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Synthesis and crystal structure of two polyoxometalate complexes $\text{NaH}_3\text{SiW}_{12}\text{O}_{40} \cdot 17\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2 \cdot 13\text{H}_2\text{O}$

Chang-Sheng Wu^a, Bi-Song Zhang^a, Jian-Ping Qiu^a & Yun-Xia Li^a

^a Institute of Materia Medica, College of Pharmaceutics and Material Engineering, Jinhua Polytechnic, Jinhua, PR China

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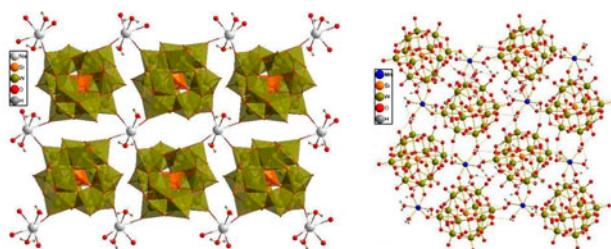
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Synthesis and crystal structure of two polyoxometalate complexes $\text{NaH}_3\text{SiW}_{12}\text{O}_{40}\cdot 17\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2\cdot 13\text{H}_2\text{O}$

CHANG-SHENG WU, BI-SONG ZHANG*, JIAN-PING QIU and YUN-XIA LI

Institute of Materia Medica, College of Pharmaceutics and Material Engineering, Jinhua Polytechnic, Jinhua, PR China

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Two polyoxometalate-based complexes, $\text{NaH}_3\text{SiW}_{12}\text{O}_{40}\cdot 17\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2\cdot 13\text{H}_2\text{O}$ (**2**), have been hydrothermally synthesized and characterized by IR spectra, thermal analysis, and X-ray single crystal diffraction. The results reveal that the Na(I) in **1** is in a distorted octahedral geometry with two coordinated waters and four O_i from four $\alpha\text{-}[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ anions, while each $\alpha\text{-}[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ is connected with four Na(I) by four O_i . The Na–O and hydrogen bonds connect **1** into a 3-D framework. Complex **2** consists of two $\alpha\text{-}[\text{H}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$ anions and two $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ cations, each Mn(II) is coordinated by four waters and two O_i from two $\alpha\text{-}[\text{H}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$ anions; the clusters are assembled into a 3-D supramolecular network by hydrogen bonds.

Keywords: Polyoxometalate-based complex; Crystal structure; Manganese; Tungstosilicate

1. Introduction

Polyoxometalate chemistry has developed as a branch of inorganic chemistry [1]. Polyoxometalates and polyoxometalate-based compounds have attracted continuous interest due to their potential applications in medicine [2–4], catalysis [5–7], materials science [6–9], and magnetic properties [10]. Specially, using polyoxometalates as building blocks to synthesize functional complexes with organic/metal ligands become a focus in

*Corresponding author. Email: zbs_jy@163.com

coordination chemistry [11]. Several polyoxometalate-based complexes [12–19] were synthesized and characterized, while their catalytic and electrochemical properties were studied. Our group is interested in synthesis and properties of polyoxometalate-supported metal complex, transition metal, organic ligands, and polyoxometalate were used to synthesis functional complexes [20]. In this paper, we report the synthesis and crystal structure of two new polyoxometalate-based complexes, $\text{NaH}_3\text{SiW}_{12}\text{O}_{40}\cdot 17\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2\cdot 13\text{H}_2\text{O}$.

2. Experimental

All chemicals of reagent grade were purchased from commercial sources and used without purification. IR spectra was recorded on a Nicolet EXUS760 FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1} . Elemental analyzes (H) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer and Si, W, Mn, Na on a PLASMA-SPEC (I) ICP atomic emission spectrometer. Thermal gravimetric analysis was performed on a Mettler-TolledoSDTA851^o analyzer at a heating rate of 10 $^\circ\text{C min}^{-1}$ from room temperature to 800 $^\circ\text{C}$. The crystal structures were determined on a Rigaku R-AXIS RAPID X-ray diffractometer.

2.1. Synthesis of $\text{NaH}_3\text{SiW}_{12}\text{O}_{40}\cdot 17\text{H}_2\text{O}$ (1)

Dropwise addition of 1.0 ML^{-1} NaOH to an aqueous solution of 0.2001 g (0.5 mM) $\text{Fe}_2(\text{SO}_4)_3$ in 5.0 mL H_2O produced brown precipitate, which was then centrifuged and washed with deionized water 5 times. A mixture of precipitate and 1.4395 g (0.5 mM) $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was added to 25.00 mL buffer solution (pH 6.84, dipotassium hydrogen phosphate, sodium dihydrogen phosphate); after stirring for 2 h, the suspension was then sealed in a Teflon reactor and heated at 160 $^\circ\text{C}$ for 100 h. After slowly cooling to room temperature, colorless block crystals were filtered, washed with distilled water, and dried in air. Anal. Calcd for $\text{NaH}_3\text{SiW}_{12}\text{O}_{40}\cdot 17\text{H}_2\text{O}$ (3206.58): Na, 0.72; Si, 0.88; W, 68.8. Found: Na, 0.79; Si, 0.80; W, 68.4%. IR (KBr): $\nu = 1016 \text{ m}, 980 \text{ s}, 924 \text{ s}, 880 \text{ m}, 789 \text{ s}, 538 \text{ m cm}^{-1}$.

2.2. Synthesis of $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2\cdot 13\text{H}_2\text{O}$ (2)

$\text{MnSO}_4\cdot\text{H}_2\text{O}$ (0.0856 g, 0.5 mM) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (1.4398 g, 0.5 mM) were added to 25.00 mL buffer solution (pH 6.84, dipotassium hydrogen phosphate, sodium dihydrogen phosphate); after stirring for 2 h, the solution was then sealed in a Teflon-lined stainless steel vessel, heated to 160 $^\circ\text{C}$ for 100 h. After naturally cooling to room temperature, the liquid was filtered off, and the filtrate then evaporated slowly at room temperature for a week, giving purple block crystals which were filtered off, washed with distilled water, and dried in air. Anal. Calcd for $[\text{Mn}(\text{H}_2\text{O})_4]_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})_2\cdot 13\text{H}_2\text{O}$ (6240.83): Mn, 1.76; Si, 0.90; W, 70.7. Found: Mn, 1.79; Si, 0.82; W, 70.4%. IR (KBr): $\nu = 1614 \text{ m}, 1400 \text{ m}, 1016 \text{ s}, 980 \text{ s}, 926 \text{ s}, 791 \text{ s}, 536 \text{ s cm}^{-1}$.

2.3. X-ray crystallography

Suitable single crystals of **1** and **2** were selected and diffraction data were collected on a Rigaku R-AXIS RAPID X-ray diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The crystal structures were solved by direct methods using SHELXTL-97 [21] and expanded with Fourier techniques by full-matrix least-squares with equivalent isotropic displacement parameters for the non-hydrogen atoms. All hydrogens were generated geometrically and treated as riding. Crystal data and structure refinement parameters of **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. Infrared spectrum

There are four characteristic asymmetric vibrations resulting from $\alpha\text{-}[\text{SiW}_{12}\text{O}_{40}]^{4-}$ below 1000 cm^{-1} , $\nu_{\text{as}}(\text{W}=\text{O}_t) = 980$, $\nu_{\text{as}}(\text{Si}-\text{O}_a) = 925$, $\nu_{\text{as}}(\text{W}-\text{O}_b) = 880$, and $\nu_{\text{as}}(\text{W}-\text{O}_c) = 781 \text{ cm}^{-1}$. As seen in figure S1 (see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.973866>), the IR spectra of **1** and **2** are very similar. Comparing the

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Compounds	1	2
Empirical formula	H ₃₇ NaO ₅₇ SiW ₁₂	H ₄₆ Mn ₂ O ₁₀₁ Si ₂ W ₂₄
Formula weight	3206.58	6240.83
Color/Shape	Colorless, block	Purple, block
Crystal size (mm)	0.36 × 0.27 × 0.14	0.56 × 0.39 × 0.10
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions (\AA , °)		
<i>a</i>	13.209(3)	13.916(3)
<i>b</i>	13.774(3)	13.929(3)
<i>c</i>	14.643(3)	14.035(3)
α	90.76(3)	92.88(3)
β	109.36(3)	112.41(3)
γ	115.21(3)	117.19(3)
<i>V</i> (\AA^3)	2236.6(8)	2152.2(7)
<i>Z</i>	2	1
<i>D</i> _{Calcd} ($\text{g}\cdot\text{cm}^{-3}$)	4.761	4.815
<i>F</i> (0 0 0)	2812	2708
<i>hkl</i> range	$-15 \leq h \leq 15$ $-16 \leq k \leq 16$ $-16 \leq l \leq 17$	$-16 \leq h \leq 16$ $-14 \leq k \leq 16$ $-16 \leq l \leq 16$
μ (mm^{-1})	30.90	32.36
θ range (°)	3.00–27.47	3.17–25.00
Total no. of data	17,642	16,910
Unique reflections [<i>R</i> _{int}]	7832 [0.1380]	7543 [0.1415]
No. of obs. data [<i>I</i> > 2 σ (<i>I</i>)]	5646	5812
Goodness of fit on <i>F</i> ²	1.053	1.037
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0950, 0.1544	0.1012, 0.2137
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0734, 0.1386	0.0836, 0.1991
Extinction	0.00182(15)	0.00091(11)
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} ($\text{e}\text{\AA}^{-3}$)	4.66, -4.15	4.37, -5.92

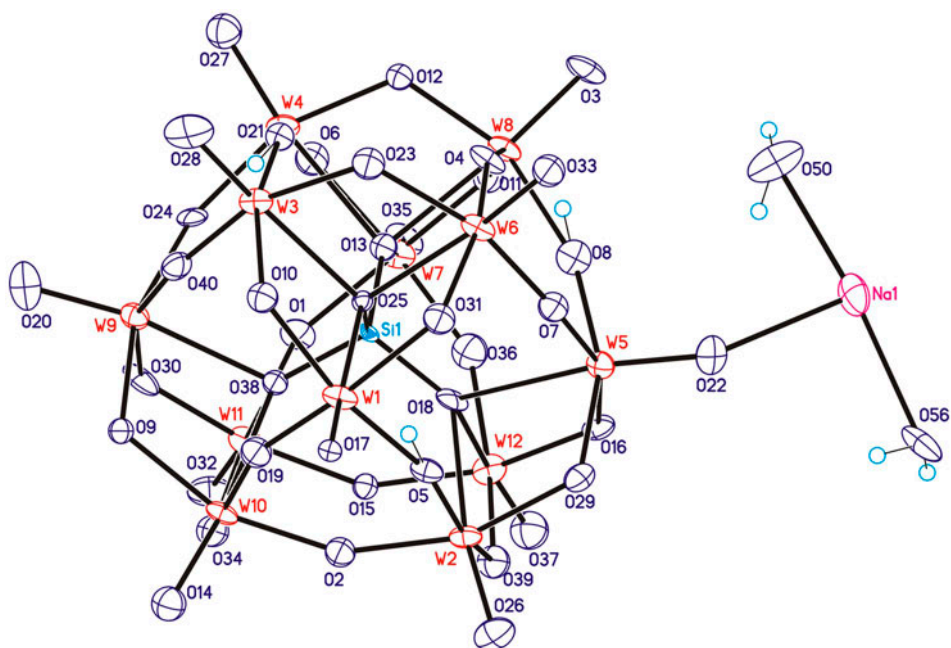


Figure 1. Molecular structure of **1** (lattice waters and three O_i from other Keggin clusters were omitted for clarity).

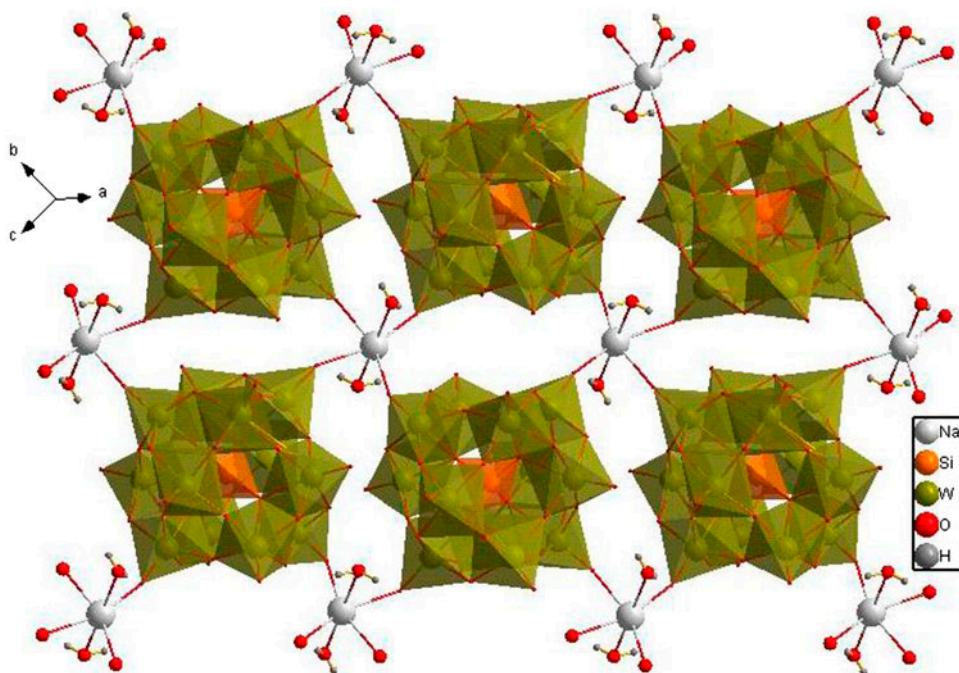


Figure 2. View of the 2-D framework of **1** (lattice water and H-bonds are omitted for clarity).

data with those of α -[SiW₁₂O₄₀]⁴⁻, the vibrations of W = O_t and Si–O_a are nearly the same, and the W–O_c bond vibration shifts from 781 to 791 cm⁻¹, while the peak of W–O_b bond nearly disappears. These results show that in **1** and **2**, α -[SiW₁₂O₄₀]⁴⁻ structures still exist in the classical α -Keggin form, and as the influence of coordinated Na(I) and Mn(II) ions, the absorptions due to the W–O_c and W–O_b bonds are blue-shifted, which makes vibrations of Si–O_a and W–O_b overlap (figure S1, Supplementary material).

3.2. Thermal analyses

Thermal analysis was carried out from 38 to 800 °C, with **1** and **2** heated at a heating rate of 10 °C min⁻¹. As seen in figure S2-1, **1** has a rapid weight loss of 5.05% from 38 to 300 °C, corresponding to release of nine crystal water molecules. Upon further heating, nearly no further weight loss suggests that **1** is very stable below 800 °C. For **2**, the TG curve (figure S2-2) exhibits a rapid weight loss from 38 to 207 °C, giving total loss of 3.83% (calcd 3.75%), for release of 13 crystal water molecules. With temperature increase to 800 °C, weight loss of 4.87% (calcd 4.90%) reveals that four more coordinated waters are removed from the complex (figure S2, Supplementary material).

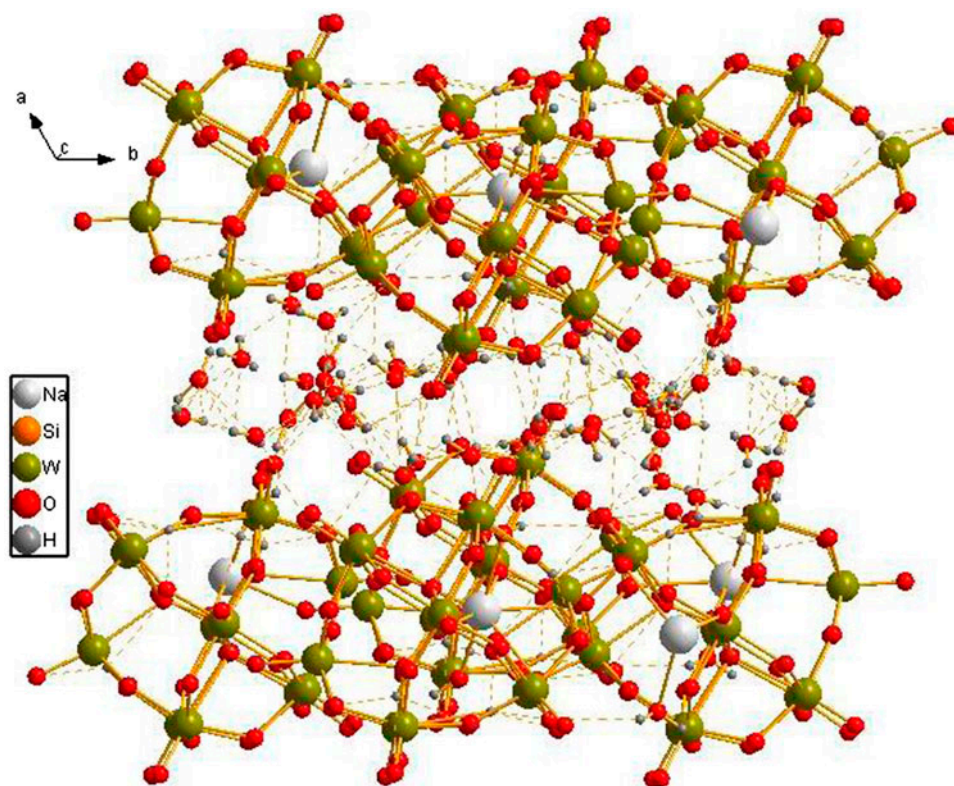


Figure 3. The crystal packing of **1** showing hydrogen bonding (dashed line) along the *c* axis.

3.3. Description of crystal structures

For **1**, the $[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ remains a typical Keggin type (figure 1), four types of oxygens exist in the structure according to their coordination surroundings: O_a connect Si and three W, O_b share corners between two W_3O_{13} units, O_c connect edge-sharing WO_6 octahedra in the same W_3O_{13} unit, O_t terminal oxygens connect to one W. A central SiO_4 tetrahedron is surrounded by 12 WO_6 octahedra, 3 WO_6 connect by sharing edges of octahedra to form a W_3O_{13} unit, then four W_3O_{13} units and one SiO_4 tetrahedron connect by tetrahedral O_a and corner-sharing O_b to form a $\alpha\text{-}[\text{SiW}_{12}\text{O}_{40}]^{4-}$ structure. In the central SiO_4 tetrahedron, the bond lengths of Si-O_a vary from 1.609(14) to 1.640(11) Å, and the bond angles of $\text{O}_a\text{-Si-O}_a$ are 107.8(7)–110.3(7)°. Four types of oxygens have different distance with W: W-O_a , 2.330(13)–2.380(14) Å, W-O_b , 1.849(12)–1.973(14) Å, W-O_c , 1.889(15)–1.969(11) Å and W-O_t , 1.664(16)–1.729(17) Å. Some selected bond lengths and angles of **1** are listed in table S1. Each Na(I) is in a distorted octahedral geometry, two coordinated waters and four O_t from four $\alpha\text{-}[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ anions are coordinated with one Na, the Na–O distances vary from 2.348(14) to 2.781(13) Å, each Na connects four $\alpha\text{-}[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ clusters, while each $\alpha\text{-}[\text{H}_3\text{SiW}_{12}\text{O}_{40}]^-$ is connected with four Na(I) by four terminal O_t . Molecules of **1** are interlinked into a 2-D layer structure by Na– O_t and hydrogen bonds (figure 2). Hydrogen bond lengths and angles are shown in table S2, and intermolecular and intramolecular hydrogen bonds connect **1** into a 3-D framework (figure 3).

As shown in figure 4, **2** consists of two $\alpha\text{-}[\text{H}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$ anions and two $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ cations. For the central SiO_4 tetrahedron of each $\alpha\text{-}[\text{H}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$ anion, the bond lengths

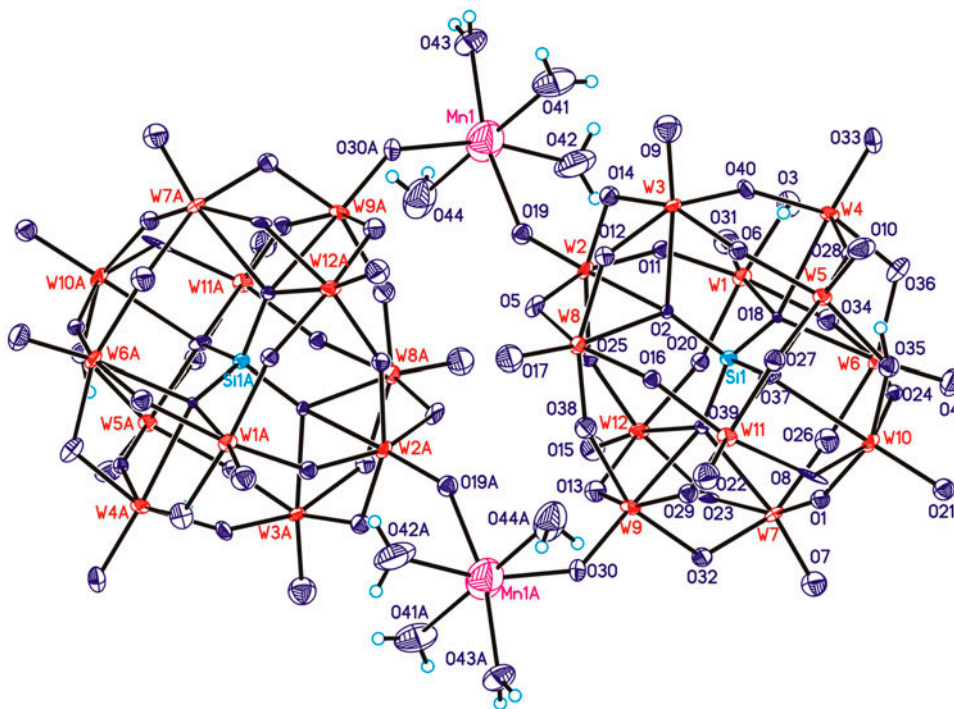


Figure 4. Molecular structure of **2** (lattice water molecules are omitted for clarity).

of Si–O_a vary from 1.583(15) to 1.628(15) Å, while the O_a–Si–O_a angles are 107.8(8)–110.8(8)°. Four types of oxygens with different coordinated surroundings have different distances with W: W–O_a, 2.305(17)–2.388(15) Å, W–O_b, 1.853(14)–1.951(16) Å; W–O_c, 1.883(15)–1.947(18) Å and W–O_d, 1.673(16)–1.738(16) Å. Some selected bond lengths and angles are listed in table S3. Each Mn(II) is six-coordinate with six oxygens, four from four coordinated waters and two terminal O_t from two α -[H₂SiW₁₂O₄₀]²⁻ anions, the distances of Mn–O (from coordinated water molecule) are 2.25(2)–2.35(3) Å and the distances of Mn(1)–O(19) and Mn(1)–O(30)^{#1} are 2.262(17) and 2.36(2) Å, respectively, while the angle of O(19)–Mn(1)–O(30)^{#1} is 87.8(7)°, and that of W(9)–O(30)–Mn(1)^{#1} and W(2)–O(19)–Mn(1) are 136.5(10) and 147.0(9)°. Hydrogen bonding exists between coordinated water molecules and terminal O_t from Keggin clusters, these interactions, as well as H-bonds between coordinated water and lattice water molecules, lattice water and terminal O_t connect **2** into a 2-D layer structure (figure 5); hydrogen bond lengths and angles are shown in table S4. Hydrogen bonds between lattice water and O_t from different layers assemble **2** into a 3-D framework (figure 6).

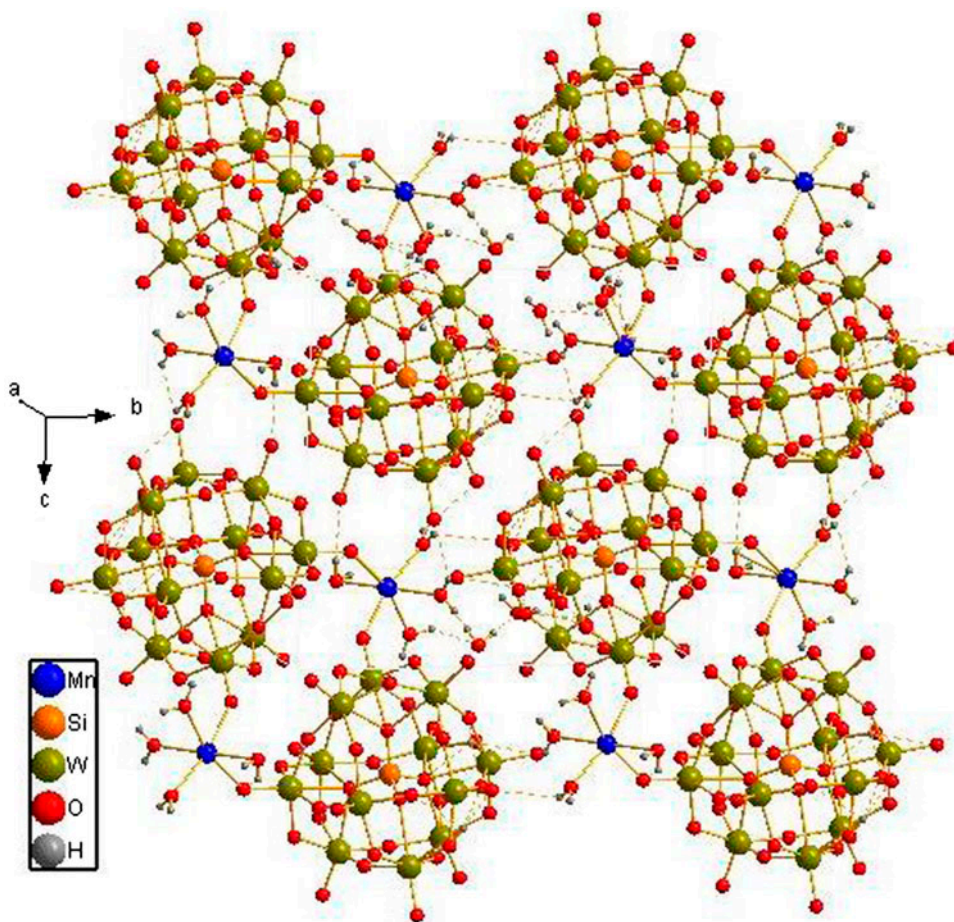


Figure 5. View of the 2-D framework structure of **2** showing hydrogen bonding (dashed lines).

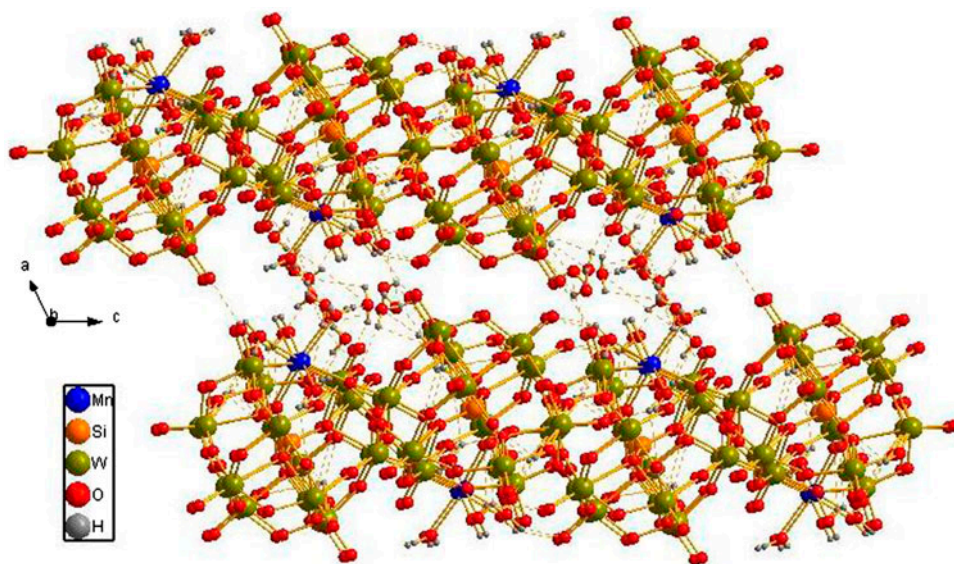


Figure 6. The crystal packing of **2** showing hydrogen bonding (dashed lines) along the *b* axis.

4. Conclusion

Two polyoxometalate-based complexes have been synthesized and characterized by IR spectra, thermal analysis, and single crystal X-ray diffraction. In **1**, the Na–O_t and hydrogen bonds connect the [H₃SiW₁₂O₄₀][−] clusters to form 2-D supramolecular layers. In **2**, two [Mn(H₂O)₄]²⁺ cations connect two [H₂SiW₁₂O₄₀]^{2−} to form a dinuclear complex. The crystal structures of both complexes are stabilized by intermolecular and intramolecular hydrogen bonds.

Supplementary material

The IR spectra and TG/DTA curves of **1** and **2**, selected bond distances, bond angles, and hydrogen bond parameters are included. CCDC 990988 and CCDC 990993 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223/336–033; Email: deposit@ccdc.cam.ac.uk].

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