

# Synthesis, crystal structure, theoretical study and luminescence property of a butterfly-like W/Cu/S cluster with 1,10-phenanthroline

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**Abstract.** A new butterfly-like cluster,  $[\text{WOS}_3\text{Cu}_2(\text{phen})_2] \cdot 3\text{H}_2\text{O}$  (**1**) (phen = 1,10-phenanthroline) has been synthesized and characterized by elemental analysis, infrared spectroscopy, ultraviolet-visible spectroscopy, X-ray single crystal analysis and fluorescent analysis. Its crystal structure is monoclinic with space group  $C2/c$  and cell parameters:  $a = 31.928(6)$  Å,  $b = 10.653(2)$  Å,  $c = 23.097(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 133.11(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5735(2)$  Å<sup>3</sup>,  $Z = 8$ . This complex displays a favourable pairwise  $\pi$ - $\pi$  stacking. Density functional theory and time-dependent density functional theory calculations at the B3LYP/LanL2DZf+6-31G\* level were performed on complex **1** to rationalize its experimental absorption spectra. Complex **1** exhibits luminescence in EtOH solution at room temperature.

**Keywords.** Heterothiometallic clusters; crystal structure; DFT calculations; luminescence.

## 1. Introduction

Over the past decade, heterothiometallic clusters have received much attention due to their well-defined structures and potential applications in catalytic reactions and material science.<sup>1–6</sup> W/Cu/S clusters are important types of clusters and have received considerable attention for their interesting structural chemistry and potential applications in biological systems like, development of structural and functional models for the active sites of enzymes.<sup>7–10</sup> A common synthetic strategy for the preparation of W/Cu/S clusters is to employ neutral species  $\text{CuX}$  ( $X = \text{halogen or pseudo-halogen}$ ), to react with  $[\text{WO}_n\text{S}_{4-n}]$  ( $n = 0-2$ ).<sup>11,12</sup> These reactions result in the formation of a large number of heterometallic compounds with different structural configurations such as cubane-like, butterfly, nest-shaped, hexagonal prism-shaped, and polymeric structures. However, most of these clusters reported in the literature are derived from tetrathiometalates, while clusters containing terminal oxygen atoms are relatively rare.<sup>13–16</sup> A few examples are known in which heterothiometallic

clusters W/Cu/S are assembled with organic ligands.<sup>17–20</sup> Herein, we present the synthesis and crystal structure of a new butterfly-like cluster  $[\text{WOS}_3\text{Cu}_2(\text{phen})_2] \cdot 3\text{H}_2\text{O}$  (**1**), which displays a favourable pairwise  $\pi$ - $\pi$  stacking. The 1,10-phenanthroline (phen) was introduced as a highly efficient organic ligand in the construction of this complex. Till now, phen is of major interest to diverse scientific communities due to its excellent coordinating ability and large conjugated system which can easily form  $\pi$ - $\pi$  interactions.<sup>21,22</sup> The  $\pi$ - $\pi$  interactions is one of the most powerful non-covalent intermolecular interactions and undoubtedly play important roles in determining the crystal packing and molecular assemblies of the coordination compounds.<sup>23,24</sup> Theoretical study and luminescent property of **1** have also been investigated in detail.

## 2. Experimental

### 2.1 Materials and physical measurements

All chemicals and solvents used for the syntheses were reagent grade and used without further purification. The starting material  $[\text{NH}_4]_2\text{WOS}_3$  was obtained according

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to the literature procedure.<sup>25</sup> Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C system. Infrared spectra were recorded in the region 400–4000  $\text{cm}^{-1}$  on a Nicolet Nexus 470 spectrometer (Germany) with samples as KBr disks. The UV-Vis absorption spectra were obtained with a FLASH EA 1112 spectrophotometer. Steady-state fluorescence spectra were measured on a Fluoro-Max-P instrument; samples were dissolved in dry EtOH solution, filtered, transferred to a long quartz cell, and then capped and deoxygenated by bubbling with  $\text{N}_2$  before measurement.

## 2.2 Synthesis of $[\text{WOS}_3\text{Cu}_2(\text{phen})_2] \cdot 3\text{H}_2\text{O}$ (**1**)

CuI (57.1 mg, 0.3 mmol) and  $[\text{NH}_4]_2\text{WOS}_3$  (33.2 mg, 0.1 mmol), Phen- $\text{H}_2\text{O}$  (59.5 mg, 0.3 mmol) were added to 8 mL dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and the resultant solution was stirred at room temperature for 3 h and then filtered. Slow evaporation of the filtrate produced red blocks of **1** in 3 days, which was collected by filtration, washed with diethyl ether, and dried in air. Yield: 37.7 mg, 45% (based on W). Complex **1** is stable in air when dried but is relatively unstable in aqueous and polar media (after 1–2 days the colour changes to green, typical of a  $\text{Cu}^{\text{II}}$  oxidized product). Analysis calculated for  $\text{C}_{24}\text{H}_{22}\text{Cu}_2\text{N}_4\text{O}_4\text{S}_3\text{W}$ : C 34.42, H 2.65, N 6.69%; found: C 34.37, H 2.61, N 6.72%. IR data (KBr pellets,  $\text{cm}^{-1}$ ): 3443.6(m), 3033.3(w), 1619.1(m), 1574.9(s), 1507.3(m), 1419.6(s), 910.9(s), 841.2(s), 723.9(s), 448.1(s).

## 2.3 X-ray data collection and structure refinement

Single crystal X-ray diffraction data for complex **1** at 293 K were collected with the use of graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku Saturn 724<sup>+</sup> CCD diffractometer. The SMART and SAINT program packages were used for data collection and integration, respectively. The collected data were also corrected for absorbance using equivalent reflections and SADABS based upon Laue symmetry. The structure was solved by direct methods and refined on  $F^2$  by the full-matrix least-squares calculations with the use of SHELX-97 program package.<sup>26–28</sup> All the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. All the hydrogen atoms were placed at the calculated positions and refined following the riding model. Several attempts to refine a satisfactory solvent model in the lattice failed, and in the final refinement of the data it was treated with the SQUEEZE<sup>29</sup> procedure to

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

Formula	$\text{C}_{24}\text{H}_{22}\text{Cu}_2\text{N}_4\text{O}_4\text{S}_3\text{W}$
Formula weight	83757
Temperature /K	293(2)
Wavelength / $\text{\AA}$	0.71073
Crystal system	monoclinic
Space group	$C2/c$
$a$ / $\text{\AA}$	31.928(6)
$b$ / $\text{\AA}$	10.653(2)
$c$ / $\text{\AA}$	23.097(5)
$\alpha$ / $^\circ$	90
$\beta$ / $^\circ$	133.11(3)
$\gamma$ / $^\circ$	90
Volume / $\text{\AA}^3$	5735(2)
$Z$	8
$\rho_{\text{calcd}}$ / $\text{Kg/m}^3$	1.940
$\mu$ ( $\text{mm}^{-1}$ )	5727
Reflections collected/unique	13440/5017
$F(000)$	3248
Crystal size ( $\text{mm}^3$ )	$0.15 \times 0.12 \times 0.1$
$\theta$ ranges ( $^\circ$ )	3.25 to 25.00
$h/k/l$	$-3730/-1211/-27,26$
Reflections collected	13440
Independent reflections	5017 [R(int) = 0.0401]
Data/restraints/parameters	5017 / 0 / 316
Goodness-of-fit on $F^2$	1.115
Final R indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0454, wR_2 = 0.0972$
R indices (all data)	$R_1 = 0.550, wR_2 = 0.1027$
Largest peak and hole ( $\text{e}\text{\AA}^{-3}$ )	0.691 and -0.898

remove reflections contributing to the area of the solvent. Details of the crystal parameters, data collection and refinement of complex **1** are summarized in table 1. The selected bond lengths and angles for complex **1** are listed in table 2.

## 2.4 Density Functional Theory Study

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed to characterize the experimental absorption spectra by using the Gaussian 09 program.<sup>30</sup> The model compound of **1** was selected from experimental X-ray single-crystal structure. The restricted singlet wave function in DMF (dielectric constant  $\epsilon = 36.71$ ) solution was tested to be stable with the framework of the polarized continuum model (PCM) using B3LYP functional.<sup>31,32</sup> Herein, the basis set 6-31G\*+LanL2DZ\* (using 6-31G\* basis set for S, C, N, O, and H atoms, adding the f-type polarization functions to Cu and W atoms at the basis set LanL2DZ) was employed in view of the influence of d and f functions on the absorption spectra. The exponents of f orbitals for Cu (3.525) and W (0.823) atoms, were selected as

**Table 2.** Selected bond lengths (Å) and bond angles (°) of **1**.

Bond lengths (Å)		Bond lengths (Å)	
W(1)-O(1)	1.748(5)	W(1)-S(1)	2.236(2)
W(1)-S(2)	2.251(2)	W(1)-S(3)	2.272(2)
W(1)-Cu(1)	2.6759(12)	W(1)-Cu(2)	2.6501(14)
Cu(1)-N(1)	2.056(6)	Cu(1)-N(2)	2.116(6)
Cu(1)-S(2)	2.265(2)	Cu(1)-S(3)	2.272(2)
Cu(2)-N(3)	2.136(6)	Cu(2)-N(4)	2.026(6)
Cu(2)-S(1)	2.257(2)	Cu(2)-S(3)	2.278(2)
Bond angles (°)		Bond angles (°)	
O(1)-W(1)-S(1)	108.67(19)	O(1)-W(1)-S(2)	109.09(17)
O(1)-W(1)-S(3)	110.6(2)	S(1)-W(1)-S(2)	112.20(8)
S(1)-W(1)-S(3)	108.59(7)	S(2)-W(1)-S(3)	107.73(7)
N(1)-Cu(1)-N(2)	79.5(2)	N(1)-Cu(1)-S(2)	121.88(17)
N(1)-Cu(1)-S(3)	118.24(18)	N(2)-Cu(1)-S(2)	104.60(18)
N(2)-Cu(1)-S(3)	123.33(17)	S(2)-Cu(1)-S(3)	107.24(8)
N(3)-Cu(2)-S(1)	116.80(17)	N(3)-Cu(2)-S(3)	105.08(16)
N(4)-Cu(2)-S(1)	118.99(18)	N(4)-Cu(2)-S(3)	124.80(17)
N(4)-Cu(2)-N(3)	79.6(2)	S(1)-Cu(2)-S(3)	107.63(8)
W(1)-S(1)-Cu(2)	72.30(6)	W(1)-S(2)-Cu(1)	72.67(6)
W(1)-S(3)-Cu(1)	72.16(6)	W(1)-S(3)-Cu(2)	71.24(6)
Cu(1)-S(3)-Cu(2)	112.47(9)		

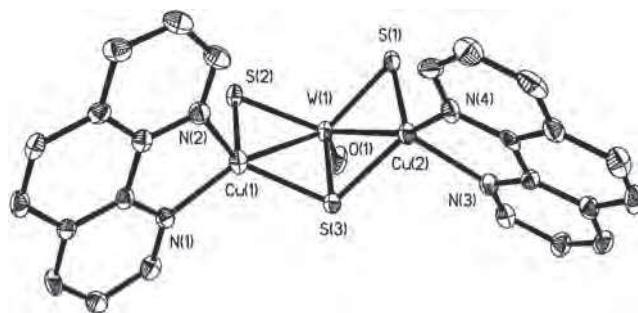
those in previous work.<sup>33</sup> The vertical electronic excitation energies of complex **1** in DMF solution were then obtained through TD-DFT/PCM calculation at the same level.

### 3. Results and Discussion

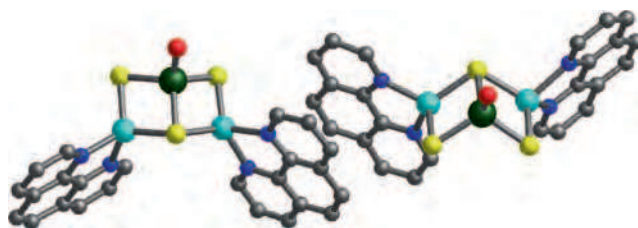
#### 3.1 Description of the crystal structure

Single crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic system with space group  $C2/c$ , and figure 1 shows the perspective view of the complex **1**. The  $[\text{WOS}_3\text{Cu}_2(\text{phen})_2]$  molecule consists of a butterfly-like  $[\text{WOS}_3\text{Cu}_2]$  core structure, and the oxidation states of W and Cu atoms in **1** are assumed to be +6 and +1, respectively. The W centre in the  $[\text{WOS}_3]^{2-}$  unit has a distorted tetrahedral configuration coordinated by one terminal O atom, one  $\mu_3$ -S atom and two  $\mu_2$ -S atoms, with S–W–S(O) bond angles ranging from 107.73(7) to 112.20(8)°. The W–O distance of 1.748(5) Å is characteristic of a W=O double bond. The average W–S bond length, 2.253 Å, falls in the range of typical W–S single bond.

The two Cu atoms exhibit the same coordination mode. Each atom adopts a distorted tetrahedral geometry and is coordinated by one  $\mu_2$ -S atom and one  $\mu_3$ -S atom from the thiometallate core and two N atoms from one phen ligand, forming two almost equivalent  $\text{CuS}_2\text{phen}$  units. These two  $\text{CuS}_2\text{phen}$  units are joined by a central W atom through two pairs



**Figure 1.** Molecular structure of complex **1**. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms were omitted for clarity.

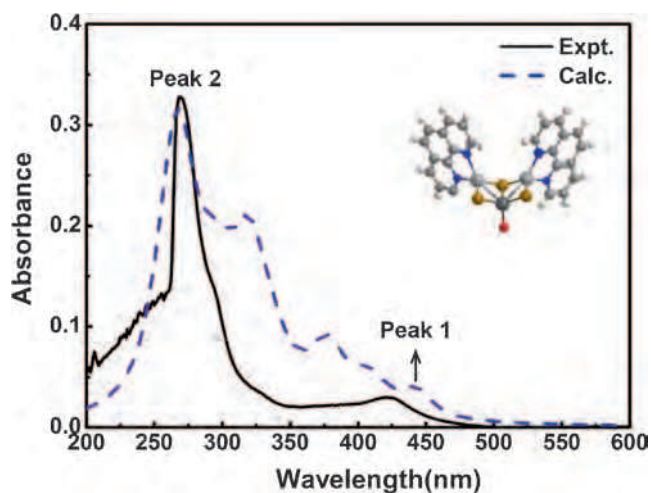


**Figure 2.** Pairwise stacking view of **1**, all H atoms have been omitted for clarity.

of S–S edges, thereby forming the skeleton of the  $[\text{WOS}_3\text{Cu}_2(\text{phen})_2]$ . The bond angles at these two Cu atoms range from 79.5(2)° to 124.80(17)°. The mean W···Cu distance (2.663 Å) is comparable to those of other clusters containing tetrahedral coordinated Cu, such as  $[\text{WOS}_3\text{Cu}_2(\text{PPh}_3)_2(\text{Py})_2]$ .<sup>34</sup>

It is worth noting that the phen ligands of two inversion-related molecules in **1** are exactly parallel and display pairwise  $\pi$ - $\pi$  stacking interactions (figure 2). The moieties of this pair are related to one another

through an inversion centre located between the phen rings. The interplanar separation is 3.3 Å, which indicates the presence of  $\pi$ - $\pi$  stacking interactions between two neighbouring phen ligands.



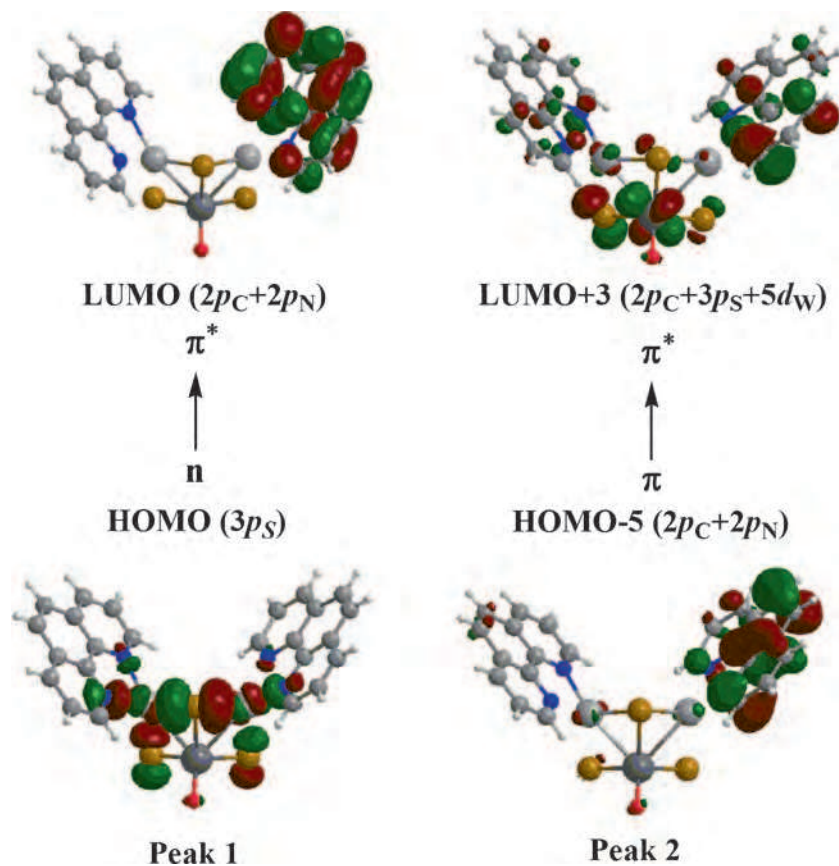
**Figure 3.** Experimental absorption spectrum of complex **1** (in black line) and TD-DFT/PCM calculation spectrum (in blue dash). For the latter, a Lorentzian function has been adopted with the spectral line width set to 70 nm.

### 3.2 Infrared Spectroscopy

In the complex **1**, the  $\nu(\text{C-H})$  vibration of aromatic ring is observed at about  $3033\text{ cm}^{-1}$ . Peaks at 1619, 1575, 1507 and  $1420\text{ cm}^{-1}$  may be attributed to the vibrations of the  $\text{C}=\text{C}/\text{C}=\text{N}$  bonds in **1**. The band at  $448\text{ cm}^{-1}$  is assigned to the  $\text{W-S}$  stretching frequency of  $[\text{WOS}_3]^{2-}$  in the complex, which is  $22\text{ cm}^{-1}$  lower than that of free  $[\text{WOS}_3]^{2-}$  in ammonium salt.<sup>35</sup> This indicates a decrease in the stretching force constant, showing that the  $[\text{WOS}_3]^{2-}$  ligand is coordinated through the sulfur atoms. The terminal  $\nu(\text{W}=\text{O})$  stretching frequency has been identified as a strong absorption band at  $911\text{ cm}^{-1}$  in accordance with literature values.<sup>36</sup>

### 3.3 Experimental and theoretical absorption spectra

To gain deeper insight into the electronic transitions and spectral characterization of this heterothiometallic



**Figure 4.** The assignment to absorption peaks of complex **1**. The molecular orbitals are obtained through DFT/PCM calculations at the B3LYP/6-31G\*+LanL2DZ\* level.

cluster, the TD-DFT/PCM calculations were performed for **1**. The experimental absorption spectra of **1** were measured in a  $1.6 \times 10^5$  mol dm<sup>3</sup> DMF solution. Figure 3 shows a comparison between the scaled absorption spectra of complex **1** with the Lorentzian function<sup>37</sup> and the experimental results, displaying a qualitative agreement in the shape of the absorption spectra. As schematically illustrated in figure 4, the lowest dipole-allowed absorption bands (Peak 1) of complex **1** are mainly assigned to be  $n \rightarrow \pi^*$  transitions. The  $n$  orbital is dominated by the  $p$  orbitals of S atoms, and the  $\pi^*$  orbital is composed of  $p$  orbitals of C and N atoms in phen ligand. The relatively stronger absorption bands (Peak 2) are mainly ascribed to the transitions from  $\pi$  to  $\pi^*$  orbitals. The  $\pi$  orbital is dominated by the  $p$  orbitals of C and N atoms in phen ligand and  $\pi^*$  orbital is mainly contributed from  $p$  orbitals of C and S atoms and  $d$  orbital of W atom.

### 3.4 Luminescence behaviour

Luminescent complexes are currently of great interest due to their potential applications in chemical sensors, photochemistry and electroluminescent displays.<sup>38</sup> In order to examine the fluorescent property of this complex, the luminescent property of **1** was investigated in EtOH solution and corresponding photoluminescent spectra is depicted in figure S1. It was observed that the emission peaks occurred at 369, 404 and 474 nm under 330 nm excitation. To further study the relative luminescence between the free ligand and its complex, the photoluminescent property of free phen ligand was also investigated in EtOH solution at room temperature (figure S1). The free phen molecule shows the fluorescent emission peak at 404 nm upon excitation at 330 nm, which may be attributed to the  $\pi \rightarrow \pi^*$  transition.<sup>39</sup> By comparing the profiles and locations of the emission peaks of complex **1** with the corresponding free phen ligand, we can presume that the emission peaks of complex **1** may originate from the combined interaction of intra-ligand  $\pi \rightarrow \pi^*$  transitions from the phen ligand and metal-to-ligand-charge-transfer (MLCT) transitions. Compared to free phen, the different emission peaks in **1** are presumably a result of coordination of the relevant ligands to a metal atom, the  $\pi$ -system is altered and therefore also the transition energy.<sup>40</sup> These observations indicate that complex **1** can serve as candidates of photoactive materials. The electrochemical behaviour of complex **1** in isopropyl alcohol solution was investigated by using Cyclic Voltammetry (CV), but no obvious redox activity and variation of conductance were observed (figure S2).

## 4. Conclusions

In summary, a new butterfly-like heterothiometallic cluster [WOS<sub>3</sub>Cu<sub>2</sub>(phen)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O has been synthesized and characterized. The  $\pi$ – $\pi$  stacking between the phen ligands plays an important role in determining the crystal packing and molecular assemblies of this complex. The theoretical absorption spectra of **1** obtained from density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are in good agreement with the experimental observations. The title complex is luminescent.

## Supplementary Information

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1006130 (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk). Luminescence spectra of complex **1** and free phen ligand and electrochemical behaviour of complex **1** can be seen in supplementary information (figures S1–S2). For details, see www.ias.ac.in/chemsci.

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