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*Full Paper*

# Crystal growth and characterisation of a unique trinuclear $V^{IV}/V^{V}$ complex

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**Abstract:** Single crystals of a mixed-valence trinuclear cluster of formula $[V_2^{V}V^{IV}O_5(C_{12}H_8N_2)_3(SO_4)_2(H_2O)_3]\cdot 6H_2O$ were grown by layer diffusion technique and characterised by single-crystal X-ray diffraction; $P2_1/c$, $a$ = 20.5448(11) Å, $b$ = 11.7647(9) Å, $c$ = 18.1871(9) Å, $\beta$ = 92.64(0)°, $V$ = 4391.22 (93) Å$^3$, $R$ = 0.0941 and $Rw$ = 0.1345. A distinct characteristic of the structure is the existence of the rare linear mono-μ-oxo $[V_2^{V}V^{IV}O_5]^{4+}$ building units and the presence of a large number of hydrogen bonds and π-π interactions. The study on the mixed valence state of vanadium by valence bond sum calculations, manganometric titration and cyclic voltammetry, and the presence of π-π interactions by calculation of the harmonic oscillator model of aromaticity indices are presented. The thermogravimetric and differential scanning calorimetric analysis is also reported. The results of UV-Vis spectroscopic study and band gap energy calculation are included.

**Keywords:** vanadium complex, trinuclear complex, crystal structure, single-crystal X-ray diffraction

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## INTRODUCTION

Prompted by a variety of valences and coordination chemistry that can be adopted by vanadium and a wide range of potential applications of its complexes [1-3], the interest in vanadium complexes has been unceasing, particularly in those of high nuclearity and mixed valence state. The bi-nuclear complexes containing a mono-μ-oxo $[V_2O_3]^{2+}$ core are thus far the largest class in which the mixed valence state of vanadium is common. Examples of polynuclear $V^{IV}/V^{V}$ complexes with mono-μ-oxovanadium cores are still limited: the tetra-nuclear $[V_4O_6(C_2H_5O)_6(C_{12}H_8N_2)_2]$, penta-nuclear $\{[V_2O_4(C_{12}H_8N_2)_2(PO_4)]2VO(OH)\}_{3/4}\{[V_2O_4(C_{12}H_8N_2)_2(HPO_4)]_2\}_{1/4}\cdot 4.5H_2O$ and nona-nuclear $K_7[V_9O_{16}(bdta)_4]\cdot 27H_2O$ (bdta = butanediaminetetraacetate) are known [4-6]. To the best of our knowledge, the first example of the tri-nuclear vanadium complex of this kind with a chemical formula of $[VO_2(\textit{phen})(SO_4)(H_2O)]_2(VO(\textit{phen})(H_2O)]\cdot 4H_2O$ (*phen* = phenanthroline ligand) was reported by Huang et al. in 2008 [7]. Its hydrothermal synthesis and the novel characteristic of its structure in exhibiting a practically linear $[V_3O_5]^{4+}$ core were reported with a brief description on the EPR and UV-Vis study of the complex.

As a continuation of our interest in the synthesis of new polyoxovanadates using organodiamines of different molecular flexibility and aromaticity, we embark on the synthesis and growing of single crystals of compound $[V_2^{V}V^{IV}O_5(C_{12}H_8N_2)_3(SO_4)_2(H_2O)_3]\cdot 6H_2O$ **(1)**. Although reported earlier [7], the synthesis and crystal growth of **1** by a different route carried out in this study and a detailed description of its crystal structure should be worth reporting. Different ways of determining the mixed valence state of vanadium are presented. The UV-Vis spectroscopic study, cyclic voltammetric analysis and thermorgravimetric-differential scanning calorimetric analysis of **1** were also performed.

## MATERIALS AND METHODS

### Chemicals

All chemicals were used as-received: 1,10-phenanthroline ($C_{12}H_8N_2$; Fluka, 99%), ethyl alcohol (Merck, 99.9%), ammonium metavanadate (Ajax, 99.5%), sodium hydroxide (Merck, 99%), sulfuric acid (Merck, 95-97%), potassium permanganate (BDS, 99%), sodium sulphite (Ajax, 98%) and potassium bromide (BDH 98.5%).

### Crystal Growth and Characterisation

An ethanolic solution of organic ligand (solution A) was prepared by dissolving 0.495 g of 1,10-phenanthroline (*phen*) in 15.0 $cm^3$ of ethyl alcohol. An aqueous solution of $VO_2^+$ (solution B) was prepared by dissolving 2.00 g of ammonium metavanadate in 50.0 $cm^3$ of warm 1.00 mol $dm^{-3}$ sodium hydroxide solution, followed by addition of 80.0 $cm^3$ of 1.00 mol $dm^{-3}$ sulfuric acid . A portion of solution B (1.50 $cm^3$) was gently loaded into a glass test tube of 5 mm in diameter and 10 cm in length, followed by 1.50 $cm^3$ of solution A. Dark green crystals of **1** appeared at the boundary between solutions A and B after leaving for 5 days at atmospheric condition.

The elemental composition of the crystals was semi-quantified using an energy-dispersive X-ray microanalyser equipped with a field-emission scanning electron microscope (JEOL JSM-6335F), whereupon a consistent V:S:O:C:N atomic ratio of 2.8:1.0:3.2:6.7:1.5 (exp.) compared to 2.4:1.0:5.5:6.7:1.3 (calc.) was obtained. A Fourier transform infrared (FTIR) spectrum of the ground crystals as a KBr pellet was collected on a Bruker Tensor 27 FT-IR instrument (4000-400 $cm^{-1}$, resolution 0.5 $cm^{-1}$): 3450 $cm^{-1}$, ν(O–H); 3065 $cm^{-1}$, ν(aromatic C–H); 1626, 1583, 1519 and 1427 $cm^{-1}$, ν(aromatic C=C); 1187, 1125 and 1032 $cm^{-1}$, $\nu(SO_4)$; 970 and 937 $cm^{-1}$, ν(V=O); 870, 848, 778, 736 and 723 $cm^{-1}$, $\delta_{oop}$(aromatic C-H); 647 and 593 $cm^{-1}$, δ(V–O–V).

The purity of **1** was assured by X-ray powder diffraction pattern collected on a Bruker D8 Advance diffractometer (Ni filter, Cu $K\alpha$, $\lambda$=1.540558 Å, 48 kV, 30 mA). In order to determine the amount of $V^{IV}$ and total $V^{IV,V}$, the aqueous solutions of **1** and its reduced form were titrated against standardised potassium permanganate solution. The solution of the reduced form of **1** was obtained by a reaction with sulphur dioxide generated from sodium sulphite. Cyclic voltammetry (CV) was also conducted using a BAS CV-50W voltammetric analyser (Bioanalytical System, Inc., USA) with Pt (MF-2013, 1.6 mm in diameter), Ag/AgCl (MF-2063) and Pt wire (MW-1032) as working, reference and auxiliary electrodes respectively.

Themogravimetric-differential scanning calorimetric (TG-DSC) analysis was performed using ETZSCH STA 409 PC/PG thermal analyser (Netzsch-Gerätebau GmbH, Germany) (20-1200°C, rate 10°C/min, $N_2$ gas) to evaluate the thermal stability of **1**. A UV-Vis spectrum of an aqueous solution of **1** from 200 nm to 800 nm was measured with a Perkin Elmer UV LAMDA 25 spectrophotometer. The loss of crystal colour after complete dissolution was noted.

## Crystal Structure Determination

Data of 8699 independent reflections were collected in a range of $2.5 \leq \theta/° \leq 26.1$ on a 0.45×0.25×0.15 $mm^3$ greenish lozenge crystal of **1** using a Stoe IPDS2 diffractometer (Stoe & Cie GmbH, Germany) and Stoe *X*-Area software [8]. A face indexed absorption correction was applied within the Stoe *X*-RED software using Tompa method [9-10]. The data were then reduced and refined resulting in 5365 reflections with $I > 2\sigma(I)$ and internal R of 0.070. The structure was determined by direct method and refined by full-matrix least-square methods using SHELXS97 and SHELXL97 programs via the WinGx program interface [11-13]. The structure was solved and refined in $P2_1/c$, $a$ = 20.5448(11) Å, $b$=11.7647(9) Å, $c$ = 18.1871(9) Å, $\beta$ = 92.64(0)°, $V$ = 4391.22 (93) $Å^3$, $Z$ = 4, $R$ =0.0941 and $Rw$ = 0.1345. The data were of reasonable quality. However, it was not possible to locate hydrogen atoms of the included water molecules. Some disorder in the positions of the water molecules was also detected. Details on data collection and structural deduction and refinement are summarised in Table 1. A rather large deviation of the goodness of fit from unity due to local disorder in the structure of **1** may be noted.

The structure of **1** was first reported by Huang et al. in 2008 [7]. The synthesis by hydrothermal route and the uniqueness of the complex as the first mixed-valence polynuclear vanadium with linear mono-μ-oxo $[V_3O_5]^{4+}$ core were briefly reported. The study of the EPR and electronic spectrum was included. Crystallographic data of the formerly reported structure were compared with the presently reported structure as shown in Table 1, which suggests an approximate equivalence.

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

| | **1** | Data abstracted from Huang et al. [7] |
|---|---|---|
| Formula | $[V_2^{V}V^{IV}O_5(\mathit{phen})_3(SO_4)_2(H_2O)_3]\cdot 6H_2O$ | $[VO_2(\mathit{phen})(SO_4)(H_2O)]_2[VO(\mathit{phen})(H_2O)]\cdot 4H_2O$ |
| Formula weight | 1117 | 1091.66 |
| Crystal description | Dark green | *N/A* |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_{1/c}$ | $P2_{1/c}$ |
| $a$/ Å | 20.5448(11) | 20.747(4) |
| $b$/ Å | 11.7647(9) | 11.828(2) |
| $c$/ Å | 18.1871(9) | 18.316(4) |
| $\beta$ / ° | 92.639(4) | 93.07(3) |
| Unit cell volume/ Å$^3$ | 4391.2(5) | 4488.2(16) |
| $Z$ | 4 | 4 |
| $\rho_{calc}$/g.cm$^{-3}$ | 1.691 | 1.616 |
| $T$/K | 150(4) | 293(2) |
| Radiation ($\lambda$/Å) | Mo $K_\alpha$(0.71073) | Mo $K_\alpha$(0.71073) |
| Total data collected | 24523 | 37068 |
| $R_{int}$ | 0.070 | 0.0384 |
| Data ($I>2\sigma(I)$) | 8699 | 10059 |
| Goodness of fit ($S$) | 0.797 | 1.049 |
| $R$, $R_w$ (all data) | 0.0941, 0.1345 | *N/A* |
| $R$, $R_w(I>2\sigma(I))$ | 0.055, 0.135 | 0.0558, 0.1488 |

## RESULTS AND DISCUSSION

### Crystal Structure of 1

Compound **1,** $[V_2^{V}V^{IV}O_5(C_{12}H_8N_2)_3(SO_4)_2(H_2O)_3]\cdot 6H_2O$, crystallises in monoclinic space group $P2_1/c$ with cell parameters $a$ = 20.5448(11) Å, $b$ = 11.7647(9) Å, $c$ = 18.1871(9) Å, $\beta$ = 92.64(0)°, $V$ = 4391.22 (93) Å$^3$ and $Z$ = 4, which are similar to those of the previously reported structure [7]. Figure 1 shows an asymmetric unit of **1**, depicting three distinct vanadium atoms linked by two $\mu_2$-O11 and $\mu_2$-O12 to form an approximately linear trinulcear vanadium oxide backbone with bond angles being close to linearity: V1-O11-V2 = 163.1° and V(2)-O(12)-V(3) = 159.2°. Selected bond lengths and bond angles in **1** are listed in Table 2 and Table 3 respectively. The terminal V1 and V3 share the common distorted octahedral geometry, coordinated to two N atoms of the chelating *phen* and four O atoms from a monodentate sulphate, a terminal aqua ligand, the vanadyl bond and the oxo-bridge. Similar distorted octahedral geometry is adopted by the mediating V2, coordinated to two N atoms of the chelating *phen*, two *trans* $\mu_2$-O atoms of oxo-bridges, and the vanadyl and sulfate O atoms. The chemical formula of $[V_3O_5(\mathit{phen})_3(SO_4)_2(H_2O)_3]$ can thus be derived. A common question for polynuclear vanadium complexes is, however, the valence states of the vanadium atoms.

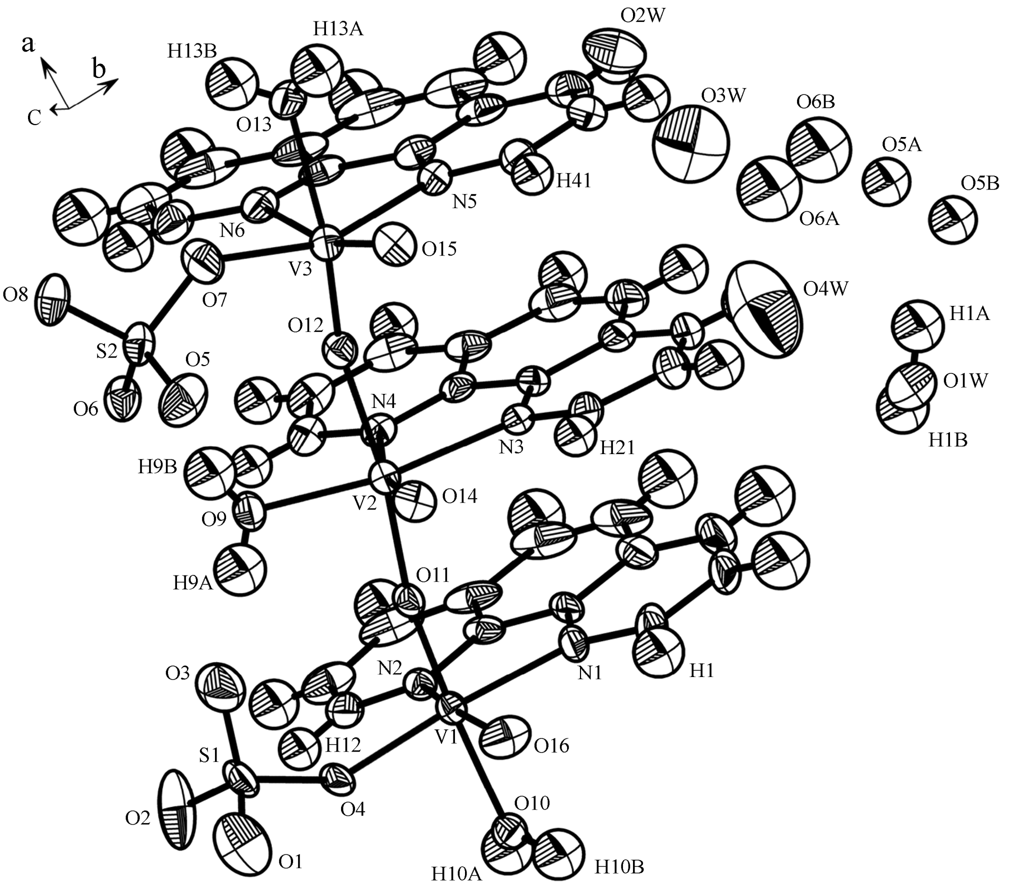

**Figure 1.** Asymmetric unit of **1** with atomic numbering scheme and drawn with 50% thermal elliptical possibility

**Table 2.** Selected bond distances (Å) in **1** with standard deviations in brackets

| | | | |
|---|---|---|---|
| V1—O16 | 1.600(3) | V3—O12 | 1.677(3) |
| V1—O11 | 1.675(3) | V3—O7 | 1.930(3) |
| V1—O4 | 1.917(3) | V3—O13 | 2.123(4) |
| V1—N1 | 2.132(4) | V3—N5 | 2.136(4) |
| V1—O10 | 2.149(4) | V3—N6 | 2.296(4) |
| V1—N2 | 2.249(3) | S2—O5 | 1.430(4) |
| V2—O14 | 1.592(3) | S2—O8 | 1.455(3) |
| V2—O12 | 1.932(3) | S2—O6 | 1.468(3) |
| V2—O11 | 1.947(3) | S2—O7 | 1.521(4) |
| V2—O9 | 1.998(3) | S1—O2 | 1.421(4) |
| V2—N3 | 2.124(4) | S1—O1 | 1.457(4) |
| V2—N4 | 2.307(3) | S1—O3 | 1.462(5) |
| V3—O15 | 1.596(3) | S1—O4 | 1.510(3) |

**Table 3.** Selected bond angles (°) in **1** with standard deviations in brackets

| | | | | | |
|---|---|---|---|---|---|
| O16—V1—O11 | 104.73(16) | O12-V2-N3 | 87.57(13) | N5-V3-N6 | 73.96(13) |
| O16—V1—O4 | 104.79(18) | O11-V2-N3 | 96.01(13) | O5-S2-O8 | 113.5(2) |
| O11—V1—O4 | 99.86(14) | O9-V2-N3 | 159.64(14) | O5-S2-O6 | 111.2(2) |
| O16—V1—N1 | 92.14(18) | O14-V2-N4 | 166.12(15) | O8-S2-O6 | 110.40(19) |
| O11—V1—N1 | 88.54(15) | O12-V2-N4 | 80.55(12) | O5-S2-O7 | 109.1(2) |
| O4 —V1—N1 | 158.32(14) | O11-V2-N4 | 82.81(12) | O8-S2-O7 | 103.9(2) |
| O16—V1—O10 | 87.57(16) | O9-V2-N4 | 86.43(14) | O6-S2-O7 | 108.3(2) |
| O11—V1—O10 | 165.39(13) | N3-V2-N4 | 73.57(13) | O2-S1-O1 | 109.3(3) |
| O4 —V1—O10 | 84.22(13) | O15-V3-O12 | 104.37(16) | O2-S1-O3 | 116.4(3) |
| N1 —V1—O10 | 83.05(14) | O15-V3-O7 | 104.52(17) | O1-S1-O3 | 105.5(3) |
| O16—V1—N2 | 161.26(17) | O12-V3-O7 | 97.97(15) | O2-S1-O4 | 106.8(2) |
| O11—V1—N2 | 88.14(14) | O15-V3-O13 | 93.89(15) | O1-S1-O4 | 107.2(2) |
| O4 —V1—N2 | 85.91(13) | O12-V3-O13 | 161.30(13) | O3-S1-O4 | 111.2(2) |
| N1 —V1—N2 | 74.35(14) | O7-V3-O13 | 81.01(15) | S1-O4-V1 | 140.7(2) |
| O10-V1-N2 | 78.10(13) | O15-V3-N5 | 89.66(15) | S2-O7-V3 | 137.3(2) |
| O14-V2-O12 | 99.86(15) | O12-V3-N5 | 95.24(14) | V1-O11-V2 | 163.10(18) |
| O14-V2-O11 | 98.38(15) | O7-V3-N5 | 157.48(16) | V3-O12-V2 | 159.23(18) |
| O12-V2-O11 | 161.23(12) | O13-V3-N5 | 80.64(14) | | |
| O14-V2-O9 | 107.45(16) | O15-V3-N6 | 162.33(16) | | |
| O12-V2-O9 | 85.36(14) | O12-V3-N6 | 84.12(14) | | |
| O11-V2-O9 | 85.00(13) | O7-V3-N6 | 89.31(16) | | |
| O14-V2-N3 | 92.56(15) | O13-V3-N6 | 77.20(13) | | |

The bond valence sum (BVS) calculation was attempted using the refined bond lengths listed in Table 2 with the following assumed parameters: $R_0(\mathrm{V}^{\mathrm{V,IV}}–\mathrm{O}^{\mathrm{-II}}) = 1.735$, $R_0(\mathrm{V}^{\mathrm{V}}–\mathrm{O}^{\mathrm{-II}}) = 1.803$, $R_0(\mathrm{V}^{\mathrm{IV}}–\mathrm{O}^{\mathrm{-II}}) = 1.780$, $R_0(\mathrm{V}^{\mathrm{V,IV}}–\mathrm{N}^{\mathrm{-III}}) = 1.875$, and $b = 0.370$ [14]. The BVS of 4.81, 4.15 and 4.85 were obtained for V1, V2 and V3 respectively, indicating the presence of the expected $\mathrm{V}^{\mathrm{IV}}$ and $\mathrm{V}^{\mathrm{V}}$ with twice the amount of the latter. The result of manganometric titration confirms the calculation: 0.915 mol of $\mathrm{V}^{\mathrm{IV}}$ per formula unit. The CV analysis confirms this by the presence of an irreducible reduction peak of $\mathrm{V}^{\mathrm{V}}$ to $\mathrm{V}^{\mathrm{IV}}$ at +0.242 V vs Ag/AgCl with a maximum current of 4.48 A. Based on the BVS calculation, manganometric titration and the CV experiment, a mixed $2\mathrm{V}^{\mathrm{V}}:\mathrm{V}^{\mathrm{IV}}$ valence state for vanadium and the precise formula of $[\mathrm{V}_2{}^{\mathrm{V}}\mathrm{V}^{\mathrm{IV}}\mathrm{O}_5(\mathrm{C}_{12}\mathrm{H}_8\mathrm{N}_2)_3(\mathrm{SO}_4)_2(\mathrm{H}_2\mathrm{O})_3]$ can thus be deduced. This leads to the conclusion on charge neutrality for the cluster, which confirms the presence of only water molecules as the extra-cluster species and justifies the assignment of the extra-cluster O atoms as water during the crystal structure deduction and refinements. The chemical formula with six extra-cluster water molecules, viz. $[\mathrm{V}_2{}^{\mathrm{V}}\mathrm{V}^{\mathrm{IV}}\mathrm{O}_5(\mathrm{C}_{12}\mathrm{H}_8\mathrm{N}_2)_3(\mathrm{SO}_4)_2(\mathrm{H}_2\mathrm{O})_3]\cdot 6\mathrm{H}_2\mathrm{O}$, is then established.

The phenanthroline (*phen*) ligands are located on the same side of the vanadium oxide backbone with the distances of 3.689 Å and 3.670 Å between the centroids of two adjacent molecular planes as shown in Figure 2. These distances are in a range possible for the π-π interactions to occur [15-17], which can be regarded as an important parameter regulating the spatial arrangement of these chelating ligands. It is apparent that these phenanthroline ligands are not exactly parallel to each other but slightly converge towards the free end of the molecule. Figure 3 depicts the centroids of the central benzene rings of the *phen* ligands, showing the panning angles of 9.48° and 21.80° for the superjacent and subjacent ligands from the middle one. The relative arrangement of these organic ligands indicates that other interactions are present that subjugate the weak π-π interactions, which favour the superimposed position of the ligands.

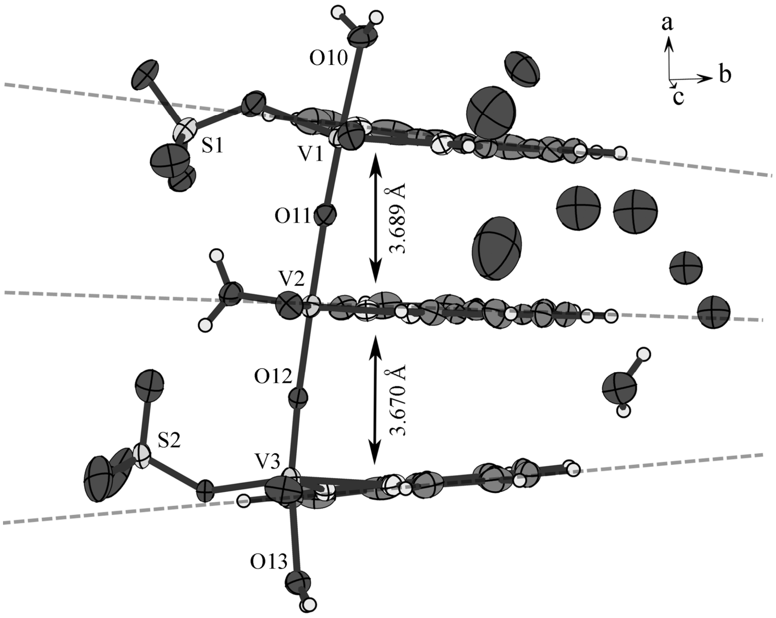

**Figure 2.** Illustration showing the relative spatial arrangement of *phen* and the corresponding inter-molecular planar distances

The interaction between π electrons commonly encountered in the stacking of aromatic molecules should impart an influence on their aromaticity. Here, the harmonic oscillator model of aromaticity (HOMA) index was used to evaluate the presence of this interaction [18-20]. According to a survey of structures consisting of *phen* in the molecules both in coordination and non-coordination modes found in the Cambridge structural databases [21], it is evident that the values of HOMA indices are distributed in different ranges depending on both the coordination and the π-π interaction. For non-coordinated *phen*, the average indices of three fused benzene rings are distributed in a range of 0.25-0.50 for those without π-π interactions and 0.66-0.83 for those with the interactions. On the other hand, the presence of π-π interactions seems to be common with coordination with average indices distributed in a higher range of 0.70-0.94, suggesting the preference of these aromatic ligands to arrange themselves in such a way as to maximise the interactions. In the structure of **1**, the HOMA indices were calculated at similar values of ca. 0.80 for each *phen* ligand. This is in very good

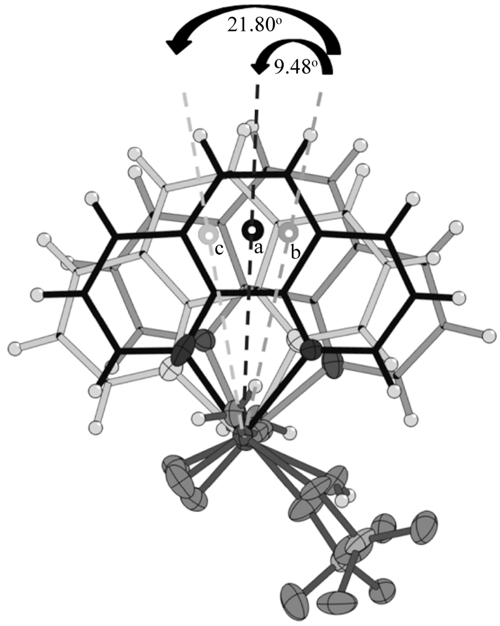

**Figure 3.** Illustration showing relative locations of the centroids (*a*, *b* and *c*) of the central benzene rings of the superjacent, middle and subjacent *phen* ligands respectively, with relative panning angles of a and c from b

agreement with the surveyed HOMA indices for those complexes with π-π interacting *phen* ligands, hence the suggested presence of such weak interaction in **1**.

The analysis for hydrogen bonding according to the definition proposed by Jeffrey [22] was performed on the crystal structure and revealed a large number of hydrogen bonding interactions as depicted in Figure 4 and listed in Table 4. The weak C-H···O hydrogen bonds formed between *phen* and the neighbouring O atoms of both ligated and free water molecules as well as the nearby sulphate group may account for the subjugation of the π-π interactions and the consequent orientation of these organic ligands. The strong hydrogen bonds of O-H···O type between the ligated water of the mediated V2 and the nearby sulphates also provide explanation for the orientation of the pending $SO_3$ motifs of V1 and V3 that incline towards each other with the bending angles of 140.71° and 137.32° for V1-O3-S1 and V3-O7-S2 respectively.

Compared to the complex, $[VO_2(phen)(SO_4)(H_2O)]_2(VO(phen)(H_2O)]\cdot 4H_2O$, reported by Huang et al. [7], structure **1** contains two more molecules of water of crystallisation and therefore a larger number of hydrogen bonding interactions. This may stem from the difference in crystal growth technique and condition. Crystals of **1** were grown at ambient temperature and pressure, whereas those of the former were obtained hydrothermally. The larger number of water outside the coordination sphere, however, does not significantly affect the solid state registry of the compound.

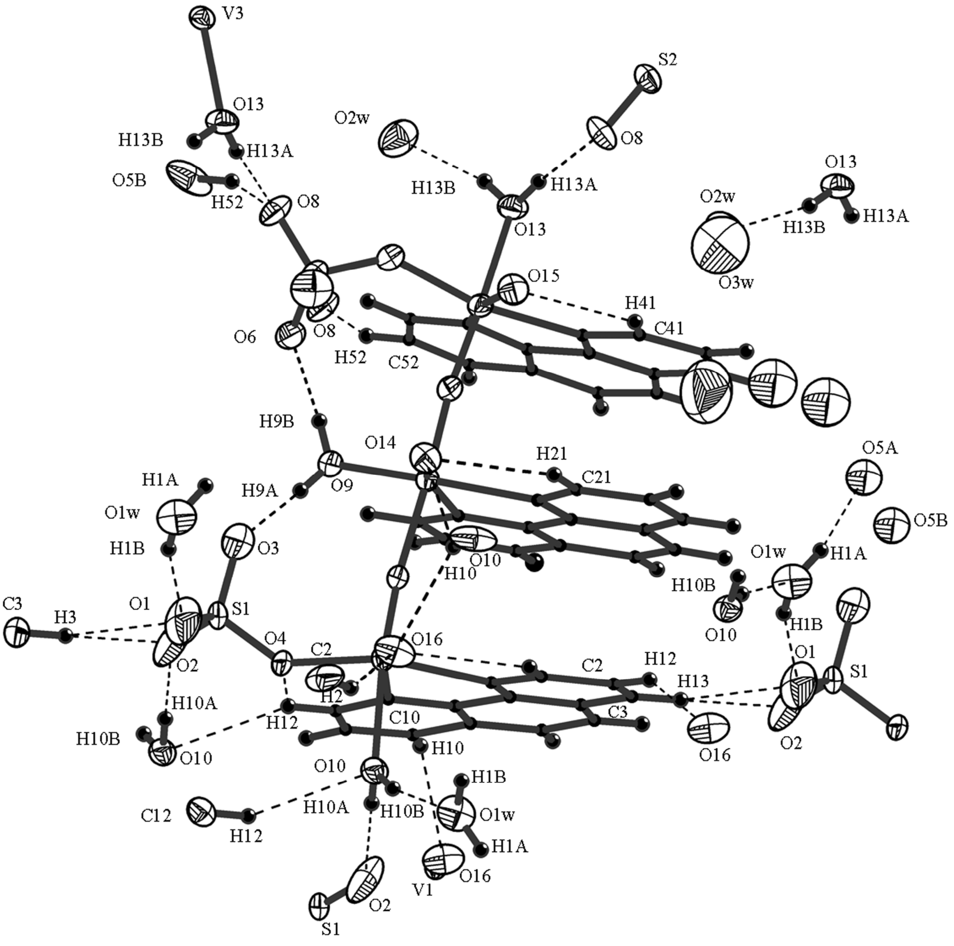

**Figure 4.** Hydrogen bonding interactions (dotted lines) of different types as listed in Table 4

## UV-Vis Spectroscopic Study

The UV-Vis spectrum measured on the aqueous solution of **1** at a concentration of 5x10$^{-4}$ mol dm$^{-3}$ (Figure 5) exhibits absorption only in the UV region. The absorption bands characteristic of *phen* are clearly present with the maxima at 230 nm (3,205 dm$^3$mol$^{-1}$cm$^{-1}$) and 264 nm (2,150 dm$^3$mol$^{-1}$ cm$^{-1}$), both of which are attributable to the intraligand $\pi$-$\pi$* transitions. The most intense band at 206 nm (10,584 dm$^3$mol$^{-1}$cm$^{-1}$) can be assigned to the LMCT process of the terminal oxygen while a broad band appearing as shoulder at 270 nm is the characteristic band associated to the LMCT of the bridging oxygen [23-25]. The absorption coefficients ($\alpha$) can be calculated from the maximum ($\lambda_{max}$) of each band, and the plot between $(\alpha h\nu)^2$ and $h\nu$ can be made (inset of Figure 5) if only the direct electronic transition is assumed [26]. The band gap energy for each transition can be obtained by extrapolation of the positive tangent line for each $h\nu$ to $\alpha$=0: 4.3017, 5.2317 and 5.8182 eV for the transitions with $\lambda_{max}$ at 264, 230 and 206 nm respectively.

**Table 4.** Summary of hydrogen bonding geometry for **1** (Standard deviations are in brackets)

| D | A | H···A (Å) | D···A (Å) | ∠ D-H···A (°) |
|---|---|---|---|---|
| $O1_W$ | $O5_A$ | 2.17(5) | 2.981(7) | 158(5) |
| $O1_W$ | O1 | 1.99(4) | 2.807(5) | 161(6) |
| O9 | O3 | 1.72(4) | 2.560(5) | 175(7) |
| O9 | O6 | 1.76(4) | 2.604(5) | 176(5) |
| O10 | O2 | 1.91(4) | 2.750(5) | 179(7) |
| O10 | $O1_W$ | 1.87(5) | 2.690(5) | 164(5) |
| O13 | O8 | 1.82(5) | 2.656(5) | 174(5) |
| O13 | $O2_W$ | 1.93(5) | 2.728(5) | 163(4) |
| C1 | O16 | 2.57 | 2.994(7) | 108 |
| C2 | O16 | 2.46 | 3.308(7) | 149 |
| C3 | O1 | 2.50 | 3.270(7) | 138 |
| C3 | O2 | 2.35 | 3.272(8) | 163 |
| C10 | O14 | 2.56 | 3.243(7) | 129 |
| C10 | O16 | 2.49 | 3.212(7) | 133 |
| C12 | O4 | 2.56 | 3.058(5) | 113 |
| C12 | O10 | 2.57 | 3.365(6) | 142 |
| C21 | O14 | 2.49 | 2.957(6) | 110 |
| C41 | O15 | 2.43 | 2.894(6) | 110 |
| C52 | O8 | 2.45 | 3.246(7) | 142 |

It is intriguing that there was no absorption in the visible light region (325-800 nm) for the solution of **1**, which was also colourless. This might be due to the loss of long-range order of the solid state structure when it was made into solution. It has been reported, however, that a broad absorption band which should be evidence for the inter-valence charge transfer between $V^{IV}$ and $V^{V}$ was observed in this region for the spectrum collected on a solid sample [7].

## Thermogravimetric and Differential Scanning Calorimetric Analysis

On heating **1** under the flow of $N_2$ gas, four stages of endothermic weight loss were observed (Figure 6). The first weight loss of 9.86% occurring between 80-150°C agrees well with the weight of six non-coordinating water molecules (9.58%), while the second loss of 5.14% observed at 150-340°C is approximately equivalent to the weight of three coordinating water molecules (4.79%). The corresponding endothermic features found in the DSC curve reflect the influence of the hydrogen bonding interactions involved with these water molecules. The next two subsequent weight losses found from 340°C to 700°C totalled 45.00%, which corresponds well with the release of three coordinated *phen* ligands. It should be noted that the argument is made based only on the agreement of weight percentages; further experiments on identification of the liberated species have to be performed if a definite conclusion is to be obtained.

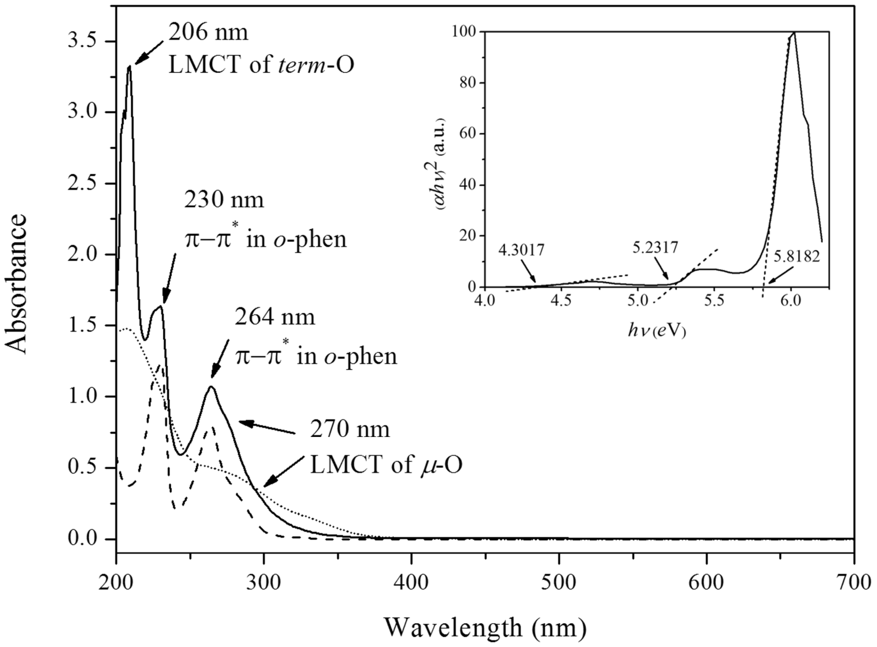

**Figure 5.** The UV-Vis spectrum of aqueous solution of **1** ($5 \times 10^{-4}$ moldm$^{-3}$, solid line) compared with those of the ligand (dash line) and vanadium precursor (dotted line). The plot between $(\alpha h\nu)^2$ and hν is provided in the inset

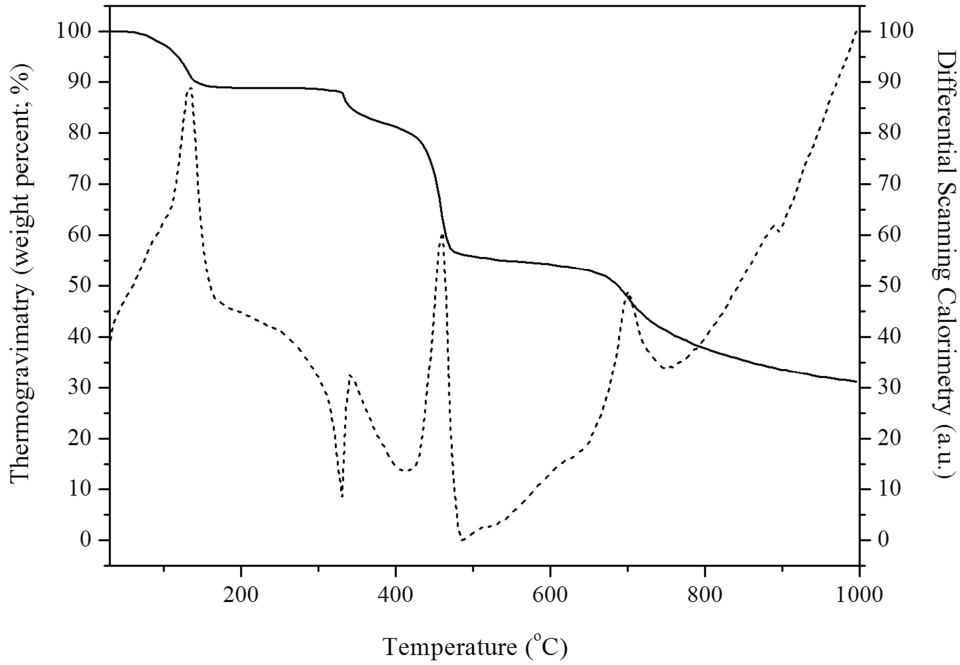

**Figure 6.** Thermogravimetric (solid line) and differential scanning calorimetric (dash line) graphs collected on **1**

## CONCLUSIONS

A rare example of mixed-valence trinuclear cluster, $[V_2^{V}V^{IV}O_5(C_{12}H_8N_2)_3(SO_4)_2(H_2O)_3]\cdot 6H_2O$, has been synthesised at ambient atmosphere. Its crystal structure has been determined and refined with excellent agreement with the previously reported structure which had fewer water of crystallisation. Detailed analysis of the structure indicates the presence of both π-π interactions and a large number of intra- and inter-cluster hydrogen bonds, which impart influence on spatial orientation of the cluster-building motifs. According to the bond valence sum calculations, the manganometric titration and cyclic voltammetry, the mixed valence of $V^{IV}$ and $V^{V}$ in the ratio of 1:2 can be deduced. The presence of six molecules of water of crystallisation is consistent with the results of the thermogravimetric/differential scanning calorimetric analysis, which suggest sequential loss of water of crystallisation, ligated water and the phenanthroline ligands.

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## SUPPLEMENTARY MATERIAL

Crystallographic data for compound **1** is available as supplementary material of this article in cif format [download].

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