

Magnetic behaviour of hybrid organo/inorganic compounds with tetranuclear copper (II) units

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Abstract

The structure and magnetic properties of two hybrid VPO compounds $[(\text{Cu}_2\text{bipy}_2)_2\text{V}_4\text{O}_{11}(\text{PO}_4)_2] \cdot 5\text{H}_2\text{O}$ **1** and $[\text{Cu}_2\text{phen}_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{V}_2\text{O}_5)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ **2** are reported. The magnetic behaviour of compound **1** can be described with the DFT calculated magnetic exchange constants, $J_1 = +4.93 \text{ cm}^{-1}$, $J_2 = -0.63 \text{ cm}^{-1}$, $J_3 = -24.2 \text{ cm}^{-1}$. Compound **2** presents intradimeric antiferromagnetism with $J_1 = -30 \text{ cm}^{-1}$, and interdimeric antiferromagnetism with $J_2 = -8.5 \text{ cm}^{-1}$.

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1. Introduction

The oxovanadium phosphate compounds present a great diversity of structures, which is in part related to the oxidation state of vanadium, and to the way in which the different polyhedra of vanadium and phosphorus are condensed, sharing corners, edges and/or faces [1]. The source of phosphorus can be simple tetrahedral phosphate anions or organic derivatised moieties of the tetrahedral phosphate subunits, in the form of diphosphonates, among others [2]. The latter present variations in the tether length $(-\text{CH}_2-)_n$ which can be used to modify the framework. The organic parts can also be introduced as ligands of complex cationic species containing a secondary paramagnetic transition metal ion, for example, copper (II). When these paramagnetic centres are bridged by phosphate groups, antiferromagnetic exchange interactions are observed between these metal centres [3]. In the present work, the structure and magnetic properties of two hybrid compounds $[(\text{Cu}_2\text{bipy}_2)_2\text{V}_4\text{O}_{11}(\text{PO}_4)_2] \cdot 5\text{H}_2\text{O}$ **1** and $[\text{Cu}_2\text{phen}_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{V}_2\text{O}_5)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ **2**

(phen = 1,10-phenantroline; bipy = 2,2'-bipyridine) are reported.

2. Computational details

All the calculations for compound **1** were performed using the crystal structure of the molecule [4]. Single-point calculations were performed with the Gaussian03 code [5] using the quadratic convergence approach with the hybrid B3LYP functional [6] and a guess function generated with the Jaguar 5.5 code [7]. We have employed a triple- ζ all electron Gaussian basis set for all atoms [8]. A detailed description of the procedure used to obtain the exchange coupling constants can be found in previous work of Ruiz et al. [9,10]. We have considered a general spin Hamiltonian that includes three first-neighbour coupling constants (J_1 , J_2 , J_3), where \hat{S}_i are the spin operators of each paramagnetic Cu^{II} centre (Fig. 1a). Therefore, the studied system presents $2J_1$, $2J_2$ and $2J_3$.

$$\hat{H} = -(J_1[\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4] + J_2[\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4] + J_3[\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3]).$$

In order to obtain the three different J values, four calculations are needed: a high spin solution ($S = 2$), and

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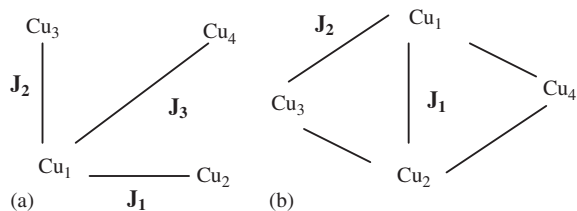


Fig. 1. Schematic representation of magnetic interactions for compound **1** (a) and compound **2** (b).

three solutions with $S = 0$; the first one with Cu₁ and Cu₂ showing spin down, the second solution with Cu₂ and Cu₄ showing spin down and the third solution with Cu₂ and Cu₃ showing spin down.

3. Results and discussion

The structure of **1** consists of phospho-vanadate chain-like fragments $\{V_4P_2O_{19}\}$ based on VO₄ and PO₄ tetrahedra by sharing common μ_2 -oxo bridges. The $\{V_4P_2O_{19}\}$ chains are coordinated to the Cu-bipy species via oxo-bridges. Edge sharing of the $\{CuN_2O_3\}$ pyramids involving μ_3 -oxo links results in dinuclear copper species with Cu–Cu distances as short as 3.19 Å (J_1). In turn, the copper dimers condense by μ_3 -oxo links of the phosphate groups to form Cu₄-units in a rectangular geometry with longer Cu–Cu distances of 4.10 Å (J_2). The diagonal of the rectangle with Cu–Cu distance of 5.01 Å corresponds to two phosphate groups bridging two metal centres (J_3), as can be seen in Fig. 1a.

The structure of **2** [11] consists of vanadium tetrahedra and the diphosphonate groups sharing common corners to form infinite zig-zag chains $[(V_2O_5 O_3PCH_2PO_3)]$. Edge-sharing of CuN₂O₃ tetragonal pyramids involving μ_3 -oxo links results in dinuclear copper species with Cu–Cu distances as short as 3.25 Å (J_1). In turn, two copper atoms are linked to the dimer through two phosphonate groups to form tetranuclear copper units with longer Cu–Cu distances of 5.13 Å (J_2), as shown in Fig. 1b. The infinite chains are connected by the tetrameric units to form layers.

Both compounds show Curie–Weiss behaviour in the high-temperature region ($T > 100$ K). Magnetic data gave a magnetic moment per Cu of $1.74\mu_B$ ($\theta \sim -9$ K) and $2.17\mu_B$ ($\theta \sim -52.6$ K) for compounds **1** and **2**, respectively. For compound **1**, the magnetic behaviour below 100 K is complex, with antiferromagnetic interactions evidenced by the lowering of the χT product with the decreasing temperature (Fig. 2).

The existing models to fit the experimental magnetic susceptibility data did not reproduce the observed experimental behaviour. DFT calculations for compound **1** gave $J_1 = +4.93$ cm⁻¹, $J_2 = -0.63$ cm⁻¹ and $J_3 = -24.2$ cm⁻¹.

For compound **2**, the χ^{-1} vs. T curve shows a minimum at about 64 K indicative of antiferromagnetic interactions and a maximum at about 35 K. The fit of the magnetic

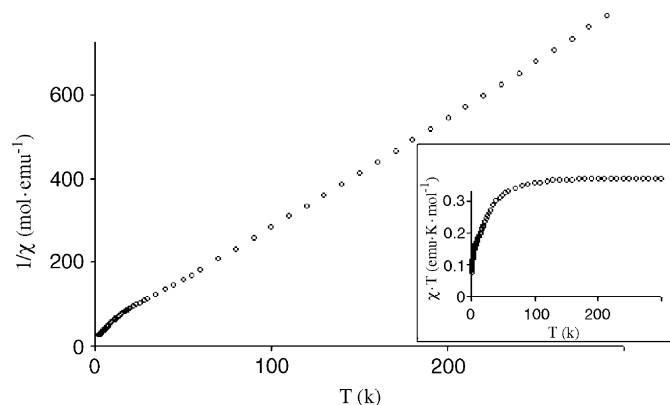


Fig. 2. The χ^{-1} vs. T curve (inset: χT vs. T) for **1**.

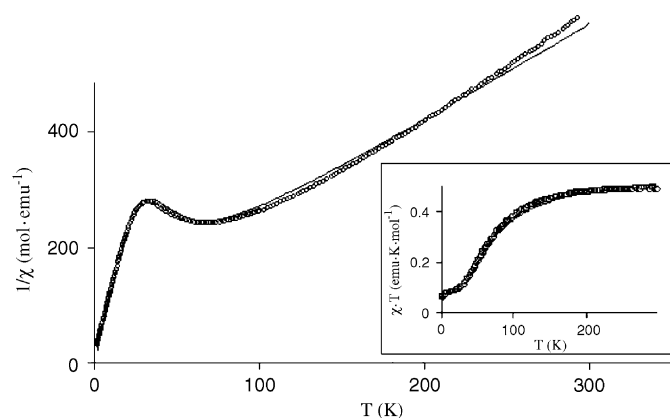


Fig. 3. The χ^{-1} vs. T curve (inset: χT vs. T) for **2**.

experimental data with the tetranuclear model previously described by Koval et al. [12] leads to $J_1 = -30$ cm⁻¹, $J_2 = -8.5$ cm⁻¹ and $g = 2.0$ (Fig. 3).

This result clearly indicates that, as expected, the prevailing antiferromagnetic interactions occur between the two central copper atoms, while weakest antiferromagnetic interactions are observed with the bis phosphato-bridged copper. A paramagnetic impurity was introduced to fit the upturn of χ vs. T at low temperature. 7.5% of impurity gives the most satisfying fit. This result is in good agreement with the extrapolated value ($\chi T \approx 0.08$ emu K mol⁻¹) of the χT curve at low temperature.

4. Concluding remarks

The use of an organic derivatised phosphate subunit to generate compound **2** produces a structure with a tetrameric copper unit with a connectivity different from that observed for the tetrameric copper phosphate bridged compound **1**.

The magnetic behaviour of **1** can be described with a model which presents three magnetic coupling constants, while **2** presents two different magnetic exchange pathways.

Compound **2** presents an antiferromagnetic intradimer exchange interaction, with a J_1 value of -30 cm⁻¹ and an interdimer J_2 value of -8.5 cm⁻¹. However, compound **1**

has an intradimer interaction which is ferromagnetic ($J_1 = +4.93 \text{ cm}^{-1}$). This can be attributed to the existence of three magnetic exchange pathways between $\text{Cu}_1\text{-Cu}_2$: a phosphate with a syn/syn-like bonding mode, a phosphate bridging through only one oxygen atom, and a oxovanadium also bridging through only one oxygen atom. The two interdimer magnetic exchange interactions are antiferromagnetic with $J_2 = -0.63 \text{ cm}^{-1}$ and $J_3 = -24.2 \text{ cm}^{-1}$, even though the distance between $\text{Cu}_1\text{-Cu}_3$ (J_2) is shorter than $\text{Cu}_1\text{-Cu}_4$ (J_3), $|J_2| < |J_3|$. This can be rationalised with the fact that the phosphate bridge responsible of the magnetic exchange pathway J_2 shows an unusual syn/anti-like bonding mode.

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