Magnetic properties of hybrid organo-inorganic copper(II) oxovanadate(V) phosphate and phosphonate bridged systems

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Abstract

The hybrid organo-inorganic compounds $[Cu_4(bipy)_4V_4O_{11}(PO_4)_2]nH_2O$ ($n \sim 5$) (**1**), $[Cu_2(phen)_2(PO_4)(H_2PO_4)_2(VO_2) \cdot 2H_2O]$ (**2**) and $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]H_2O$ (**3**) which present different bridging forms of the phosphate/phosphonate group, show different bulk magnetic properties. We herein analyze the magnetic behaviour of these compounds in terms of their structural parameters. We also report a theoretical study for compound (**1**) assuming four different magnetic exchange pathways between the copper centres present in the tetranuclear unit. For compound (**1**) the following J values were obtained $J_1 = +3.29$; $J_2 = -0.63$; $J_3 = -2.23$; $J_4 = -46.14\ cm^{-1}$. Compound (**2**) presents a Curie–Weiss behaviour in the whole range of temperature (3–300 K), and compound (**3**) shows a maximum for the magnetic susceptibility at 64 K, typical for antiferromagnetic interactions. These data where fitted using a model previously reported in the literature, assuming two different magnetic exchange pathways between the four copper(II) centres, with $J_1 = -30.0$ and $J_2 = -8.5\ cm^{-1}$.

Keywords: Magnetic properties; DFT calculations; Copper(II); Organo-inorganic systems; Phosphate; Phosphonate

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 derivatized moieties of the tetrahedral phosphate subunits, in the form of diphosphonates, among others [2–7]. The presence of paramagnetic coordination complexes as part of these VPO structures offers an interesting way to obtain polynuclear magnetic interacting centres isolated from each other [8–10].

The VPO structures offer different types of bridges which can produce the magnetic superexchange phenomena between paramagnetic centres. For example, phosphate and oxo-vanadium can bind two or more metal centres in a 1,1 or 1,3 bridging mode [11]. The existence of more than one of these bridges between interacting paramagnetic centres can produce a different type of magnetic phenomena, as observed when a single bridge is present. On the other hand, small structural variations can affect the magnitude of the magnetic interaction.

Theoretical studies, from a quantum mechanical point of view, are necessary since for most compounds with polynuclear magnetic interacting centres and with various different exchange pathways, the existing analytical models are too limited to explain the variety of the reported magnetic behaviour. The aim of the theoretical study reported in this paper was to obtain the different exchange pathways

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present in $[Cu_4(bipy)_4V_4O_{11}(PO_4)_2]nH_2O$ ($n \sim 5$) (**1**), for which the used analytical models did not give a good fit of the experimental magnetic data. The theoretical methods used in the present work are based on density functional theory [12–14].

In the present work, we will discuss the magnetic behaviour of three hybrid organo-inorganic compounds which present different bridging forms of the phosphate/phosphonate/oxovanadium groups, showing different bulk magnetic properties. Compounds (**2**) and (**3**) correspond to $[Cu_2(phen)_2(PO_4)(H_2PO_4)_2(VO_2) \cdot 2H_2O]$ and $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]H_2O$, respectively.

2. Experimental

The syntheses of compounds (**1**), (**2**) and (**3**) were previously reported [9,15,10].

3. Computational details

All the calculations for compound (**1**) were performed using the crystal structure of the molecule [10]. Single point calculations were performed with the GAUSSIAN03 code [16] using the quadratic convergence approach (convergence criteria 0.02 cm^{-1}) with the hybrid B3LYP functional [17] and a guess function generated with the JAGUAR 5.5 code [18]. We have employed a triple-ζ all electron Gaussian basis set for all atoms [19]. Since the crystal structure corresponds to an extended system which contains tetranuclear copper cores connected by phosphovanadates moieties, a tetranuclear unit was used for the calculations, see Fig. 1. This tetranuclear unit was obtained using four pentacoordinated copper(II) centres, each metal centre bonded to a bipyridine and to three oxygen atoms from phosphate and oxovanadium groups. In the case of an oxo-vanadium group bridging in a 1,1 form, hydrogen atoms were added to the two oxygen atoms which were originally bonded to a phosphate group. In the case of a phosphovanadate group bridging in a 1,3 form, one hydrogen atom was added to a oxygen atom originally bonded to a phosphate group. The hydrogen atoms added to the structure were optimized with MM+ molecular mechanics force field using the TITAN package [20]. The fragment has four different Cu–Cu distances (3.19; 4.10; 5.38 and 5.01 Å), and therefore four different exchange coupling constants (J_1, J_2, J_3 and J_4) are expected. Therefore, the studied system can be described with the phenomenological Hamiltonian

$$\hat{H} = -J_1[\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4] - J_2[\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4] - J_3[\hat{S}_2\hat{S}_3] - J_4[\hat{S}_1\hat{S}_4]$$

In order to obtain the four different J values, five calculations are needed: a high spin solution ($S = 2$), three solutions with $S = 0$, and one solution with $S = 1$. The calculated temperature dependence of the magnetic susceptibility was obtained with the MAGPACK code [21] using $g = 2.00$.

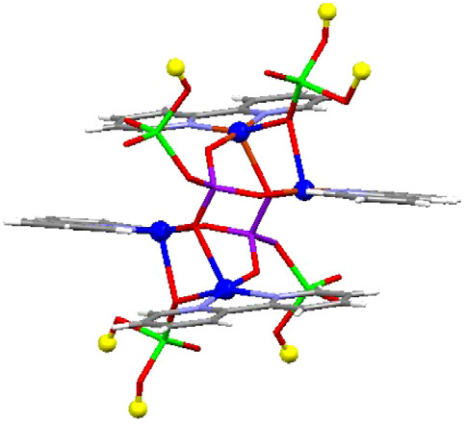

Fig. 1. Tetranuclear copper(II) model of compound (**1**) used for the calculations. The four central deep blue spheres correspond to copper atoms. The six peripherical yellow spheres correspond to added hydrogen atoms. Phosphorous, purple; vanadium, green; oxygen, red; nitrogen, light blue; carbon, grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Results and discussion

4.1. Structural description

The three reported hybrid organo-inorganic copper(II) compounds, based on the vanadium(V)/phosphorus/oxygen substructure (VPO) have different extended structures. In compound (**1**), the existing tetranuclear copper(II) species are connected by the $V_4P_2O_{19}$ chain-like fragments to form infinite chains running parallel [1 0 0] [9]. In compound (**2**), the vanadium octahedral and phosphorous tetrahedra share common corners to form infinite chains based on the VP_2O_{12}. An extra phosphorous tetrahedron acts as a single bridge between two copper(II) centres, giving rise to the existence of $Cu_2(phen)_2(PO_4)^+$ species. These cationic species are interconnected by μ_2-oxo bridges of phosphorous and vanadium forming infinite chains, which propagate along the a direction [15]. In compound (**3**), the vanadium tetrahedra and diphosphonate groups share common corners to give infinite zig-zag chains, $[V_2O_5O_3PCH_2PO_3]$ running along the [1 0 0] direction. The infinite chains are connected by the tetrameric units to form layers [10].

In all the reported copper(II) compounds, the metal centres present a square pyramidal geometry. However, different type of bridges between the copper(II) centres are observed in each case. The copper(II) tetranuclear unit present in compound (**1**) is the most complex, in relation to the bridges that exist between the metal centres. The two nearest copper(II) centres (d_{Cu-Cu} 3.19 Å) are linked by three bridges: a 1,1-oxo-vanadium group, a 1,1-phosphate group, and a 1,3-phosphate group. These dinuclear species are interconnected by two 1,3-phosphate group, thus giving rise to a rhombohedral tetranuclear unit (d_{Cu-Cu} 4.10 Å). The internal diagonals of this rhombohedral struc-

ture correspond to two 1,3-phosphate bridges each, with distances of 5.03 and 5.38 Å (Fig. 2).

In compound (**2**), the dinuclear copper(II) unit is formed with the presence of one 1,3-phosphate bridge ($d_{Cu–Cu}$ 3.46 Å) (Fig. 3). In compound (**3**), the tetranuclear species is formed by the central bis 1,1-oxo bridged dimer ($d_{Cu–Cu}$ 3.25 Å) and the two external copper(II) atoms with 1,3-bis phosphate bridges ($d_{Cu–Cu}$ 5.13 Å) (Fig. 4).

5. Magnetic behaviour

Only compound (**2**) presents Curie–Weiss behaviour in the whole temperature range (3–300 K), while all three compound show this behaviour for the high temperature region (>100 K). The magnetic behaviour of compound (**3**) has been analyzed elsewhere; the obtained J values being $J_{intra} = -30\ cm^{-1}$ and $J_{inter} = -8.5\ cm^{-1}$ [10].

For compound (**1**) the magnetic behaviour below 60 K is complex, and the analytical expression used did not give a good fit of the experimental magnetic data. A theoretical model with four exchange pathways was used in order to describe the magnetic behaviour of the rhombohedral tetranuclear species. The experimental magnetic data for compound (**1**) (Fig. 5a) is well described with the following calculated J parameters: $J_1 = +3.29$, $J_2 = -0.63$, $J_3 = -2.23$ and $J_4 = -46.14\ cm^{-1}$ (Fig. 5b). The overall antiferromagnetic behaviour at low temperatures is due mainly to a inter-dimer exchange interaction, while the intra-dimer exchange interaction due to the existence of the three bridges results slightly ferromagnetic. Therefore, the 1,1-oxo-vanadium bridge present in the dinuclear unit may be acting counter complementary in relation to the two phosphate bridges. The Cu_2–Cu_3 diagonal ($d_{Cu–Cu}$ 5.01 Å) presents the phosphate ligands with the most symmetrical copper–oxygen distances (Cu_2O: 1.92; Cu_3O: 1.95; Cu_2O': 1.95 and Cu_3O': 1.92 Å). This fact may influence the magnitude of the J value ($J_4 = -46.14\ cm^{-1}$), in comparison to the much smaller obtained J values ($J_2 = -0.63$, $J_3 = -2.23\ cm^{-1}$). For this latter exchange pathways greater differences in the Cu–O distances are observed, ranging from 1.89 Å (shortest) to 2.29 Å (longest). It is known that geometrical factors greatly influence the magnitude of the magnetic exchange coupling between paramagnetic metal centres.

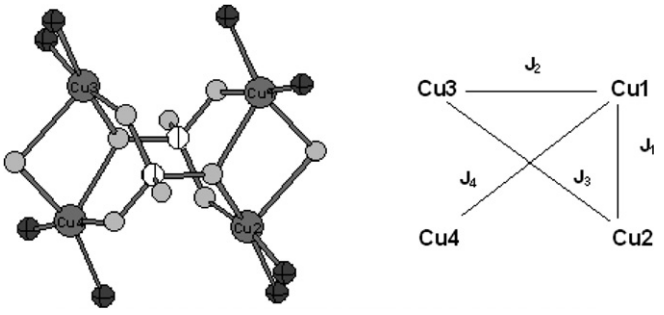

Fig. 2. Tetranuclear copper(II) core of compound (**1**) with all the oxygen atoms involved in the magnetic exchange phenomenon. Dark gray, nitrogen; light gray, oxygen; dashed, phosphorus. Schematic diagram of the four different magnetic exchange pathways.

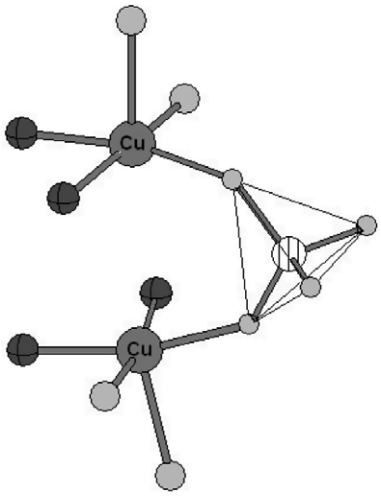

Fig. 3. Binuclear copper(II) core of compound (**2**) showing the 1,3-phosphato bridge. Dark gray, nitrogen; light gray, oxygen; dashed, phosphorus.

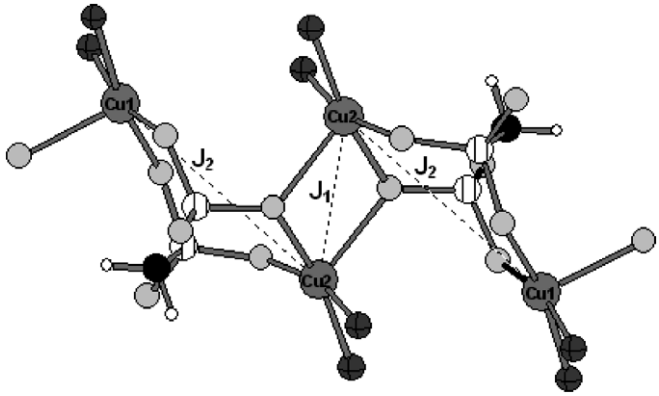

Fig. 4. Tetranuclear copper(II) core of compound (**3**) showing all the phosphate bridges involved in the magnetic exchange phenomenon. Dark gray, nitrogen; light gray, oxygen; dashed, phosphorus. J_1, J_2: magnetic exchange constants.

When a simpler model was used to describe the tetranuclear unit of compound (**1**) in which the two diagonals are taken as equal, assuming a perfect rectangular geometry for the species, the following j values were obtained: $J_1 = +4.93$, $J_2 = -0.63$, $J_3 = -24.2\ cm^{-1}$ [11]. Even though the same trend is obtained in the sign of the j values, these do not reproduce the low temperature behaviour of compound (**1**) as can be seen in Fig. 5c. It is interesting to point out that the J_3 value of the rectangular model corresponds to the mean value of the J_3 and J_4 values of the rhombohedral model.

The fact that compound (**2**) does not show antiferromagnetism in the whole temperature range, may be due to the fact that the bridged copper(II) centres of the

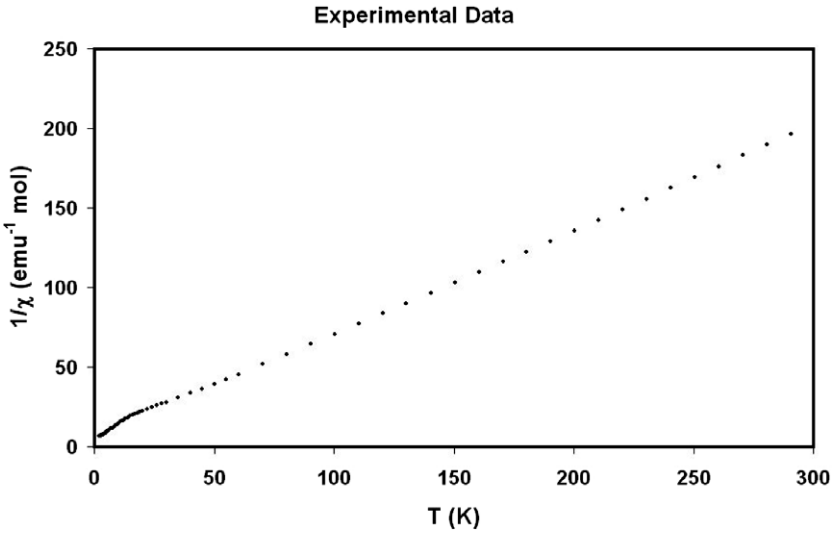

Fig. 5a. Experimental magnetic data of compound (**1**). $1/\chi$ vs. T.

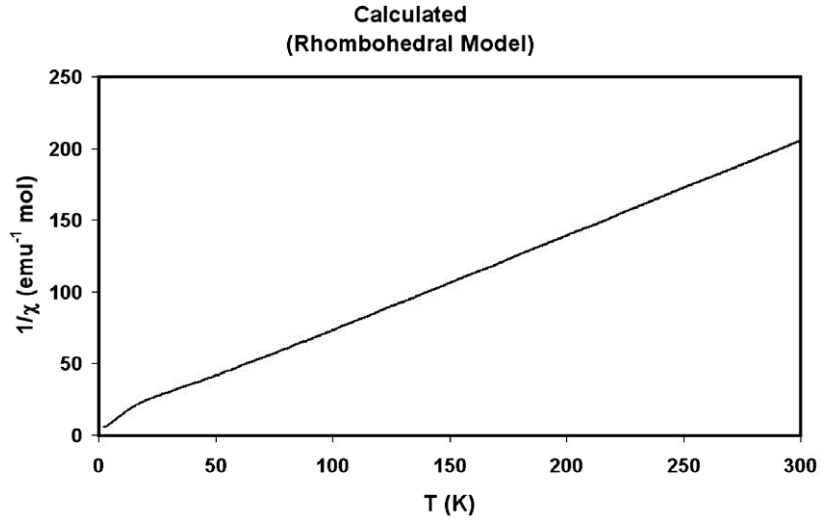

Fig. 5b. Calculated magnetic data of compound (**1**) using the rhombohedral model. $1/\chi$ vs. T.

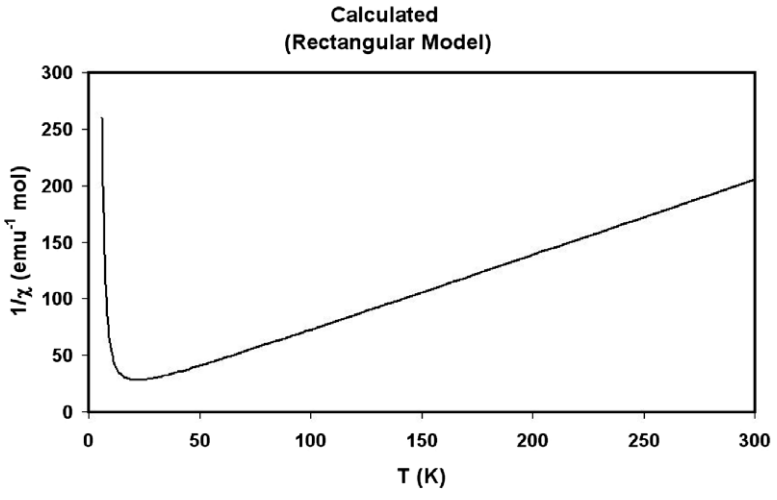

Fig. 5c. Calculated magnetic data of compound (**1**) using the rectangular model. $1/\chi$ vs. T.

$Cu_2(phen)_2(PO_4)^+$ fragment are located on different planes, and present only one chelate phosphate bridge. Thus the only possible pathway for the magnetic exchange interaction is not adequately located to be effective.

Compound (**3**) presents a typical antiferromagnetic behaviour with a maximum at 64 K. The two 1,1-phosphate bridges link the two copper(II) centres at a short distance of 3.25 Å, and represent adequate magnetic exchange pathways ($J_1 = -30.0\ cm^{-1}$). The 1,3 mode of bridging of the two phosphate groups of the phosphonate ligands assure an inter-dimer antiferromagnetic exchange interaction with $J_2 = -8.5\ cm^{-1}$.

6. Conclusions

The different modes of bridging of the phosphate and oxo-vanadium ligands give rise to completely different magnetic behaviour of the three hybrid organo-inorganic copper(II) compounds.

Phosphates bridges permit the existence of antiferromagnetic exchange coupling between the copper(II) centres. The exchange interaction being stronger when the copper(II) oxygen distances involved are similar in length giving a more symmetrical structure.

Acknowledgements

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References

[1] S. Boudin, A. Guesdon, A. Leclaire, M-M. Borel, Int. J. Inorg. Mater. 2 (2000) 561, and references therein.
[2] R.C. Finn, J. Zubieta, J. Chem. Soc., Dalton Trans. (2000) 1821.
[3] R.C. Finn, J. Zubieta, Inorg. Chim. Acta 332 (2002) 191.
[4] R.C. Finn, J. Zubieta, Inorg. Chim. Acta 335 (2002) 131.
[5] G. Yucesan, V. Golub, Ch. J. O'Connor, J. Zubieta, Solid State Sci. 7 (2005) 133.
[6] R.C. Finn, R. Lam, J.E. Greedan, J. Zubieta, Inorg. Chem. 40 (2001) 3745.
[7] R.B. Fu, X.T. Wu, S.M. Hu, W.X. Du, J.J. Zhang, Z.Y. Fu, Inorg. Chem. Com. 6 (2003) 694.
[8] Y. Moreno, A. Vega, S. Ushak, R. Baggio, O. Pena, E. Le Fur, J.Y. Pivan, E. Spodine, J. Mater. Chem. 13 (2003) 2381.
[9] S. Ushak, E. Spodine, D. Venegas-Yazigi, E. Le Fur, J.Y. Pivan, O. Pena, R. Cardoso-Gil, R. Kniep, J. Mater. Chem. 15 (2005) 4529.
[10] S. Ushak, E. Spodine, E. Le Fur, D. Venegas-Yazigi, J.Y. Pivan, W. Schnelle, R. Cardoso-Gil, R. Kniep, Inorg. Chem. 45 (2006) 5393.
[11] E. Spodine, D. Venegas-Yazigi, S. Ushak, E. Le Fur, J.Y. Pivan, Physica B 384 (2006) 120.
[12] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, J. Am. Chem. Soc. 119 (1997) 1297.
[13] E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, in: J.S. Miller, M. Drillon (Eds.), Electronic Structure and Magnetic Behavior in Polynuclear Transition-metal Compounds, Weinheim, 2001.
[14] E. Ruiz, Struct. Bond. 113 (2004) 71.
[15] S. Ushak, Doctoral Thesis, University of Chile, 2006.
[16] M.J. Frisch et al., GAUSSIAN 03 (Revision B.4), Gaussian, Inc., Pittsburgh, PA, 2003.
[17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[18] Jaguar 5.5, Schrödinger, Inc., Portland, 2003.
[19] A. Schaefer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.
[20] Titan, V.1.08, Wavefunction Inc. and Schrodinger Inc. Von Karman Av., Suite 370, Irvine, CA, USA.
[21] MAGPACK Software: J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, B.S. Tsukerblat, J. Comp. Chem. 22 (2001) 985.