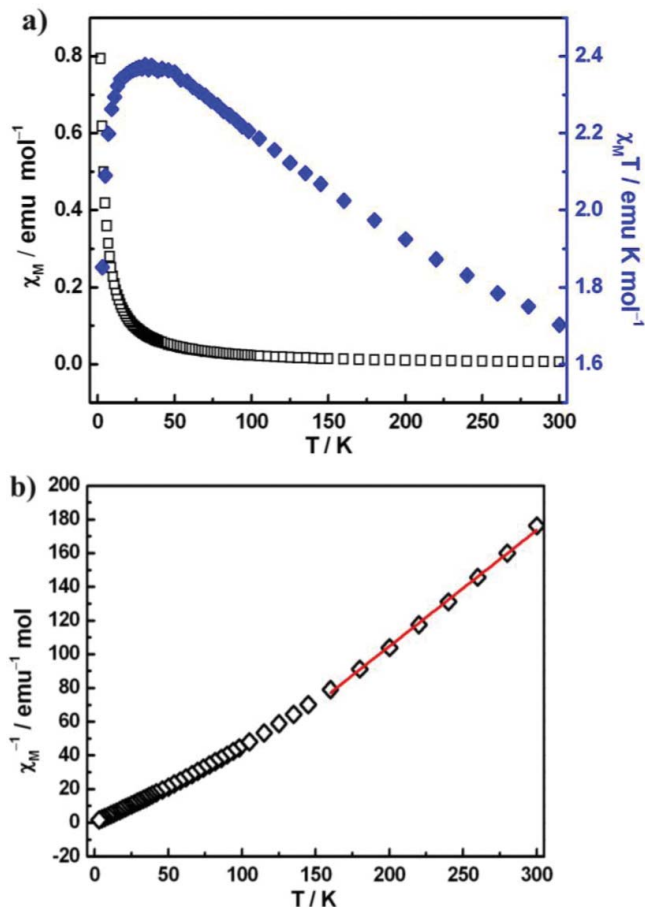


Fig. 3. (a) Temperature dependence of the molar magnetic susceptibility and the product of the molar magnetic susceptibility and temperature for **1** between 2 and 300 K. (b) Temperature evolution of the inverse magnetic susceptibility for **1** between 2 and 300 K. The red solid line between 300 K and 160 K was generated from the best fit by the Curie–Weiss expression.

with copper centers. As a matter of fact, ferromagnetic copper-cluster containing POMs have been observed in the hexa- Cu^{II} sandwiched POTs such as $[\text{Cu}(\text{enMe})_2(\text{H}_2\text{O})_2]_2 [\text{Cu}_6(\text{enMe})_2(\text{B}-\alpha\text{-SiW}_9\text{O}_{34})_2] \cdot 4\text{H}_2\text{O}$,^[33] $[\text{Cu}(\text{en})_2]_2 [\text{Cu}(\text{deta})(\text{H}_2\text{O})_2]_2 [\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 6\text{H}_2\text{O}$,^[34] $(n\text{-BuNH}_3)_{12} [\text{Cu}_6\text{Cl}_6(\text{B}-\alpha\text{-AsW}_9\text{O}_{33})_2] \cdot 4\text{H}_2\text{O}$,^[35] $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2 [\text{Cu}(\text{en})_2] [\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})(\text{B}-\alpha\text{-AsW}_9\text{O}_{34})_2] \cdot \text{en} \cdot 9\text{H}_2\text{O}$ ^[17] and the octa- Cu^{II} sandwiched POTs such as $[\text{Cu}(\text{H}_2\text{O})_2]_2 [\text{Cu}_8(\text{dap})_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-GeW}_9\text{O}_{34})_2]$,^[36] and $[\text{Cu}^{\text{II}}_2(\text{H}_2\text{O})_2(2,2'\text{-bpy})_2] \{[\text{Cu}^{\text{II}}(\text{bdyl})]_2 [\text{Cu}^{\text{II}}_8(2,2'\text{-bpy})_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-GeW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$.^[37]

Conclusions

In summary, an organic–inorganic hybrid silicotungstate with binuclear copper complex cations $[\text{Cu}_2(\text{phen})_2\text{Cl}(\text{H}_2\text{O})(\text{OH})]_2 [\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$ (**1**) has been synthesized and structurally characterized by elemental analyses, IR spectroscopy, ICP–AES analyses, and single-crystal X-ray diffraction. As far as we know, **1** is a rare organic–inorganic hybrid

saturated Keggin silicotungstate modified by two di-copper copper complexes containing two copper-phen cations bridged by one μ_2 -Cl and one hydroxyl bridges. The magnetic measurements of **1** reveal the ferromagnetic coupling interactions within copper centers.

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 941870 (**1**). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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