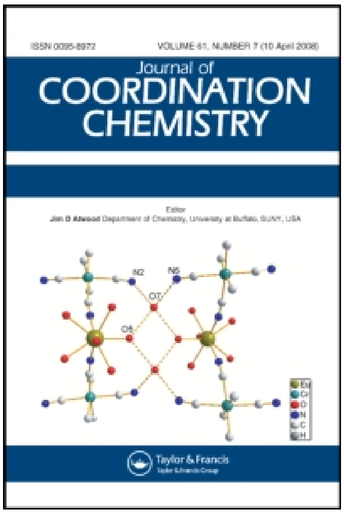

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Syntheses and crystal structures of two compounds based on saturated keggin-type polyoxotungstates and mixed ligands

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Two new polyoxotungstates with dafo and 4,4′-bipy ligands, $[Ag(dafo)_2]_2\{[Ag(4,4'\text{-}bipy)]_2SiW_{12}O_{40}\}$ (**1**) and $[Cd_2(dafo)_4(4,4'\text{-}bipy)(H_2O)_2](dafo)\ SiW_{12}O_{40}$ (**2**) (dafo = 4, 5-diazafluoren-9-one, 4,4′-bipy = 4,4′-bipyridine), have been hydrothermally synthesized and characterized by elemental analyses, IR, TG and single crystal X-ray diffraction. Compound **1** consists of a one-dimensional (1D) chain constructed from $[Ag(4,4'\text{-}bipy)]^+$ cations. With the connection of $[Ag(4,4'\text{-}bipy)]^+$ cations and $\alpha\text{-}[SiW_{12}O_{40}]^{4-}$ anions, two-dimensional (2D) structure was built. Because of the π–π stacking interactions between pyridyl rings of 4,4′-bipy from adjacent chains, three-dimensional (3D) structure was generated. Furthermore, the C–H $\cdots$ O weak interaction between $[Ag(dafo)_2]_2^{4+}$ and polytungstate made the structure more stable. Like **1**, compound **2** is a three-dimensional (3D) supramolecular compound constructed from a transition-metal complex fragment $[Cd_2(dafo)_4(4,4'\text{-}bipy)(H_2O)_2]^{4+}$, $SiW_{12}O_{40}^{4-}$ and free dafo through C–H $\cdots$ O weak interactions. To our best knowledge, it is the first time that saturated Keggin-type polyoxotungstates interact with dafo and 4,4′-bipy at the same time.

Keywords: Polyoxotungstates; Keggin; Weak interaction; Dafo; 4,4′-bipy

1. Introduction

The rapid progress of exploring organic-inorganic hybrid materials is driven by their structural diversity and fascinating properties with applications to catalysis, ion exchange, sorption, magnetism, electrical conductivity and photochemistry [1]. Incorporation of metal organic moieties into inorganic oxide clusters provides a promising approach for structural modification and synthesis of metal organic-inorganic hybrid materials that combine the features of both substructures. Furthermore, it is expected that novel structures can be synthesized by

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introducing mixed ligands into the polyoxometalate (POMs) system. For example, Gutiérrez-Zorrilla's group prepared a series of novel compounds [2] under different buffer conditions, containing polyoxometalates and mixed organoamine and dicarboxylate ligands. Liu and co-workers reported $[Co(en)_2][Co(2,2'\text{-bipy})_2]_2[PMo^{VI}{}_5Mo^{V}{}_3V^{IV}{}_8O_{44}]\cdot 4.5H_2O$ (en=ethylenediamine) [3], the first example of a 2D framework where polyoxoanions are linked by two types of complex fragments. An unusual one-dimensional (1D) chain-like material $[4,4'\text{-Hbipy}][\{Cu_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})_{2.5}\}PW_{11}CuO_{39}]\cdot 6H_2O$ [4] with a mixture of 2,2′-bipy and 4,4′-bipy has been characterized by the Dolbecq group. As part of our continuing efforts in construction of organic-inorganic hybrid materials, our group synthesized [5], $[Cu^{II}(en)(2,2'\text{-bipy})]_3[P_2W_{18}O_{62}]\cdot 3H_2O$, which is a novel Wells–Dawson polyoxoanion supported by two copper(II) complex fragments with mixed en and 2,2′-bipy ligands in a single W_3O_{13} triplet.

The mixed ligands in these compounds are usually organoamine and dicarboxylate ligands, or two chelating organoamine ligands, but are rarely with one linear organoamine and one chelating organoamine ligand. Inspired by the aforementioned considerations, the bidentate ligands, dafo and 4,4′-bipy, seized our attention because of the following considerations: (1) The chelating dafo ligand presents structural versatility. First, the adjacent nitrogen atoms chelate to metal atoms the same as 1,10-phen. Second, it can form hydrogen bonds through oxygen from carbonyl to generate high dimensional structures. Third, the π–π stacking interaction between the pyridyl rings can enforce supramolecular interactions. (2) The linear rigid 4,4′-bipy ligand contains two pyridyl groups in the opposite position, which has been explored in constructing extended structures, especially in the POMs field. Therefore, intriguing structures are expected to be synthesized by introducing the dafo and 4,4′-bipy ligands into a single structure.

Herein we report two new organic-inorganic hybrid polyoxotungstates with mixed dafo and 4,4′-bipy ligands: $[Ag(dafo)_2]_2\{[Ag(4,4'\text{-bipy})]_2SiW_{12}O_{40}\}$ (**1**), and $[Cd_2(dafo)_4(4,4'\text{-bipy})(H_2O)_2](dafo)SiW_{12}O_{40}$ (**2**). Compound **1** exhibits a new 3D structure in which supramolecular interactions make the whole structure more stable. Compound **2** has an unusual 3D structure constructed from 1D hybrid chains linked via weak C–H$\cdots$O interactions. To the best of our knowledge, there are no polyoxotungstates constructed with mixed dafo and 4,4′-bipy ligands.

2. Experimental section

2.1. *General methods and materials*

All organic solvents and materials used for synthesis were reagent grade and used without further purification. $K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ and dafo were prepared according to the literature methods [6, 7]. Elemental analyses (C, H, N,) were performed on a Perkin-Elemer 2400 CHN elemental analyzer. The W, Ag, Cd and

Si contents were determined by a Leaman inductively coupled plasma (ICP) spectrometer. FT/IR spectra were recorded in the range 4000–400 $\mathrm{cm^{-1}}$ on an Alpha Centaut FTIR spectrophotometer using a KBr pellet. TG analysis was performed on a Perkin-Elmer TGA-7 instrument in flowing N_2 with a heating rate of 10°C $\mathrm{min^{-1}}$.

2.2. *Syntheses*

2.2.1. $[Ag(dafo)_2]_2\{[Ag(4,4'\text{-}bipy)]_2SiW_{12}O_{40}\}$ (1). The best crystals of **1** were prepared from a mixture of $AgNO_3$ (0.1 g, 0.59 mmol), 4,4′-bipy (0.05 g, 0.32 mmol), dafo (0.05 g, 0.29 mmol), $K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ (0.15 g, 0.05 mmol) and H_2O (8 mL, 444.05 mmol) adjusted to pH ($5\sim 6$) by adding NaOH (1 mol $\mathrm{L^{-1}}$), then the mixture was stirred for 20 min in air. The mixture was then transferred to a teflon-lined autoclave (23 mL) and kept at 130°C for 5 days. After slow cooling to room temperature, yellow crystals obtained were filtered, washed with distilled water and dried in a desiccator at room temperature to give a 19% yield based on W. Elemental analysis (%) found: C, 17.86; H, 1.04; N, 3.95. Calcd: C, 17.68; H, 0.93; N, 3.87. The ICP analysis (%) showed that **1** contained W, 51.56; Ag, 9.76; Si, 0.73. Calcd: W, 50.75; Ag, 9.93; Si, 0.65. IR spectra: 3436 (m), 1731 (m), 1607 (s), 1567 (m), 1470(w), 1409 (m), 1012 (m), 962 (s), 920 (s), 882 (m), 790 (s), 760 (s) $\mathrm{cm^{-1}}$.

2.2.2. $[Cd_2(dafo)_4(4,4'\text{-}bipy)(H_2O)_2](dafo)SiW_{12}O_{40}$ (2). The same synthetic method as for **1** was used except that $AgNO_3$ was replaced by $Cd(NO_3)_2\cdot 4H_2O$ (0.1 g, 0.32 mmol), affording yellow block crystals in 15% yield based on W. Elemental analysis (%) found: C, 18.65; H, 1.10; N, 3.85. Calcd: C, 18.59; H, 0.96; N, 4.00. The ICP analysis (%) showed that **2** contained W, 52.85; Cd, 5.21; Si, 0.70. Calcd: W, 52.52; Cd, 5.35; Si, 0.67. IR spectra: 3444 (m), 1734 (m), 1611 (s), 1574 (m), 1465(w), 1412 (m), 1011 (m), 970 (s), 921 (s), 883 (m), 790 (s), 757 (s) $\mathrm{cm^{-1}}$.

2.3. *X-ray crystallography*

Single crystals of **1** and **2** were carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a R-axis RAPID IP diffractometer equipped with a normal focus, 18kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 200 mA. Data processing was accomplished with the RAXWISH processing program. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL 97 software [8]. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The crystal data and structure refinement of **1** and **2** are summarized in table 1.

Table 1. Crystal data and Structure Refinement of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{64}H_{40}Ag_4N_{12}O_{44}SiW_{12}$	$C_{65}H_{42}Cd_2N_{12}O_{47}SiW_{12}$
Formula weight	4346.85	4198.16
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.357(2)	11.979(2)
b (Å)	13.727(3)	14.549(3)
c (Å)	14.047(3)	14.655(3)
α (°)	74.17(3)	70.83(3)
β (°)	83.13(3)	67.35(3)
γ (°)	82.93(3)	72.21(3)
V (Å3)	2082.4(7)	2179.0(8)
Z	1	1
μ (mm^{-1})	17.527	16.356
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0657$, $wR_2 = 0.1504$	$R_1 = 0.0743$, $wR_2 = 0.1814$
R indices (all data)	$R_1 = 0.0775$, $wR_2 = 0.1596$	$R_1 = 0.0846$, $wR_2 = 0.1872$

Note: $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction analysis reveals that **1** consists of α-$[SiW_{12}O_{40}]^{4-}$ polyoxoanion, $[Ag(4,4'\text{-bipy})]^+$ and $Ag(dafo)_2^+$ cations. As shown in figure S3, the α-$[SiW_{12}O_{40}]^{4-}$ polyoxoanion exhibits a disordered Keggin structure. The central Si1 atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. The Si–O distances range from 1.606(2) to 1.674(2) Å. This structure feature often appears in $XMo_{12}O_{40}{}^{n-}$ with the Keggin structure, which has been explained by several groups [9]. The W–O distances can be grouped into three sets: W–Ot (terminal) 1.664(1) – 1.690(1) Å, W–Ob (bridge) 1.856(1) – 1.928(2) Å, W–Oc (central) 2.323(2) – 2.428(2) Å. Such α-$[SiW_{12}O_{40}]^{4-}$ unit connects with two Ag (I) ions with oxygen atoms with Ag–O bond distance 2.707(2) Å. The Ag (I) has a "T" shape coordination mode, and the other two coordination sites are occupied by two nitrogen atoms from 4,4′-bipy (Ag1–N5 = 2.152(1) Å and Ag1–N6 = 2.147(1) Å) (figure S4). Based on this connection mode, the $[Ag(4,4'\text{-bipy})]^+$ complex links the α-$[SiW_{12}O_{40}]^{4-}$ unit along the *a*-axis to form a two-dimensional layer as shown in figure S5. Furthermore, adjacent two-dimensional layers are connected to form a three-dimensional structure with π–π interactions from 4,4′-bipy as shown in figure 1. The distance of the adjacent pyridine rings range from 3.479(3) to 3.909(3)′. The three-dimensional structure was stabilized with C–H ··· O weak interactions between $Ag(dafo)_2^+$and polyoxometalates (C–H ··· O distance in the range of 3.179(4) to 3.360(7)′) as shown in figure S6.

The structure of **2** is a three-dimensional supramolecular structure. There exist two parts in the single unit: one is α-$[SiW_{12}O_{40}]^{4-}$ building unit, the other one is the transition-metal-complex fragment $[Cd_2(dafo)_4(4,4'\text{-bipy})(H_2O)_2]^{4+}$. Only one crystallographic independent Cd(II) exists in the transition-metal-complex fragment, Cd(1) connects with four nitrogen atoms from two dafo ligands with the Cd–N bond in the range from 2.345(7) to 2.436(5) Å, one nitrogen atom of 4,4′-bipy

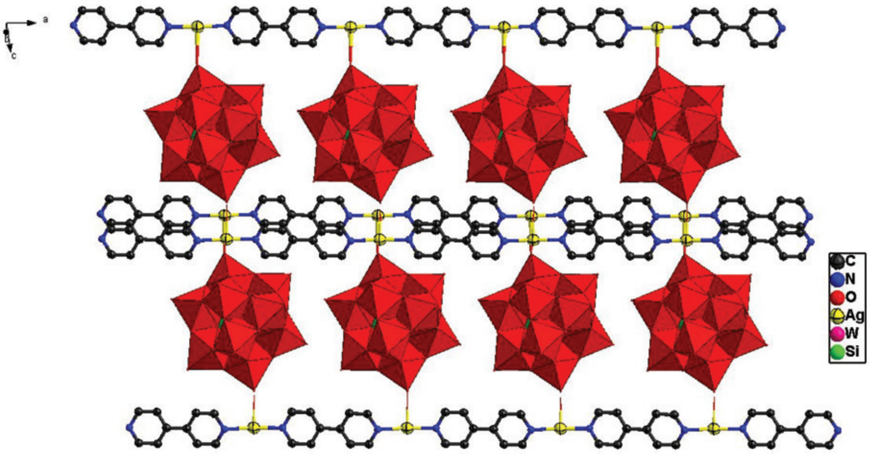

Figure 1. Three-dimensional structure of compound **1**.

(Cd–N=2.305(5) Å) and one oxygen atom from water (Cd–O=2.288(6) Å), forming a distorted octahedral geometry. Two such octahedra are connected with bridging 4,4'-bipy to form a rod-like structure (dafo-Cd-4,4′-bipy-Cd-dafo). Furthermore, there exists a free dafo in this unit as shown in figure S7. Because the C–H $\cdots$ O weak interaction among the α-$[SiW_{12}O_{40}]^{4-}$ anions, dafo and 4,4′-bipy (C–H $\cdots$ O bonds in the range from 3.099(7) to 3.636(9) Å), the **2** is generated to a 1D chain-like structure along the *b*-axis, as shown in figure 2(a). Such adjacent 1D chains are connected by C–H $\cdots$ O weak interactions between dafo ligands to form a 2D layer structure (C–H $\cdots$ O distances range from 3.341(7) to 3.418(7) Å), as shown in figure 2(b). Adjacent layers further extend to form a 3D supramolecular network through the same kind of weak interaction as shown in figure S8.

3.2. *IR spectra*

There exist four characteristic peaks in **1** (figure S1). The peaks appear at 790, 882, 962 and 1012 cm^{-1}, ascribed to ν(W–Ob–W), ν(W–Oc–W), ν(W–Ot), and ν(Si–Oc), respectively. The other four peaks at 1409, 1470, 1567 and 1607 cm^{-1} are attributed to characteristic vibration of 4,4′-bipy [10]. Like **1**, compound **2** (figure S2) possesses bands at 790, 883, 970, 1011 cm^{-1} attributed to ν(W–O–W) and ν(Si–O). All the peaks experience a slight shift to lower wave numbers, compared to the typical Keggin-type heteropolyoxoanion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ [11]. This may be due to interaction between $[SiW_{12}O_{40}]^{4-}$ and transition-metal coordination polymers. A series of bands in the 1412–1611 cm^{-1} region are associated with the 4,4′-bipy group. It has a medium strong band at 3444 cm^{-1}, characteristic of water.

3.3. *Thermogravimetric analyses*

The thermal stabilities of **1** and **2** have been determined on single crystalline samples in nitrogen by thermogravimetric analysis (TGA). For compound **1**, the

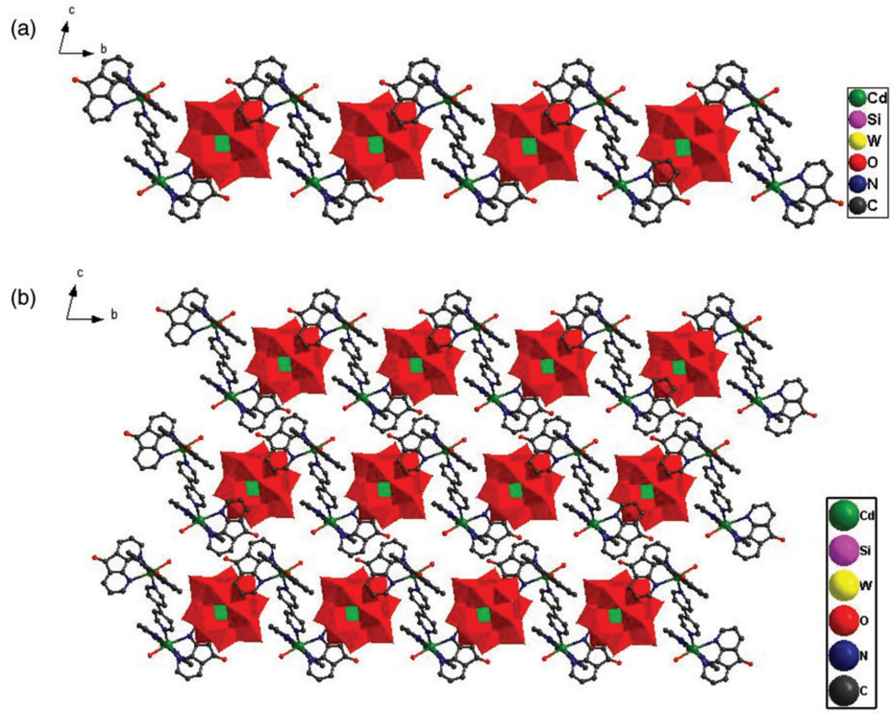

Figure 2. (a) One-dimensional chain structure in compound **2**; (b) Two-dimensional layer structure of compound **2**.

weight loss of 23.76% from 314 to 595°C indicates loss of organic ligands (Calcd 23.95%). For **2**, TGA exhibits two weight losses: one (0.93%) from 140°C to 180°C is attributed to loss of coordinated water (Calcd 0.86%). Another weight loss (25.49%) from 290°C to 470°C, corresponds to removal of 4,4′-bipy and dafo ligand (Calcd 25.36%).

4. Conclusion

In this article, we combined the merits of polyoxotungstates, dafo and 4,4′-bipy and synthesized two new three-dimensional supramolecular compounds with different structures. In the two compounds, weak interactions (C–H $\cdots$ O weak interaction and π–π stacking interactions) [12] were very important for generation of the two new frameworks, not only stabilizing the whole structure but also expanding the low-dimension to high-dimensional compounds. Furthermore, their synthesis confirms the advantages of hydrothermal methods in preparing new organic-inorganic hybrid solids and suggests a way to introduce mixed ligands into POMs systems. More work in the field is underway.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 648341 for **1**, CCDC reference number 632871 for **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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