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ARTICLE TYPE

## A new vanadium sulfate with ferrimagnetic and NLO properties constructed from novel discrete umbrella-like $[\text{V}^{\text{V}}(\mu_3\text{-O})_4\text{V}^{\text{IV}}_4\text{O}_5(\text{SO}_4)_4(\text{en})]^{5-}$ anions

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A new vanadium sulfate,  $[\text{H}_2\text{N}(\text{CH}_3)_2]_{19/3}(\text{en})[\text{V}_5\text{O}_5(\mu_3\text{-O})_4(\text{SO}_4)_4(\text{SO}_4)_{2/3}[\text{HN}(\text{CH}_3)_2]_{2/3}]$  **1**, constructed from novel umbrella-like  $[\text{V}^{\text{V}}(\mu_3\text{-O})_4\text{V}^{\text{IV}}_4\text{O}_5(\text{SO}_4)_4(\text{en})]^{5-}$  anions was synthesized and structurally characterized using single-crystal X-ray analysis. While the magnetic and optical studies of **1** indicate the title compound exhibits the presence of significant ZFS, interesting ferrimagnetic interactions and strong two photon absorption.

The widespread attention in POM-based materials arises from their structural diversity and potential functional applications including catalysis, sorption, electronics, medicine, environmental sciences.<sup>1-3</sup> Among the polyoxometalates, polyoxovanadates (POVs) have attracted extensive interests owing to its vibrant abilities such as oxidation-reduction property, exceptional performance in magnetic materials and heterogeneous catalysts.<sup>4-6</sup> Therefore, a wide variety of novel structures based on vanadium oxide clusters have been reported.<sup>7-</sup>

Although significant methods have been made to rationally design and prepare new hybrid organic-inorganic vanadate compounds which including phosphates, borates, and silicates,<sup>10-12</sup> vanadium sulfates are relatively less investigated due to the difficulties of crystallization.<sup>12d</sup> Up to now, few vanadium sulfate units including only  $[(\text{V}^{\text{IV}}\text{O})_2(\text{OH})_2(\text{SO}_4)_2]$ ,  $[\text{V}^{\text{III}}(\text{OH})(\text{SO}_4)_2]$ ,  $[(\text{V}^{\text{IV}}\text{O})(\text{H}_2\text{O})(\text{SO}_4)_2]$ ,<sup>13</sup> were obtained by using amine as template, and all reported vanadium sulphates are infinite structures with 1D V-O-S chains or 2D layers. It is therefore in vital to design new functionalised discrete V-O-S cluster, in order to explore their magnetic and optical properties, which may be applied in microwave device materials<sup>2c</sup> and optical storage medium<sup>3c</sup>, respectively.

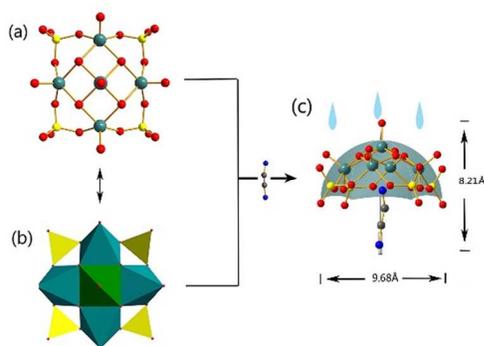
In the field of magnetism, magnetic clusters especially nano-sized clusters display novel properties that make them promising candidates for future applications. The important family of magnetic polyoxometalates including the fully reduced V (III or IV) and the mixed valence (IV/V or III/IV) oxometalates exhibit amusing magnetic property. In most cases, magnetic studies performed on polyoxovanadates have shown antiferromagnetic coupling between  $\text{V}^{\text{IV}}$  ions.<sup>5c</sup> To date, ferrimagnetic vanadium compounds are limited to fully reduced vanadium (III) and it is rare to be reported in mixed valence  $\text{V}^{\text{IV/V}}$  oxometalates.<sup>5d</sup> We

herein reported a new vanadium sulfate formulated as  $[\text{H}_2\text{N}(\text{CH}_3)_2]_{19/3}(\text{en})[\text{V}_5\text{O}_5(\mu_3\text{-O})_4(\text{SO}_4)_4(\text{SO}_4)_{2/3}[\text{HN}(\text{CH}_3)_2]_{2/3}]$  **1**, containing a novel umbrella-like building unit  $[\text{V}_5\text{O}_5(\mu_3\text{-O})_4(\text{SO}_4)_4(\text{en})]^{5-}$ . To the best of our knowledge, **1** represents the first known discrete umbrella-like V-O-S cluster, which is different from the reported 'cover' stabilized by arsenates or phosphates.<sup>14-16</sup> While the magnetic studies of **1** indicate the title compound exhibits the presence of significant ZFS and interesting ferrimagnetic interactions between  $\text{V}^{4+}$  ions in mixed-valent unit  $\{\text{V}^{\text{V}}(\mu_3\text{-O})_4\text{V}^{\text{IV}}_4\text{O}_5(\text{SO}_4)_4\}$ . While the optical study of **1** indicates the title compound exhibits strong two photon absorption. The nonlinear absorption coefficient and 2PA cross section are calculated as 0.005278 cm/GW and 622 GM.

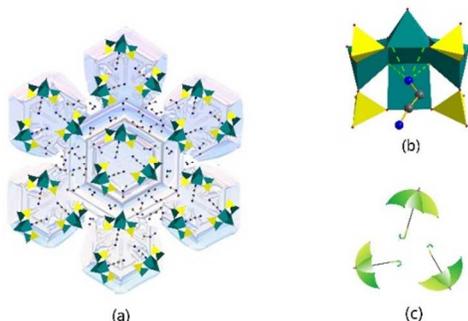
The dark green block crystal of **1** was prepared by the solvothermal reaction of  $\text{VOSO}_4$ , en, DMF and  $\text{H}_2\text{SO}_4$  at 180°C for 5 days, and cooling to room temperature. In the structure of **1**, ethylenediamine and dimethylamine function as template, and protonated dimethylamine cations are also used to balance the charges. The unexpected free dimethylamine cations are the byproduct of the DMF decomposition,<sup>17, 18</sup> which plays an indispensable role in producing **1** together with ethylenediamine.

The single-crystal X-ray crystallographic analysis shows that compound **1** crystallizes in the hexagonal space group  $P6_3/m$ , and consisted of interesting umbrella-like V-O-S cluster,  $[\text{V}_5\text{O}_9(\text{SO}_4)_4(\text{en})]^{5-}$ , protonated dimethylamine cations and sulfate group. As shown in Fig. 1a, umbrella-like nanosized anion of **1** composed of a convex mixed-valent  $\{\text{V}^{\text{V}}\text{O}(\mu_3\text{-O})_4\text{V}^{\text{IV}}_4\text{O}_4(\text{SO}_4)_4\}$  unit, of which the topmost  $\text{V}^{\text{V}}(\text{V}2)$  polyhedron sharing common edges with its four surrounding  $\{\text{V}^{\text{IV}}\text{O}_5\}$  (V1, V3, V3, V4) polyhedra. There are two types of five-coordinated vanadium atoms in the polyanion of **1** (square-pyramidal geometry, as shown in Fig. 1b). Central vanadium atom (V2) is coordinated by four  $\mu_3\text{-O}$  (O3, O4) and one terminal oxygen atoms to form a very regular square-pyramidal. Other four V atoms are bonded by five O atoms to make four distorted  $\text{VO}_5$  square-pyramids, which are connected by sharing corners to generate a V4 ring. While central  $\text{VO}_5$  pyramid joins in V4 ring by sharing edges to form a  $\text{V}_5\text{O}_{17}$  unit. Further, four  $\text{SO}_4$  tetrahedra are attached to  $\text{V}_5\text{O}_{17}$  unit by sharing corners, an umbrella cover of mixed-valence  $\{\text{V}^{\text{V}}\text{O}(\mu_3\text{-O})_4\text{V}^{\text{IV}}_4\text{O}_4(\text{SO}_4)_4\}$  is generated. Interestingly, a free en molecule acts as an umbrella handle just perpendicular to the horizontal

plane composed by V1, V3, V3 and V4. N atom (N2A) of en molecule is involved very strong hydrogen bonding interactions with  $\mu_3$ -O atoms (O3 and O4) to form umbrella cover  $\{V^V O(\mu_3-O)_4 V^{IV} O_4(SO_4)_4\}$ . The N...O distances are between 2.92(2) and 2.96(2) Å (Fig. 2b). The remaining dimethylamine cations and sulfate group surround the umbrella. Bond valence sum (BVS) analyses indicate the valence state of topmost V atom is +5, while other vanadium atoms are +4.<sup>14c, 19</sup> The absorption between 500 and 900 nm in the UV-vis spectra of **1** (Fig. S2) is attributed to d-d transition. So the sulfates-stabilized pentanuclear core carries an overall charge of -5, which is compensated by protonated dimethylamine cations in **1**. In central  $V^V O_5$  quadrangular, the O-V-O angles range from 83.6(2) to 141.73(17)°, whereas in surrounding  $V^{IV} O_5$  quadrangulars, the O-V-O angles range from 178.2(2) to 150.42(16)°. The  $V^{IV}$ -O bond distances vary from 1.581(5) to 2.007(4) Å which is comparable with the reported  $V^{IV}$  compounds,<sup>20</sup> while  $V^V$ -O bond distances are expectedly shorter and between 1.590(6) and 1.887(4) Å.



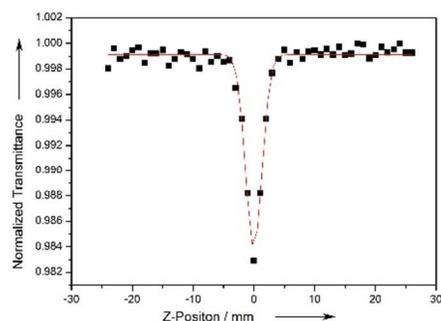
**Fig. 1** (a) The structure of umbrella cover  $\{V_5O_9(SO_4)_4\}$  unit in **1**; (b) Polyhedral structure of mixed-valent cover; (c) Viewing of umbrella unit in **1**. The colour codes are as follows: V, green; O, red; S, yellow; N, blue; C, grey.



**Fig. 2** (a) Polyhedral view of the 3D structure formed by the  $\{V_5O_9(SO_4)_4\}$  clusters and amines along [001] direction in **1**; (b) Hydrogen bonding interactions between en molecule and umbrella cover. (c) Umbrella. Green dotted line: hydrogen bonds.

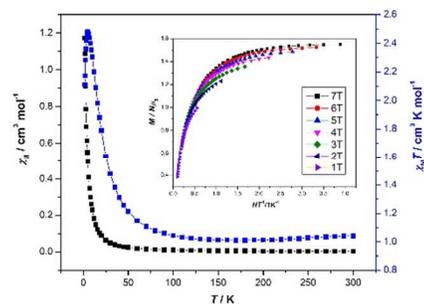
In the structure of **1**, it is noticeable that the umbrella like anionic of  $[V_5O_9(SO_4)_4]^{5-}$  units are packing regularly. As show in Fig. 2, every three umbrella units form a trangle type of  $[V_5O_9(SO_4)_4]_3$ , which is surrounded by six trangle units. The dimethylamine cations flood the interspace through the hydrogen bonding interactions to generate 3D supermolecule with the oxygen atoms belonging to the sulfate group and umbrella  $[V_5O_9(SO_4)_4]^{5-}$  anion. The trangle type of  $[V_5O_9(SO_4)_4]_3$  units

keep a staggered-array arrangement with the dissociative dimethylamine residing in clearance to make a snowflake clusters via hydrogen bonds as shown in Fig. 2a.  $[N-H...O]$  hydrogen bonds distances range from 2.928(6) Å ( $N1-H1A...O17$ ) to 3.250(7) Å ( $N1-H1B...O3$ ), whereas the  $[C-H...O]$  bond distances are from 3.166(10) Å ( $C2-H2A...O8$ ) to 3.37(4) Å ( $C4-H4C...O2$ ). Such layers are heaped up one over another along *c*-axis to form an assembly work (Fig. S5, ESI†). The selected values of the bond distances and angles of **1** are listed in Table. S2 (ESI†) and the various hydrogen bonds are listed in Table. S3 (ESI†).



**Fig. 3** The open aperture z-scan data for compound **1** in water at  $3.5 \times 10^{-4}$  mol L<sup>-1</sup>. The unfilled circles are the experimental data and the solid curve represents the theoretical data.

The third-order NLO responses, 2PA cross sections ( $\delta$ ) of **1** is obtained by open-aperture Z-scan technique. Fig. 3 shows that the nonlinear absorption coefficient and 2PA cross section are calculated as 0.005278 cm/GW and 622 GM (1 GM =  $10^{-50}$  cm<sup>4</sup>s/photon) for **1** (ESI†). To our knowledge, above third-order NLO property has not been found in other reported vanadates. The third-order NLO responses indicate that the umbrella like clusters compounds **1** has potential application in nonlinear optical field.



**Fig. 4** Temperature dependence of  $\chi_m T$  for **1** at 2kOe. (Inset: reduced magnetization date for **1** at low temperature.)

The variable-temperature magnetic susceptibility of compound **1** was measured at 2000 Oe in the temperature range of 2-300 K. It can be considered to contain squares of  $S = 1/2$  spin centres with a central diamagnetic  $V^V$ . The effective magnetic moment ( $\mu_B$ ) calculated at 300 K is  $2.89 \mu_B$  by the equation

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_m T} \quad (1)$$

which is smaller than expected value  $3.46 \mu_B$  for total uncoupled 4  $V^{IV}$  ( $S=1/2$ ) ions. As plotted in Fig. 4, the  $\chi_m T$  values of

compound **1** slowly decreases to a minimum value of 1.01 cm<sup>3</sup> K mol<sup>-1</sup> upon cooling to 169 K and increases to the maximum value of 2.48 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K, then decreases again sharply. The shapes of curve shows a ferrimagnetic property, indicating that antiferromagnetic coupling between vanadium ions dominates the magnetic properties of **1** but the ground state spin is not zero. Therefore, the very low  $\chi_m T$  value at room temperature indicates that the antiferromagnetic coupling exists in higher temperature even than 300 K and the experimental value of  $\chi_m T$  may approach the Curie constant. The low-temperature (<5 K) decrease may be assigned to the presence of ZFS (zero field splitting) in the ground state and the antiferromagnetic interaction between the clusters. To further verify the magnitude of the spin ground state for complex, magnetization data were collected in the ranges 1–7 Tesla (see the inset in Fig. 4). The antiferromagnetic coupling between metal ions in **1** is further confirmed by the unsaturated magnetization value of 1.55  $N\mu_B$  at 7 T as shown in Fig. S6 (ESI<sup>†</sup>). Since no signal was observed in the plot of out-of-phase AC susceptibilities (Fig. S7, ESI<sup>†</sup>), compound **1** did not exhibit single-molecule magnet (SMM) behaviour.<sup>21</sup> However, the presence of significant ZFS and interesting ferrimagnetic interactions in mixed valence V<sup>IV/V</sup> oxometalates has not been discovered before.

## Conclusions

In conclusion, we have described a novel amine-templated vanadium sulfate constructed from {V<sub>5</sub>O<sub>9</sub>(SO<sub>4</sub>)<sub>4</sub>} cluster and organic amines at the condition of solvothermal synthesis. The cluster contains the umbrella-like unit [V<sub>5</sub>O<sub>9</sub>(SO<sub>4</sub>)<sub>4</sub>(en)]<sup>5-</sup> and stabilize the whole complex through extensive H-bonds. It is firstly synthesized {V<sub>5</sub>O<sub>9</sub>} unit constructed by sulfates. Magnetic study reveals the ferrimagnetic interactions in complex **1**. And compound **1** shows very good NLO activities which are very rare in compounds containing POM anions. The present work provides a contribution to further systematic and multifunctional exploration of the V-O-S system.

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## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

<sup>‡</sup> Crystal Data for [H<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>6.34</sub>(en)[V<sub>5</sub>O<sub>9</sub>(μ<sub>3</sub>-O)<sub>4</sub>(SO<sub>4</sub>)<sub>4</sub>](SO<sub>4</sub>)<sub>0.67</sub>[HN(CH<sub>3</sub>)<sub>2</sub>]<sub>0.66</sub> **1**: Mr =1229.07, Hexagonal, space group P6<sub>3</sub>/m, a = 20.4115(17) Å, b = 20.4115(17) Å, c = 25.444(2) Å, α = β = 90 ° γ = 120 °, V = 9180.3(17) Å<sup>3</sup>, Z = 6, ρ<sub>calcd</sub> = 1.347 Mg m<sup>-3</sup>, final R1 = 0.0703 (wR2 = 0.1862) for independent reflections 5460 [I > 2(θ)]. CCDC-1043088

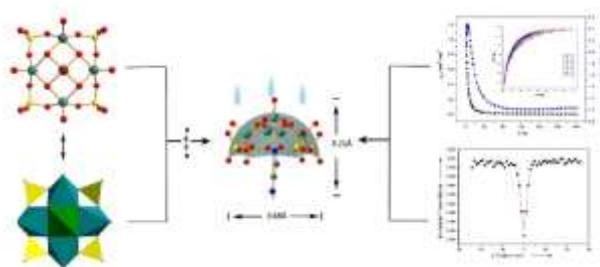
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## Table of Contents

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A new umbrella-like vanadium sulfate shows significant ZFS and strong two photon absorption.