

# A new $\alpha$ -Keggin type polyoxometalate coordinated to four silver complex moieties: $\{PW_9V_3O_{40}[Ag(2,2'-bipy)]_2[Ag_2(2,2'-bipy)_3]_2\}^\dagger$

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A new polyoxometalate derivative  $\{PW_9V_3O_{40}[Ag(2,2'-bipy)]_2[Ag_2(2,2'-bipy)_3]_2\}$  **1** has been hydrothermally synthesized and structurally characterized by the single crystal X-ray diffraction. X-Ray analysis showed that both  $[Ag(2,2'-bipy)]^+$  and  $[Ag_2(2,2'-bipy)_3]^{2+}$  units are supported on the  $\alpha$ -Keggin polyoxoanion  $[PW_9V_3O_{40}]^{6-}$  via the surface bridging oxygen atoms. **1** represents the first  $\alpha$ -Keggin type polyoxoanion coordinated with four transition metal complex moieties, which further acts as a neutral molecular units for the construction of an interesting three-dimensional supramolecular framework.

## Introduction

The design and synthesis of organic-inorganic hybrid compounds is of great interest owing to their extensive theoretical and practical applications in molecular adsorption, catalysis, electromagnetism and photochemistry.<sup>1-8</sup> In polyoxometalate (POM) chemistry, a brand-new advance in this field is the decoration of polyoxoanions with various organic and/or transition metal complex moieties.<sup>12-17</sup> These kinds of decorated polyoxometalate derivatives can be regarded as an ideal atomic-level structural model for the determination of the mechanisms of oxide-supported catalysts.<sup>9</sup> Furthermore, such kinds of compounds can be molecularly fine-tuned and provide potentially new types of catalyst systems as well as interesting functional materials with optical, electronic and magnetic properties.<sup>10,11</sup> To date, in contrast to extensive reports on the isopolyoxometalate-supported transition metal complexes,<sup>12,13</sup> examples of Keggin- and Dawson-type heteropolyoxoanion-supported transition metal complexes are limited and concentrate on such compounds in which only one transition metal complex fragment is supported on the POMs, such as  $[Ni(2,2'-bipy)_3]_1[PW_{12}O_{40}Ni(2,2'-bipy)_2(H_2O)] \cdot 0.5H_2O$ ,<sup>14</sup>  $[CpRh \cdot SiW_9Nb_3O_{40}]^{5-}$ ,<sup>15</sup> and  $[CpRh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ .<sup>16</sup> Owing to the deficient charge density on the surface oxygen atoms of many Keggin- and Dawson-type POMs,<sup>9</sup> the number of transition metal complexes that are supported on these kinds of POMs rarely exceeds two or more.<sup>17</sup> If the charge density on the surface oxygen atoms of POMs is increased, there would exist potential capability for these polyoxoanions to coordinate with two or more transition metal complex cations. An effective method to obtain such high negative polyoxoanions is substituting the six valent metal centers [for example the W(vi) and Mo(vi)] with lower valent metal atoms [such as V(v) and Nb(v)]. However, no such kind of highly negative polyoxoanions coordinated with two or more transition metal complex fragments has been reported yet.

In this paper, we report the hydrothermal synthesis and crystal structure of a novel  $\alpha$ -Keggin type polyoxometalate derivative  $\{PW_9V_3O_{40}[Ag(2,2'-bipy)]_2[Ag_2(2,2'-bipy)_3]_2\}$  **1**. In the crystal structure of **1**, both  $[Ag(2,2'-bipy)]^+$  and  $[Ag_2(2,2'-bipy)_3]^{2+}$  groups are coordinated to the  $\alpha$ -Keggin-type polyoxoanion  $[PW_9V_3O_{40}]^{6-}$  via the surface bridging oxygen atoms. To the best of our knowledge, **1** represents the first  $\alpha$ -Keggin-type polyoxoanion coordinated to four transition metal complex moieties. Furthermore, **1** acts as a neutral molecular unit for the construction of an interesting three-dimensional (3-D) supramolecular framework.

## Experimental

### Materials and methods

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. P, V, W and Ag were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectrum was recorded on an Alpha Centaur FT/IR spectrometer with a pressed KBr pellet in the 4000–400  $cm^{-1}$  region. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg-K $\alpha$  (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at  $6.2 \times 10^{-6}$  Pa during analysis. The TG curve was obtained on a Perkin-Elmer TGA7 thermogravimetric analyzer in flowing N<sub>2</sub> with a temperature ramp rate of 10 °C min<sup>-1</sup>.

### Synthesis

A mixture of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, NH<sub>4</sub>VO<sub>3</sub>, AgNO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, 2,2'-bipy and H<sub>2</sub>O in a molar ratio of 5 : 2 : 3 : 2 : 2 : 700 was sealed in a 25 mL of Teflon-lined autoclave with 70% filling and heated at 160 °C for 120 h. Then, the autoclave was cooled at 10 °C h<sup>-1</sup> to room temperature. The brown crystals of **1** were filtered off, washed with water, and dried in a desiccator at ambient temperature (yield 56% based on V). Anal. calc. for C<sub>80</sub>H<sub>64</sub>N<sub>16</sub>Ag<sub>6</sub>PV<sub>3</sub>W<sub>9</sub>O<sub>40</sub>: C, 21.96; H, 1.47; N, 5.12; P, 0.71; V, 3.49; W, 37.82; Ag, 14.80. Found: C, 22.07; H, 1.54; N, 5.26; P, 0.68; V, 3.54; W, 37.89; Ag, 14.88%. IR (cm<sup>-1</sup>): 1633(w),

<sup>†</sup> Electronic supplementary information (ESI) available: thermal ellipsoid plot of  $[Ag_2(2,2'-bipy)_3]^{2+}$ , schematic representation of the molecular building blocks of **1**, simplified 2-D representation of the supramolecular network of **1**, IR spectra, XPS spectra and a TG curve for **1**. See <http://www.rsc.org/suppdata/dt/b2/b208531c/>

1587(m), 1462(m), 1435(s), 1072(m), 1057(m), 951(s), 872(s), 788 (s) and 762(s).

### X-Ray crystallography

A brown crystal was affixed to the end of a glass capillary. Data were collected on a Siemens P4 four-circle diffractometer. Empirical absorption correction from  $\psi$ -scans was applied. The structure was solved by the direct method and refined by full-matrix least squares on  $F^2$  using SHELXL-97 software.<sup>18</sup> All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. Selected bond lengths and angles of compound **1** are provided in Table 1.

Crystal data:  $C_{80}H_{64}N_{16}O_{40}PAg_6V_3W_9$ ,  $M = 4375.13$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.541(3)$ ,  $b = 13.702(3)$ ,  $c = 14.408(3)$  Å,  $\alpha = 69.60(3)$ ,  $\beta = 73.61(3)$ ,  $\gamma = 83.27(3)^\circ$ ,  $V = 2403.2(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 293$  K,  $\mu(\text{Mo-K}\alpha) = 12.298$  mm<sup>-1</sup>, 8740 reflections measured, 7413 unique ( $R_{\text{int}} = 0.0224$ ), 5839 observed with  $I > 2\sigma(I)$  which were used in all refinements. The final  $R(F)$  was 0.0484 for observed data.

CCDC reference number 168924.

See <http://www.rsc.org/suppdata/dt/b2/b208531c/> for crystallographic data in CIF or other electronic format.

## Results and discussion

### Crystal structure of **1**

The compound **1** consists of two  $[\text{Ag}(2,2'\text{-bipy})]^+$  units, two  $[\text{Ag}_2(2,2'\text{-bipy})_3]^{2+}$  units, and one  $[\text{PW}_9\text{V}_3\text{O}_{40}]^{6-}$  polyoxoanion as shown in Fig. 1, selected bond lengths and angles are

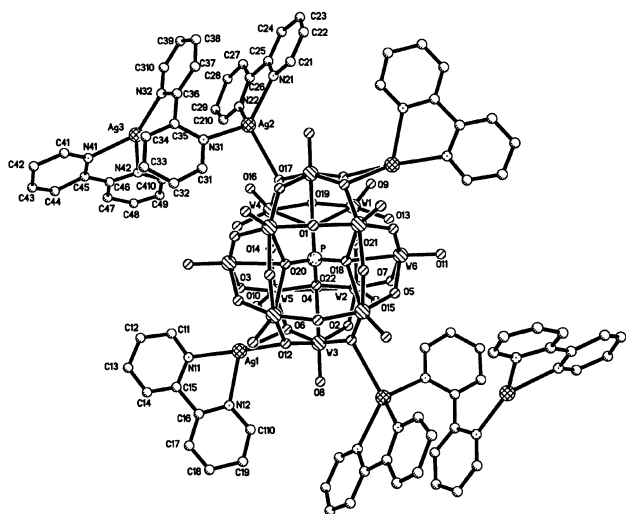


Fig. 1 Molecular structure of compound **1**.

collected in Table 1. The heteropolyanion  $[\text{PW}_9\text{V}_3\text{O}_{40}]^{6-}$  exhibits the well-known  $\alpha$ -Keggin-type structure, which is formed from twelve  $\text{MO}_6$  (W and V are crystallographically disordered, each  $M = 3/4\text{W} + 1/4\text{V}$ , and statistically occupied in the crystal) octahedra and one  $\text{PO}_4$  tetrahedron. The central P atom is located at the inversion center  $(-5000, 10000, 10000)$ , which indicates that the central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. The P–O distances are in the range of 1.484(8)–1.552(10) Å, while the O–P–O angles vary from 108.3(5) to 110.0(5)°. The M–O distances can be divided into three groups:  $M\text{-O}_t$  1.647(6)–1.667(5) Å,  $M\text{-O}_{bc}$  1.862(6)–1.925(6) Å, and  $M\text{-O}_a$  2.412(9)–2.481(8) Å. The most unusual structural feature of compound **1** is that six surface bridging oxygen atoms of the Keggin polyoxoanion  $[\text{PW}_9\text{V}_3\text{O}_{40}]^{6-}$  are coordinated to four silver-

Table 1 Bond lengths (Å) and angles (°) for compound **1**

W(1)–O(11)	1.667(5)	Ag(1)–N(12)	2.326(8)
W(1)–O(7)	1.866(7)	Ag(1)–O(6)	2.345(6)
W(1)–O(5)	1.896(6)	Ag(1)–O(12)	2.579(6)
W(1)–O(13)	1.898(6)	Ag(2)–N(31)	2.241(6)
W(1)–O(3 <sup>a</sup> )	1.901(8)	Ag(2)–N(21)	2.294(7)
W(1)–O(18)	2.434(8)	Ag(2)–N(22)	2.375(8)
W(2)–O(10)	1.647(6)	Ag(2)–O(17)	2.656(6)
W(2)–O(14)	1.879(6)	Ag(3)–N(41)	2.263(7)
W(2)–O(3)	1.887(7)	Ag(3)–N(42)	2.283(8)
W(2)–O(4)	1.894(6)	P(1)–O(20)	1.484(8)
W(2)–O(6)	1.925(6)	P(1)–O(1)	1.510(9)
W(2)–O(18 <sup>a</sup> )	2.462(11)	P(1)–O(18)	1.524(9)
Ag(1)–N(11)	2.279(7)	P(1)–O(22)	1.552(10)
O(11)–W(1)–O(7)	101.1(3)	N(31)–Ag(2)–N(21)	131.8(3)
O(11)–W(1)–O(5)	101.2(3)	N(31)–Ag(2)–N(22)	114.8(2)
O(7)–W(1)–O(5)	87.5(3)	N(21)–Ag(2)–N(22)	71.0(3)
O(11)–W(1)–O(13)	100.8(3)	N(32)–Ag(3)–N(41)	142.6(3)
O(7)–W(1)–O(13)	89.0(3)	N(32)–Ag(3)–N(42)	142.1(3)
O(5)–W(1)–O(13)	158.1(3)	N(41)–Ag(3)–N(42)	73.1(3)
N(11)–Ag(1)–N(12)	70.7(3)	O(20)–P(1)–O(1)	109.1(5)
N(11)–Ag(1)–O(6)	134.8(2)	O(20)–P(1)–O(18)	109.6(5)
N(12)–Ag(1)–O(6)	119.8(3)	O(1)–P(1)–O(18)	109.9(5)
N(11)–Ag(1)–O(12)	158.9(2)	O(20)–P(1)–O(22)	110.0(5)
N(12)–Ag(1)–O(12)	109.4(3)	O(1)–P(1)–O(22)	109.9(5)
O(6)–Ag(1)–O(12)	64.5(2)	O(18)–P(1)–O(22)	108.3(5)

Symmetry transformations used to generate equivalent atoms:  $a - x - 1, -y + 2, -z + 2$ .

2,2'-bipyridine complex cations. To our knowledge, such a type of  $\alpha$ -Keggin polyoxoanion that simultaneously supports four transition metal complexes has not been observed before.

Two bridging oxygen atoms [O(6) and O(12)] link to the Ag(1), while the bridging oxygen atom O(17) links to Ag(2). There are three kinds of Ag atoms in **1**. The Ag(1) atom is coordinated by two nitrogen atoms of the 2,2'-bipy group and two bridge-oxygen atoms of the  $\alpha$ -Keggin unit. The distances Ag(1)–O(6) and Ag(1)–O(12) are 2.345(6) and 2.579(6) Å, while the distances Ag(1)–N(11) and Ag(1)–N(12) are 2.279(7) and 2.326(8) Å, respectively. The Ag(2) atom exhibits an unusual coordination environment. It is coordinated by three nitrogen atoms of two 2,2'-bipy groups and one bridging oxygen atom of the  $\alpha$ -Keggin unit (see Fig. S1, ESI). The distance Ag(2)–O(17) is 2.656(6) Å, while the distances Ag(2)–N(21), Ag(2)–N(22), and Ag(2)–N(31) are 2.294(7), 2.375(8), and 2.241(6) Å, respectively.<sup>15,16</sup> It is noteworthy that the Ag(3) atom is in a novel  $[\text{Ag}_2(2,2'\text{-bipy})_3]^{2+}$  segment (see Fig. S1, ESI). The Ag(3) and Ag(2) atoms are coordinated by three 2,2'-bipy molecules with Ag–N distances in the range of 2.153(7)–2.375(8) Å. Among the three 2,2'-bipy molecules in the  $[\text{Ag}_2(2,2'\text{-bipy})_3]^{2+}$  units, the one that coordinates with two Ag atoms is strongly distorted, the dihedral angle between the planes of the two hexatomic rings is 60.1°. To our knowledge, such an unusual coordination mode in the  $[\text{Ag}_2(2,2'\text{-bipy})_3]^{2+}$  units has rarely been observed.<sup>19</sup>

It is also noteworthy that this neutral polyoxometalate derivative can be regarded as a windmill-type molecular unit for the construction of an interesting 3-D supramolecular framework. The basic building block of **1** is illustrated in Scheme S1 (ESI). Groups I, II and III (see ESI) are representative of the  $[\text{Ag}(1)(2,2'\text{-bipy})]$ ,  $[\text{Ag}(2)(2,2'\text{-bipy})]$  and  $[\text{Ag}(3)(2,2'\text{-bipy})]$  fragments, respectively. These three kinds of  $[\text{Ag}(2,2'\text{-bipy})]^+$  group extend along three directions. All these molecular units are connected together through  $\pi$ – $\pi$  stacking interactions between the pyridine groups of Groups I and I, II and II, and III and III, respectively. Scheme S2 (ESI) and Fig. 2 show the 2-D supramolecular network constructed by the basic neutral molecular units of **1** via the  $\pi$ – $\pi$  interactions of groups I and II. The distances between pyridine groups of I and II are 3.478 and 3.294 Å, respectively. Furthermore, these 2-D

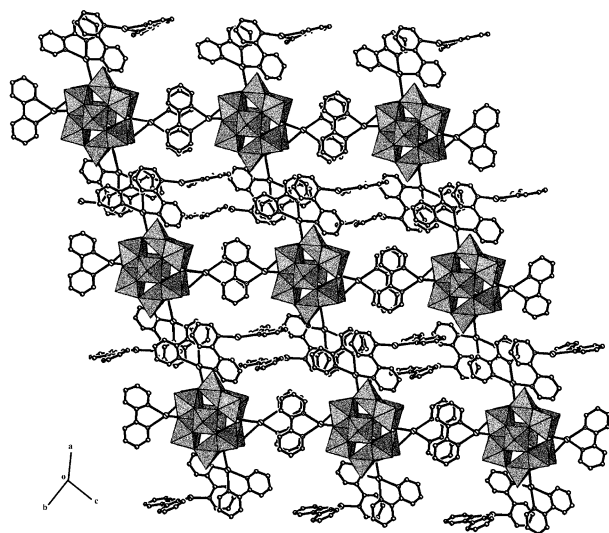


Fig. 2 The packing arrangement of compound 1.

network are linked into 3-D framework through the  $\pi$ - $\pi$  interactions of group III. The distance between pyridine groups of III is 3.442 Å.

#### IR, XPS spectrum and TG analysis

In the IR spectrum of **1** (see Fig. S2, ESI), the strong bands at 1072, 1057, 951, 872, 788 and 762  $\text{cm}^{-1}$  are due to  $\nu(\text{P-O})$ ,  $\nu(\text{W=O})$ ,  $\nu(\text{V=O})$ , and  $\nu(\text{M-O-M})(\text{M=V or W})$ , respectively. Bands in the 1633–1433  $\text{cm}^{-1}$  region are attributed to characteristic vibrations of 2,2'-bipy groups. The XPS spectra (Fig. S3, ESI) gives one peak at 517 eV, attributable to  $\text{V}^{5+}$ , a peak at 368.2 eV, attributable to  $\text{Ag}^+$ , and a peak at 35.2 eV, attributable to  $\text{W}^{6+}$  respectively. These results further confirm the composition of compound **1**.

TG analysis shows that the compound **1** exhibits strong thermal stability. In the TG curve of compound **1** (see Fig. S4, ESI), there is only one weight loss of 33.04% in the temperature range 270–550 °C, corresponding to the concomitant release of 2,2'-bipy ligands. The whole weight loss (33.04%) is in good agreement with the calculated value (32.95%).

#### Conclusion

In this paper, a novel polyoxometalate derivative  $\{\text{PW}_9\text{V}_3\text{O}_{40}\text{-}[\text{Ag}(2,2'\text{-bipy})]_2[\text{Ag}_2(2,2'\text{-bipy})_3]_2\}$  **1** has been hydrothermally synthesized and structurally characterized. The successful preparation of compound **1** confirms that the activation of surface oxygen atoms of polyoxometalates would be a promis-

ing way to decorate polyoxometalate with various organic groups and transition metal complex moieties. More work in this field is underway.

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