

A new sandwich type transition metal complex based on tungstobismuthates and 1-methylimidazole ligands exhibiting photocatalytic properties

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Abstract. A new sandwich-type transition metal complex based on tungstobismuthates and 1-methylimidazole ligands $\text{Na}_7(\text{mim})_2[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Co}^{\text{II}}(\text{mim})\}_3(\text{Bi}^{\text{III}}\text{W}^{\text{VI}}\text{O}_{33})_2]\cdot 9\text{H}_2\text{O}$ (**1**) (mim = 1-methylimidazole) has been successfully isolated in aqueous solution. The composition and structure were established by the single crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy. Single-crystal X-ray diffraction and TG analyses indicate that compound **1** consists of two tri-vacant $[\alpha\text{-B-Bi}^{\text{III}}\text{W}^{\text{VI}}\text{O}_{33}]^{9-}$ units linked through three cobalt ions. All the Co^{II} ions were sandwiched in the middle and bonded with terminal oxo atoms from $[\alpha\text{-B-Bi}^{\text{III}}\text{W}^{\text{VI}}\text{O}_{33}]^{9-}$ units as well as 1-methylimidazoles. Photocatalytic experiment indicates that compound **1** exhibit good catalytic activities for photodegradation of RhB under UV irradiation.

1. Introduction

Polyoxometalates (POMs), as a unique class of versatile metal–oxygen cluster complexes, have been attracting extensive interest due to not only their aesthetically topological properties but also their potential applications in catalysis, photochemistry, electro-chromism and magnetism [1-5]. Although this class of inorganic compounds has been known for more than a hundred years, a great number of novel polyoxoanions with unexpected shapes, sizes and properties are still being discovered [6-18].

In this aspect, transition-metal-substituted polyoxometalate (TMSP) is one of the most important species owing to their variety of building blocks, adjustable connection modes and tunable transition-metal ions that being accommodated. Among the class of TMSPs, one of the greatest subclasses is the sandwich-type polyoxoanions which are obtained by accommodate paramagnetic transition-metal cations between two lacunary polyoxoanions [19-26]. However, just as summarize by Xu and coworkers [27], although numerous sandwich-type polyoxoanions have been synthesized, almost all known structurally characterized sandwich-type POMs are based on trivacant tungstophosphate, -silicate, and -arsenate fragments, and little research was done on species that containing subvalent



main group atom Bi^{III} as heteroatom up to present, such as, [Bi₂W₂₂O₇₄(OH)₂]₁₂ as well as its derivatives [Bi₂W₂₀M₂O₇₀(H₂O)₆]⁽¹²⁻²ⁿ⁾⁻ (Mⁿ⁺=Fe^{III}, Co^{II}, Zn^{II}, Ni^{II}, Mn^{II}), [Sn₃{WO₂(OH)}(WO₂)₄(BiW₉O₃₃)₄]²¹⁻ [28-31], [Ln₃(H₂O)₁₈Bi₂W₂₂O₇₆]⁵⁻ (Ln³⁺=Ce^{III}, Eu^{III}) [32, 33], constructure from trivacant [b-B-(BiW₉O₃₃)]⁹⁻ units have been synthesized. On the other hand, tungstobismuthate anions containing [a-B-BiW₉O₃₃]⁹⁻ moieties are also contains [H₃BiW₁₈O₆₀]⁶⁻ [34], [(BiW₉O₃₃)₃Bi₆(OH)₃(H₂O)₃(V₄O₁₀)]¹²⁻ [35], [M₃(H₂O)₃(a-B-BiW₉O₃₃)₂]⁽¹⁸⁻³ⁿ⁾⁻ (Mⁿ⁺=Fe^{III}, Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}) [36], and [(VO)₃(a-B-BiW₉O₃₃)₂]¹²⁻ [37]. Moreover, until now the reports made on the combination of organic ligand and tungstobismuthates are still pretty much unexplored.

In order to enrich the family of organic ligand decorated tungstobismuthate, in this paper, 1-methylimidazole was introduced as the N-containing ligand to modify tungstobismuthate and a novel sandwich-type compound Na₇(mim)₂[{Na(H₂O)₂}₃{Co^{II}(mim)}₃(Bi^{III}W^{VI}₉O₃₃)₂].9H₂O (**1**) (mim = 1-methylimidazole) was successfully obtained. As far as we know, compound **1** represent for the first time that organic ligands simultaneously decorated to the tungstobismuthate frame work and serve as template molecules to organize the anions three-dimensional arrangement.

2. Experimental section

2.1. Materials and methods

All chemicals were commercially purchased and used without further purification. Elemental analyses Bi, W, Mn, and Na were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. IR spectrum was recorded in the range 400-4000 cm⁻¹ on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. A 752 PC UV-vis spectrophotometer was used to obtain UV-vis absorption spectrum, Perkin-Elmer TGA7 instrument was used for TG analyses under flowing N₂ with a heating rate of 10 °C min⁻¹.

Synthesis of Na₇(mim)₂[{Na(H₂O)₂}₃{Co^{II}(mim)}₃(Bi^{III}W^{VI}₉O₃₃)₂].9H₂O **1**

Na₂WO₄·H₂O (0.66 g, 2.0 mmol) was dissolved in 20 mL distilled water with vigorous stirring for 10 min. Then, a little amount of insoluble substance was removed by filtration. To above solution, 10 mL of HCl (0.1M) aqueous solution containing the Bi(NO₃)₃·H₂O (0.05g, 0.1mmol) was added dropwise within 10 min. The mixture was kept on stirring for 1 hour at room temperature until the solution turned clear. During this time, Co(NO₃)₂·6H₂O (0.06 g, 0.2 mmol (dissolved in 3 mL 1 mol/L NaOH solution) and 0.042g 1-methylimidazole was slowly added to the clear solution. The pH value of the resulting reaction mixture was adjusted to 8 at room temperature and further stirred for another 30 min at 40 °C and then cooled to the room temperature. After filtration, the purple filtrate was kept for slow evaporation at room temperature. After one week, purple-red block-like crystalline products of **1** were obtained. (yield 36.7 % based on W). Anal. Calcd for C₂₀H₃₀Bi₂Co₃N₁₀Na₆O₉₆W₁₈ **1**: Bi, 6.97; W, 55.26; Co, 2.95; Na, 2.30 %; Found: P, 7.02; W, 54.23; Co, 2.79; Na, 2.34 %.

2.2. X-ray crystallography

The crystallographic data were collected at 150 K on the Rigaku R-axis Rapid IP diffractometer using graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) and IP technique. Multi-scan absorption correction was applied. The crystal data of **1** was solved by the direct method and refined by the full-matrix least-squares method on F² using the SHELXTL-97 crystallographic software package [38]. During the refinement, The restraint command 'isor' was employed to restrain N3, N6, C7, C9, N4, C20, C13, C14 atoms so as to avoid the ADP and NPD problems on them. This command led to a restraint number 48. The polyoxoanion, 1-methylimidazole ligands and most of the water molecules were anisotropically refined, while solvent water molecules were just refined isotropically due to their unusual anisotropic thermal parameters and obvious disorder problems. H atoms on lattice water molecules cannot be found from the residual peaks and were directly included in the final molecular formula. The detailed crystal data and structure refinement for **1** were given in table 1.

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

	1
Empirical formula	C ₂₀ H ₆₀ Bi ₂ Co ₃ N ₁₀ Na ₆ O ₉₆ W ₁₈
<i>M</i>	6018.52
$\lambda/\text{\AA}$	0.71073
<i>T</i> /K	150(2) K
Crystal dimensions/mm	0.20 × 0.18 × 0.16
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>Z</i>	2
<i>D_c</i> /Mg m ⁻³	3.545
μ/mm^{-1}	22.055
θ Range/°	3.04 – 25.00
Reflections collected / unique	38030 / 18591
<i>R</i> _{int}	0.1661
Data/restraints/parameter s	18591 / 48 / 926
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.06204
<i>wR</i> ₂ (all data) ^b	0.1375
Goodness-of-fit on <i>F</i> ²	1.037
$\Delta\rho_{\text{max, min}}/\text{e \AA}^{-3}$	2.922, -4.018

$$^a R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; \quad ^b wR_2 = \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}$$

2.3. Crystal Description

The single crystal X-ray diffraction result shows that the polyoxoanion of **1** is mainly composed of two [α -B-Bi^{III}W^{VI}₉O₃₃]⁹⁻ moieties which are linked together by three 1-methylimidazole coordinated cobalt units (see figure 1). In the polyoxoanion, all the lacunary Keggin fragments [Bi^{III}W^{VI}₉O₃₃]⁹⁻ (*abbr.* {BiW₉}) exhibit the typical trivacant B- α -Keggin-type structure. Such a structural feature can be viewed as a mother α -Keggin unit that lost three edge-sharing {WO₆} octahedra. In these fragments, all Bi atoms exhibit a tri-coordination environment and all W centers display the octahedral coordination geometry. The bond lengths of Bi-O and the bond angles of O-Bi-O are in the range of 2.088 (16) ~ 2.138 (17) Å and 86.6(6) ~ 89.4(6) °, respectively. The bond lengths of W-O and bond angles of O-W-O vary from 1.696(16) ~ 2.310(16) Å and 72.1(6) ~ 171.6(6) °, respectively. 1-methylimidazole groups associated with the [α -B-Bi^{III}W^{VI}₉O₃₃]⁹⁻ fragments stabilize the metal centers. In the equatorial plane, each cobalt ion coordinates to four oxygen atoms (μ_3 -O) that derive from two different [α -B-Bi^{III}W^{VI}₉O₃₃]⁹⁻ fragments, while the apical position is occupied by a mim molecule to form a distorted square-pyramidal {MO₄N} group. The bond lengths of Co-O(N) are in the range 2.000(17) 2.083(17) Å, and the bond angles of O(N)-Co-O vary from 83.8(6) to 97.4(7)°.

Interestingly, different from most of previous organic ligands decorated tungstobismuthates all the mim molecules in **1** are slope at an angle to the equatorial plane. Three dihedral angles are 35.688(1011), 22.060(786) and 13.313(1082), respectively. Meanwhile, three sodium ions between transition metal ions in the equatorial plane are hexacoordinated with four oxygen atoms that derive from [Bi^{III}W^{VI}₉O₃₃]⁹⁻ units and two apically coordinated water molecules.

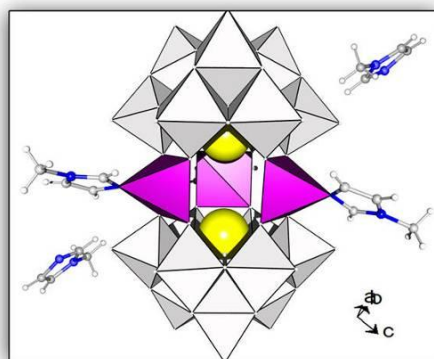


Figure 1. Polyhedral and ball-and-stick representation of **1**, lattice water molecules and free sodium ions are omitted for clarity.

Another interesting feature of compound **1** is mim molecules act as the template molecules and interact with adjacent anionic $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Co}^{\text{II}}(\text{mim})_3(\text{Bi}^{\text{III}}\text{W}^{\text{VI}}_9\text{O}_{33})_2\}]^{7-}$ units by van der Waals' force (see figure 2). Ascribing to the co-existence of mim molecules, the packing arrangement of **1** exhibits different three-dimensional structure. Meanwhile, to our knowledge, this is the first time that organic ligands simultaneously decorated to the tungstobismuthate framework and serve as template molecules to organize the anions three-dimensional arrangement.

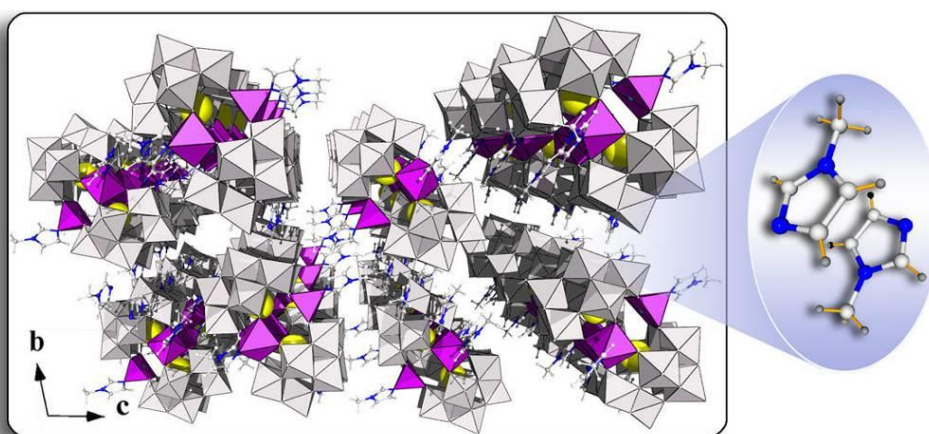


Figure 2. Ball-and-stick view of the 3-D supramolecular framework of **1** along the C-axis, water molecules omitted for clarity.

2.4. IR, UV-vis, and TG analysis

The IR spectrum of **1** shows a broad peak at 3520 cm^{-1} and strong peak at 1620 cm^{-1} attributed to the lattice water molecules. The characteristic peaks at 1091 , 939 , 852 , 706 and 429 cm^{-1} correspond to $\nu(\text{Bi}-\text{O})$, $\nu(\text{W}=\text{O}_d)$, $\nu(\text{W}-\text{O}_b)$ and $\nu(\text{W}-\text{O}_c)$ vibrations, respectively. The UV-vis spectrum of **1** displays two main peaks at 210 nm and 260 nm , which are attributable to the $\text{O} \rightarrow \text{W}$ LMCT bands. The broad bands in the visible region of $320 \sim 380\text{ nm}$ are mainly ascribed to the absorption of Co^{2+} ions [39]. Thermogravimetric (TG) analysis of **1** (see figure 3) was performed under N_2 at a rate of $10^\circ\text{C min}^{-1}$ in the range $20\text{--}600^\circ\text{C}$ on compound exhibits two steps of weight loss. The first one of ca. 5.2% in the temperature range of $35\text{--}380^\circ\text{C}$ is attributed to the loss of all lattice water molecules. This value is consistent with the calculated value of 4.9% ($\sim 15\text{ H}_2\text{O}$). The second weight loss of ca. 6.92 % between 400 and 460°C is probably the result of the loss of imi molecules.

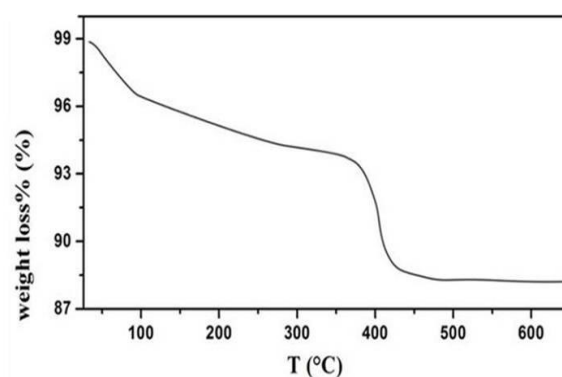


Figure 3. View of thermogravimetric analysis curve of **1**.

2.5. Photocatalytic properties

A wide range of POM possess photocatalytic ability of the degradations of recalcitrant organic pollutants under UV irradiations by oxidization of organic materials, however, the research made on amino-acid is still unexplored. We also investigated the photocatalytic performances of compounds **1** for the photocatalytic activity of RhB with UV light through a typical process: compounds **1** was dissolved in the solutions (2.40×10^{-5} mol L⁻¹) at pH=3.5 including Rhodamine-B (RhB) which were adjusted with either NaOH or HClO₄ to dilute aqueous solutions of, then vigorously stirred for 10min in the dark. Then exposed the solution to UV light from 125W Hg lamp at a distance of 4-5cm between the liquid surface and the lamp. Continuously stir the solution during irradiations. Every 60 minutes, 3.0ml of samples were taken out of the beaker for analysis. As shown in figure 4(a), the absorption peak of RhB decreased obviously from 1.4 to 0.4 and 300min ($\lambda=554$ nm). In addition, the concentrations of RhB(*K*) versus reaction time (*t*) of compound **1** were plotted in figure 4(b). The conversions of RhB(*K*) can be expressed as $K=(C_0-C_t)/C_0$, where C_0 represents the UV-vis intensity of RhB at the original reaction time ($t=0$), while I_t is the UV-vis absorption intensity at a certain irradiation time *t*. The calculation results show that the conversion of RhB is 75.67% by using **1** as the photocatalyst after 240min irradiation. Additionally, after three runs of photocatalytic tests, the photoactivity of compound **1** did not display significant loss when RhB was re-added in the system, see figure 4b. These results suggest that compound **1** may be potential photocatalysts with photocatalytic activities in the reduction of some organic dye.

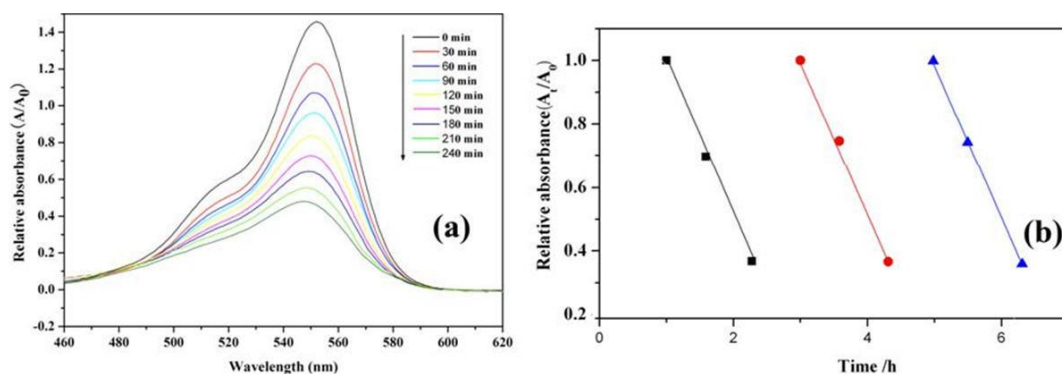


Figure 4. (a) Temporal UV-visible absorption spectral changes observed for the RhB solution as a function of irradiation time in the presence of 2×10^{-5} M compound **1**. (b) Three time of RhB degradation test by compound **1**.

3. Conclusions

In this work, we obtained a novel 1-methylimidazole decorated sandwich-type tungstobismuthate. Compared to previous organic ligand substituted tungstobismuthate anions, compound **1** shows for the

first time that organic ligands simultaneously decorated to the tungstobismuthate frame work and serve as template molecules to organize the anions three-dimensional arrangement. Photocatalytic experiment indicated that compound **1** exhibits high catalytic activity for photodegradation of RhB with UV irradiation. Further research will focus on the reactions between various other lacunary tungstobismuthate anions and different N-containing heterocycle ligands in order to obtain new type of organic ligands decorated tungstobismuthate with novel structures and interesting properties.

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