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A novel polyoxometalate tri-supported mixed-valent transition metal coordination complex

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ABSTRACT

A new compound $[Mo_8V_7O_{42}][Cu(2,2'\text{-bpy})_2]_2[Cu(2,2'\text{-bpy})]\cdot 2H_3O$ (**1**) has been synthesized under hydrothermal conditions and characterized by IR, UV–vis spectrum, elemental analysis, XRD, ESR, XPS, X-ray diffraction analysis and magnetic property study. Single-crystal X-ray structure analysis indicates that the compound **1** is a novel Keggin polyoxoanion tri-supported mixed-valent transition metal coordination complex.

It has been widely recognized that polyoxometalates (POMs) exhibit a variety of structures and properties that make them useful in catalysis, electrical conductivity, functional material and biological chemistry [1]. Recently, an important advance in this burgeoning field is that a large number of POM derivatives including substituted [2–10], capped [11–17] polyoxoanions and polyoxoanion supported transition metal coordination complexes [18–29] have been obtained. Of which, polyoxoanion supported transition metal coordination complexes, formed by the decoration of polyoxoanions with transition metal coordination complexes (TMC), are becoming extraordinarily promising because of they can be regarded as an ideal atomic level structural model for the determination of the mechanism of oxide supported catalysts [1]. 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 [1].

It is noteworthy that the Keggin polyoxoanion has been extensively employed as building blocks for the construction of POM derivatives due to its stability and diverse electronic, photochemical, magnetic and catalytic properties [1]. A large number of Keggin polyoxoanion supported transition metal coordination complexes have been hydrothermally synthesized, including Keggin polyoxoanion mono- [18–24], bi- [25,26], tri- [27], tetra- [26,28,29], penta- [30] supported transition metal coordination complexes. In general, in order to isolate polyoxoanion supported transition metal coordination complexes, two strategies have been exploited to increase the surface charge density or activate the surface oxygen atoms of polyoxoanions [1]: (I) reduce the metal centres by reducing regents [18,26,27], for instance, from W^{VI} to W^{V}; (II) replace metal centres with another lower-oxidation state metal [21,25,26,28–30], for example, from Mo^{VI} to V^{IV}. However, usually the highly reduced polyoxoanions are unstable and inclined to be oxidized in atmosphere. Therefore, it is still a great challenge to obtain stable POM supported transition metal coordination complexes.

In Keggin supported transition metal coordination complexes, linking point of transition metal coordination complex with cluster can be divided into three situations: (I) terminal-oxygen atom of cluster [18,19,22–26], (II) bridge-oxygen atom of cluster [21,27] and (III) both terminal- and bridge-oxygen atoms for multi-supported cluster [20,28–30].

Our group has focused on POM supported transition metal coordination complexes for years. We reported the first Keggin POM supported metal coordination complex [18] and consecutively reported several similar results [22–24]. Very recently, we reported the first Keggin POM tri-supported transition metal coordination complex [27]. As part of the continuing work in this system, In this paper, we report the synthesis, structure, and properties of a novel Keggin POM supported transition metal coordination complex *via* both terminal- and bridge-oxygen atoms, formulated as $[Mo_8V_7O_{42}][Cu(2,2'\text{-bpy})_2]_2[Cu(2,2'\text{-bpy})]\cdot 2H_3O$ (**1**). To our knowledge, it is the first Keggin polyoxoanion supported mixed-valent transition metal coordination complex.

1 was prepared by the conventional hydrothermal method [31,32], which is now routinely applied to the isolation of POMs. **1** was

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successfully obtained from the reaction of NH_4VO_3, $Na_2MoO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $H_2C_2O_4 \cdot 2H_2O$ in the presence of 2,2′-bpy as structure-directing agent, when the pH value was adjusted to 5 with $NH_3 \cdot H_2O$ solution [33]. The P/Mo/V or the Mo/V polyoxometalates have been studied for a long time, and a number of P/Mo/V or Mo/V polyanion species have been synthesized including $[PMo_{12}V_2O_{42}]^{5-}$ [11], $[PMo_{12}V_2O_{42}]^{4-}$ [34], $[PMo_8V_6O_{42}]^{4-}$ [34], $[PMo_8V_6O_{42}]^{5-}$ [34], $[PMo_8V_6O_{42}]^{6-}$ [34], $[Mo_8V_7O_{42}]^{7-}$ [12,34], $[PMo_8V_8O_{44}]^{6-}$ [15], $[PMo_8V_8O_{44}]^{5-}$ [34], and $[Mo_{12}V_7O_{46}]^{9+}$ [14]. These species could be classified into three groups: bi-capped-, tetra-capped-, and hexa-capped-Keggin anions. $[PMo_{12}V_2O_{42}]^{5-}$ [11], $[PMo_{12}V_2O_{42}]^{4-}$ [34], $[PMo_8V_6O_{42}]^{4-}$ [34], $[PMo_8V_6O_{42}]^{6-}$ [34], $[PMo_8V_6O_{42}]^{5-}$ [34], and $[Mo_8V_7O_{42}]^{7-}$ [12,34] are bi-capped species. The first two is not easy to be synthesized, for there are six or five molybdenum atoms that should be reduced from Mo^{VI} to Mo^{V} [11,34]. The syntheses of the rest four are easier, for there is no molybdenum atom that should be reduced from Mo^{VI} to Mo^{V}. $[PMo_8V_8O_{44}]^{6-}$ [15] and $[PMo_8V_8O_{44}]^{5-}$ [34] are tetra-capped species, which are not easy to be synthesized, for there are four vanadium atoms that should cap the Keggin core. The $[Mo_{12}V_7O_{46}]^{9+}$ [14] are the hexa-capped one, which is hard to be synthesized, for there are six vanadium atoms that should cap the Keggin core. Based on aforementioned points, though it is still very hard to determine which species will be synthesized according to its synthesis condition, the species $\{PMo_8V_6O_{42}\}$ and $\{Mo_8V_7O_{42}\}$ will be easiest to be synthesized.

The X-ray diffraction analysis [35] reveals that the compound **1** is composed of bi-capped pseudo-Keggin polyoxoanion- $[Cu(2,2'\text{-}bpy)_2]^{2+}$ and $[Cu(2,2'\text{-}bpy)]^{+}$ TMCs as well as water molecules. The building block $[Mo_8V_7O_{42}]^{7-}$ can be described as the well-known pseudo-Keggin core, consisting of four internally edge-shared triads (Mo_2VO_{13}) corner-shared to each other and disposed tetrahedrally around a central disordered VO_4 unit, with two additional VO^{2+} units capping two opposite pits. The V–O bond distances of the central VO_4 are in the range of 1.599(14)–1.716(14) Å. Each molybdenum atom has a distorted octahedral coordination environment, and the distances of Mo–O bonds can be divided into three groups: $Mo–O_c$ (O_c, central O atoms), 2.403(13)–2.482(14) Å; $Mo–O_b$ (O_b, bridging O atoms), 1.757(15)–2.099(8) Å; $Mo–O_t$ (O_t, terminal O atoms), 1.671(9)–1.690(9) Å. In addition, all vanadium atoms except the central one exhibit $\{VO_5\}$ square pyramidal geometry, the distances between the vanadium atoms and the oxygen atoms of the $\{VO_5\}$ basal planes are 1.928(8)–1.999(13) Å and the distances between the vanadium atoms and the apical oxygen atoms are in the range of 1.588(10)–1.684(7) Å. Bond valence sums (BVS) for molybdenum and vanadium atoms of **1** were calculated by using parameters given by Brown [36]. Results reveal that the oxidation state of molybdenum atoms is +6, oxidation state of the central vanadium atom is +5 and the oxidation state of the rest three independent vanadium atoms of the $[Mo_8V_7O_{42}]^{7-}$ is +4. Thus the formula for **1** is $[Mo^{VI}{}_8V^{IV}{}_6V^{V}O_{42}]^{7-}$.

An unusual feature of **1** is that the $[Mo_8V_7O_{42}]^{7-}$ anion serves as a multidentate ligand coordinating to three copper centres of the TMCs. It should be noted that the TMCs of **1** could be grouped into two types: $[Cu(2,2'\text{-}bpy)_2]^{2+}$ and $[Cu(2,2'\text{-}bpy)]^{+}$. Each Cu centre of the former not only receives the contribution of one terminal oxygen atom from the anion with Cu–O bond distance of 1.999(8) Å but also receives the contributions of four nitrogen atoms from two 2,2′-bpy ligands with Cu–N bond distances of 1.978(9)–2.116(10) Å. Thus the two copper centres of the former complete their square pyramidal coordination environments, indicating that the oxidation state of copper centres of the former is +2. The Cu centre of the latter is coordinated by one bridging oxygen atom from the anion with Cu–O bond distance of 2.214(18) Å and two nitrogen atoms from a 2,2′-bpy ligand with Cu–N bond distances of 1.869(16)–2.05(2) Å, thus the Cu centre of the latter exhibits a trigonal coordination environment, indicating that the oxidation state of copper centre of the latter is +1. In other words, the $[Mo_8V_7O_{42}]^{7-}$ anion supports two different types of TMCs: $[Cu(2,2'\text{-}bpy)_2]^{2+}$ and $[Cu(2,2'\text{-}bpy)]^{+}$ with the Cu–O contacts *via* both terminal- and bridge-oxygen atoms, forming a novel POM tri-supported mixed valent transition metal coordination complex $\{[Mo_8V_7O_{42}][Cu(2,2'\text{-}bpy)_2]_2[Cu(2,2'\text{-}bpy)]\}^{2-}$ (Fig. 1). To our knowledge, such a Keggin polyoxoanion tri-supported mixed-valent transition metal coordination complex has not been observed before. The valence of copper ions of the TMCs can be further demonstrated by bond valence sum calculations using parameters given by Brown [36], which shows that the value for the calculated oxidation states of Cu(1) in $[Cu(2,2'\text{-}bpy)_2]^{2+}$ and Cu(2) in $[Cu(2,2'\text{-}bpy)]^{+}$ is 1.67 and 0.70, respectively, consistent with the coordination environments of the copper centers of **1**.

In addition, the compound **1** contains a dinuclear water cluster $(H_2O)_2$, The water cluster is formed from Ow(1) and Ow(1a) with distance of 2.57(3) Å. The detailed analysis shows that the water cluster exhibits extensive hydrogen-bonding interactions between water molecules of the water cluster and the oxygen atoms of the polyoxoanions $[Mo_8V_7O_{42}]^{7-}$. As shown in Fig. 2, Ow(1) (and its symmetry equivalents) performs as the bridge-site and links O(20) (its symmetry equivalent) and O(7) (its symmetry equivalent) from two adjacent anions $[Mo_8V_7O_{42}]^{7-}$ via hydrogen bonds with distances of 2.78(2) Å and 3.00(3) Å, respectively. Alternatively, the dinuclear water cluster as a rod joins two neighbouring anions $[Mo_8V_7O_{42}]^{7-}$ through the hydrogen bonds between water molecules of the water cluster and the oxygen atoms of the polyoxoanions into a supramolecular chain structure.

Detailed analysis reveals that there exist π···π interactions between the phenol rings of the Phen ligands. As shown in Fig. S1, the phenol rings of the N1 Phen ligand (and its symmetry equivalents) from a $\{[Mo_8V_7O_{42}][Cu(2,2'\text{-}bpy)_2]_2[Cu(2,2'\text{-}bpy)]\}^{2-}$ unit are arranged parallel with the phenol rings of the N4 Phen ligand (and its symmetry equivalents) from an adjacent $\{[Mo_8V_7O_{42}][Cu(2,2'\text{-}bpy)_2]_2[Cu(2,2'\text{-}bpy)]\}^{2-}$ unit with interplanar distance of about 3.50 Å, which means strong π···π interactions between the phenol rings of the Phen ligands. There also exist C–H···O hydrogen bonding interactions between the carbon atoms C(11) (and its symmetry equivalents) of the Phen ligands and the oxygen atoms O(20)$(-x, 2-y, 1-z)$ (and its symmetry equivalents) of the $[Mo_8V_7O_{42}]^{7-}$ anions with bond distance and angle of 3.10(2) Å and 134°, respectively. Thus a 3-D supramolecular structure is formed through the O–H···O hydrogen bonding interactions between the water clusters and the polyoxoanions, π···π interactions between the Phen ligands and the C–H···O hydrogen bonding interactions between the Phen ligands and the polyoxoanions, as shown in Fig. 3.

The UV–vis solid diffuse reflection spectrum for the compound **1** were recorded in the range of 200–400 nm on a Shimadzu UV-3100 spectrophotometer. As shown in Fig. S2, the plot contains two characteristic bands for the ligand-to-metal (Mo) charge transfer in

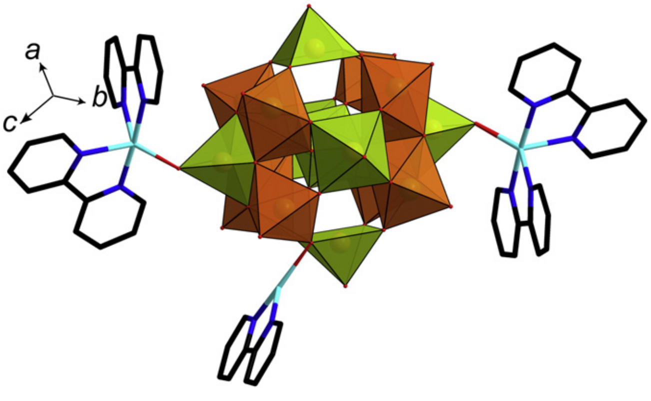

Fig. 1. The combined polyhedron and wire representation of the POM tri-supported mixed valent transition metal coordination complex $\{[Mo_8V_7O_{42}][Cu(2,2'\text{-}bpy)_2]_2[Cu(2,2'\text{-}bpy)]\}^{2-}$.