Magnetic properties of phosphate-bridged copper(II) organic–inorganic hybrid compounds

Yanko Moreno,a Andrés Vega,ᵃ Svetlana Ushak,b Ricardo Baggio,c Octavio Peña,d Eric Le Fur,c Jean-Yves Pivanc and Evgenia Spodine*a,b

a Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales (CIMAT), Universidad de Chile, Santiago, Chile
b Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile
c Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
d Laboratoire de Chimie du Solide et Inorganique Moléculaire UMR-CNRS 6511, Institut de Chimie de Rennes, Université de Rennes 1, 35042 Rennes CEDEX, France

Received 16th December 2002, Accepted 10th July 2003
First published as an Advance Article on the web 29th July 2003

Hydrothermal synthesis has allowed us to isolate and characterize three new inorganic–organic hybrid materials, the compounds [Cu2(phen)2(H2O)2(H2PO4)2]·(NO3)2·2H2O (1), [(Cu2(bipy)2(V2O5)4(P2O7))(HPO4)(H2P2O7)]·nH2O (2) and [Cu2(dpa)2(V2P2O7)2]·4n (3), which have been magnetically characterized. In addition, the magnetic behavior of the related compound [Cu2(bipy)2(V2O7)2(P2O7)]·3n (4), has been measured. Compound 1 has a dimeric structure, while compound 2 and 4 have dimer chain structures. The dependence of the magnetic susceptibility on temperature suggests antiferromagnetic coupling for 1, 2 and 3, while compound 4 can be well understood in terms of the Curie–Weiss law with θ = −23 K. The fitting of the magnetic behaviour to the Bleaney–Bowers spin–dimer coupling expression leads to J = −8.0 cm⁻¹ for 1, J = −28.8 cm⁻¹ for 2 and J = −29.0 cm⁻¹ for 3. The use of alternating chain expressions leads to J = −28.8 cm⁻¹, x = −0.03 for 2 and J = −29.4 cm⁻¹, x = −0.027 for 3.

Although a variety of coordination geometries are exhibited by the compounds in the series, all of them have O–P–O bridges connecting the cupric centres. It was possible to identify the role of the vanadyl groups of the phosphonate framework as an important factor affecting the ability of the phosphate groups to transmit magnetic interactions.

Introduction

The VOHPO₄(3−₁) system has numerous structures which range from molecular species to three dimensional structures. Among them, two dimensional lamellar compounds (2D) have been specially well studied since they undergo intercalation reactions with diverse range of species. The diversity of oxidation states and vanadium polyhedra (octahedra, pyramids, tetrahedra) and the diversity of ways in which these can be connected to the H₂PO₄(3−₁) tetrahedra, provide the basis for the preparation of structurally unprecedented oxovanadium phosphonate compounds. The use of hydrothermal techniques has allowed a large number of these materials to be obtained. When organic components that possess structure-directing properties are introduced into the reaction mixture a remarkable array of metastable inorganic–organic composite oxides is obtained. These new compounds retain some of the structural features of the synthetic precursors. The organic components can act as charge compensating cations or as ligands which are covalently linked to the inorganic backbone of the solid. Recently there has been considerable interest in the use of coordination complexes as structure directing agents. The main advantage of this strategy lies in the variety of shapes and charges presented by the complexes, as well as in the possibility of introducing a transition metal into the oxide structure. The coordination preferences of the transition metal centre will produce the necessary structural modifications of the V–P–O structures. Thus the use of copper(n) complexes with 2,2'-bipyridine (bipy), 2,2'-dipyridylamine (dpa) and 1,10-phenanthroline (phen) ligands are expected to change the 3D or 2D arrays to 0D and 1D structures, permitting the study of low dimensional magnetic phenomena. In contrast to the more extensively studied bipy ligand the dpa ligand is particularly attractive since the NH group between the two pyridyl rings permits the stabilisation of the structure through hydrogen bonding interactions, while the phen molecule allows the consequence of the steric constraints of the ligand to be investigated.

As an extension to this synthetic approach to organic–inorganic hybrid oxides, we herein report the synthesis and structure determination of new Cu(n) oxovanadium(v)-phosphate diimine compounds [diamine: 2,2'-bipyridine (bipy), 2,2'-dipyridylamine (dpa) and 1,10-phenanthroline (phen)]; [Cu₂(phen)₂(H₂O)₂(H₂PO₄)₂(NO₃)₂·2H₂O (1), [(Cu₂(bipy)₂(V₂O₅)(HPO₄)(H₂P₂O₇))]·nH₂O (2) and [Cu₂(dpa)₂(V₂P₂O₇)]·4n (4). The magnetic susceptibility data of these three compounds are also described, together with that of the related solid [Cu₂(bipy)₂(V₂O₇)₂(P₂O₇)]·3n, the structure of which was reported by Feng et al.16

Experimental

Reagents were purchased from Aldrich Chemical Co. and Fluka, and were used without further purification. All syntheses were...
carried out in 23 mL poly(tetrafluoroethylene)-lined stainless steel containers under autogenous pressure.

a) Syntheses

\[
\text{[Cu}_2\text{(phen)}_2(\text{H}_2\text{PO}_4)_2]\text{(NO}_3\text{)}_2\cdot 2\text{H}_2\text{O} \quad (1) \text{. A mixture of Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} (0.416 g, 1.72 mmol), V}_2\text{O}_5 (0.153 g, 0.84 mmol), 1,10-phenanthroline (0.6727 g, 3.397 mmol), H_3\text{PO}_4 (8.7 mmol) and H_2\text{O} (230 mmol) was heated at 120 °C for 72 h, and then the temperature was slowly lowered to 80 °C (10 °C h\textsuperscript{-1}). After the reaction vessel was cooled to room temperature, blue crystals of 1 were collected. Anal. Calcld: C, 32.8; H, 3.2; N, 9.7%. Found: C, 33.1; H, 3.2; N, 10.0%.
\]

\[
\text{[(Cu}_2\text{bipy}_2)_2(\text{VO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{PO}_4)_2)_n\text{nH}_2\text{O} \quad (2). A mixture of Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} (0.416 g, 1.72 mmol), V}_2\text{O}_5 (0.155 g, 0.85 mmol), 2,2’-bipyridylamine (0.575 g, 3.36 mmol), H_3\text{PO}_4 (8.7 mmol), H_2\text{O} (230 mmol) and Zn (0.112 g, 1.72 mmol) was heated at 120 °C for 72 h, and then the temperature was slowly lowered to 80 °C (10 °C h\textsuperscript{-1}). Green needles of 2 were collected by manual separation under a microscope from a mixture of blue and black powders. Anal. Calcld: C, 32.8; H, 3.2; N, 10.2%. Found: C, 32.8; H, 2.4; N, 10.2%.
\]

b) Structure determination. Plates of 1 (0.2 × 0.2 × 0.05 mm) and 2 (0.07 × 0.06 × 0.02 mm), and a needle shaped crystal of 4 (0.09 × 0.06 × 0.05 mm) were mounted on a glass fiber. The intensity collection was made on a Bruker SMART APEX diffractometer, using a separation of 0.3° between frames and for 10 s per frame. Data integration was made using SAINT. The structures were solved usingXS in SHELXTL by means of direct methods, completed by Fourier difference synthesis and refined until convergence using XL SHELXTL and SHELXL97. In the case of 2 the starting structure model was extracted by direct methods using SIR97 and the refinements were made on \( F^2 \) with Jana2000. For additional data collection and refinement details, see Table 1.

c) Magnetic susceptibility measurements. The magnetisation of 1–4 was measured under a constant applied field (1 or 2 kOe) within a temperature range of 5–300 K with a SHE VTS-906 SQUID susceptometer–magnetometer. Complementary magnetic data for compound 2 was also recorded at low temperatures (2–10 K). All the experimental data were corrected by diamagnetic contributions and temperature independent paramagnetism of copper(II) (TIP = 60 × 10\textsuperscript{-6} emu per Cu atom).

\[\text{[Cu}_2\text{bipy}_2(\text{VO}_4)_2(\text{PO}_4)_2)_6\text{nH}_2\text{O} \quad (4). A mixture of Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} (0.406 g, 1.68 mmol), V}_2\text{O}_5 (0.153 g, 0.84 mmol), 2,2’-dipyridylamine (0.575 g, 3.36 mmol), H_3\text{PO}_4 (8.7 mmol), H_2\text{O} (230 mmol) and Zn (0.106 g, 1.62 mmol) was heated at 120 °C for 72 h, and then the temperature was slowly lowered to 80 °C (10 °C h\textsuperscript{-1}). Green needles of 4 were collected by manual separation under a microscope from a mixture of blue and black powders. Anal. Calcld: C, 28.7; H, 2.4; N, 10.2%. Found: C, 28.7; H, 2.4; N, 10.2%.
\]

Table 1 Summary of crystal data and refinement details for [Cu\textsubscript{2}(phen)\textsubscript{2}(H\textsubscript{2}PO\textsubscript{4})\textsubscript{2}](NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O (1), [Cu\textsubscript{2}(bipy)\textsubscript{2}(V\textsubscript{2}O\textsubscript{5})(PO\textsubscript{4})\textsubscript{2}](H\textsubscript{2}P\textsubscript{2}O\textsubscript{7})·2H\textsubscript{2}O (2) and [Cu\textsubscript{2}(dpa)\textsubscript{2}(V\textsubscript{2}PO\textsubscript{4})\textsubscript{2}] (4).

\begin{tabular}{|c|c|c|}
\hline
|| & \text{1} & \text{2} & \text{4} \\
\hline
\text{Formula} & Cu\textsubscript{2}C\textsubscript{6}H\textsubscript{12}N\textsubscript{6}O\textsubscript{5}P\textsubscript{2} & Cu\textsubscript{2}C\textsubscript{6}H\textsubscript{12}N\textsubscript{6}O\textsubscript{2}P\textsubscript{2}V\textsubscript{4} & Cu\textsubscript{2}C\textsubscript{6}H\textsubscript{12}N\textsubscript{6}O\textsubscript{2}PV \\
\hline
\text{Mol. Wt.} & 877.5 & 1722.52 & 4126.55 \\
\hline
\text{Space group} & Triclinic & Triclinic & Triclinic \\
\hline
\text{Triclinic} & | & | & | \\
\hline
\text{a} [Å] & 7.136(6) & 7.413(1) & 7.391(17) \\
\hline
\text{b} [Å] & 10.615(1) & 12.992(5) & 9.863(2) \\
\hline
\text{c} [Å] & 11.063(1) & 14.968(2) & 10.311(2) \\
\hline
\text{α} [°] & 85.541(1) & 87.801(1) & 107.030(4) \\
\hline
\text{β} [°] & 83.150(1) & 78.85(1) & 105.119(4) \\
\hline
\text{γ} [°] & 70.652(1) & 78.09(1) & 98.158(4) \\
\hline
\text{V/Å}\textsuperscript{3} & 784.5(1) & 1383.9(7) & 674.1(3) \\
\hline
\text{Z} & 1 & 2 & 2 \\
\hline
\text{D}/g cm\textsuperscript{-3} & 1.858 & 2.063 & 2.033 \\
\hline
\text{F(000)} & 446 & 843 & 410 \\
\hline
\text{μ(Mo-Kα)/mm}\textsuperscript{-1} & 1.552 & 2.398 & 2.422 \\
\hline
\text{Rint} & 0.0347 & 0.0682 & 0.0570 \\
\hline
\text{R1} & 0.0426 & 0.0887 & 0.0888 \\
\hline
\text{wR1} & 0.95 & 0.95 & 0.7650 \\
\hline
\text{Max. diff. e. dens./e Å} & -0.340 & 1.25; -0.71 & 0.495; -0.453 \\
\hline
\end{tabular}

See Table 1 for additional data collection and refinement details.
Due to protonation, the distance between the two groups shows a lengthening of the P–OH bond lengths. The distance between the two copper centers inside the dimer is 5.010(1) Å. The two copper (H2P2O7)[HPO4]2−(H2PO4)2−(NO3)2 molecules are located in a chair-like arrangement at different sides of the coordination planes are parallel, but not coplanar. The basal distances are Cu–N1, 2.019(2); Cu–N2, 2.021(2); Cu–N3, 2.308(2) Å. The copper center is displaced ca. 0.15 Å towards the apical oxygen atom. The distance between the two copper centers inside the dimer is 5.010(1) Å. The two copper coordination planes are parallel, but not coplanar.

The two nitrate anions provide charge counterbalance; together with a couple of hydration water molecules and the cationic dimer units, they define a profuse 2D H-bonding network parallel to the plane (001) (Fig. 2a). Interactions along the c direction are much weaker and consist of van der Waals bonds between the aromatic groups. Table 2 shows some bond distances, angles and dihedral angles for 1.

\begin{equation}
[Cu_{2}(bipy)_{2}(V_{2}O_{12})]_{n} \quad (2).
\end{equation}

The fundamental structural motif of this compound is shown in Fig. 1b. The coordination sphere around each copper(II) is defined by two bipy nitrogen atoms, two phosphorus oxygen atoms in the basal positions, and an apical vanadyl oxygen atom, defining a square base pyramid. The nearest copper(II) centres are linked together by three bridges: two O–P–O bridges and one O–V–O bridge, involving vanadyl oxygen atoms, to form dimeric units with \(d_{Cu-Cu} = 4.481\) Å. The copper(II) centres of the dimer are interconnected by a phosphovanadate ribbon by means of phosphate and vanadyl oxygen atoms. This ribbon is composed of a tetrametallic \(V_{4}O_{13}^{2−}\) unit, formed by two \(\mu_2\)-phosphate vanadium(v) dimers interconnected through a V–O–V bridge. Besides, each tetrametallic unit is interconnected by phosphate groups, generating a chain-like structure in the \(a\)-direction. In this way, a chain of dimers is formed (Fig. 2b). Phosphate groups are present on the periphery, either as HPO4 or H2P2O7−, due to half occupancy on the phosphorus P3 site. These phosphate groups located on the periphery ensure additional links between adjacent chains, through hydrogen bonds generating a two-dimensional inorganic framework. The chelating bipy groups extend from the inorganic layer at an angle of ca. 76°. Additionally, each of these non-covalent layers interacts with its nearest neighbours through the stacking of the bipy fragments to produce a “zipper-like” crystal structure. The distance between the stacked bipy molecules is about 3.5 Å and is indicative of the presence of intermolecular interactions.

Compounds which contain both orthophosphate and diphosphate groups have been described previously mostly for vanadium(II) and (IV) compounds. In the present work we have been able to isolate a vanadium(v) phosphate copper(II) complex (2), where both PO4 tetrahedra and P2O7 groups coexist. Relevant geometrical parameters like bond distances, angles and dihedral angles are given in Table 2.

\begin{equation}
[Cu(dpa)]_{2}(V_{2}P_{2}O_{12})_{m} \quad (4).
\end{equation}

The table shows selected bond distances and angles for 4. The structure of 4 is constructed of the dimeric \(Cu(dpa)_{2}(V_{2}O_{12})_{m}\) unit (see Fig. 1c) forming an infinite covalent chain oriented along the \(a\) cell axis. The Cu(iii) ion has a distorted square planar coordination sphere composed of two nitrogen atoms from the chelating dpa ion and two oxygen atoms from two different phosphate groups. The \(V_{2}P_{2}O_{12}^{3−}\) anion, which is formed by the corner sharing of \(VO_{2}^{+}\) cations with \(PO_{4}^{3−}\) anions, acts as a bridge between two \(Cu(dpa)\) units using the phosphate oxygen atoms. The chain is then defined by the alternation of the phosphovanadate anions and the \(Cu\)-dpa units (Fig. 2c). The distance between two nearest copper(iii)-copper(II) neighbours inside the dimer is 5.035 Å and 7.396 Å along the chain. The distance of each copper(II) centre to the uncoordinated O6 of the \(VO_{2}^{+}\) group is 2.905(2) Å. Every copper(II) centre deviates slightly (0.1 Å) from the least-squares plane defined by the chelating dpa ligand. The least-squares planes corresponding to two nearest neighbours copper centres are parallel (dihedral angle of 0°).

This chain pattern has been previously described by Finn and Zubiena for \(Cu(phen)(V_{2}P_{2}O_{12})_{n}\), with the difference that in this compound the vanadyl oxo atoms of \(V_{2}P_{2}O_{12}\) are coordinated to the Cu(dimine)2− unit instead of the phosphate ones.

The individual chains are interpenetrated by the dpa ligands, that are perpendicular to the direction of the \([Cu(dpa)]_{2}(V_{2}P_{2}O_{12})_{m}\) chain. The distance between the stacked dpa is about 3.7 Å. The interpenetration permits hydrogen bonding...
interactions between the NH groups of the dpa ligands of one chain with the terminal oxo groups of the VO₄ tetrahedra of the vicinal chain, defining a “zipper-like” structure. The distances and angle involved are H1···O8, 1.85 Å; O4···O8, 2.82 Å; and O4···H1···O8: 164.1°. As a consequence a 2D hydrogen-bonded network is formed.

Although a variety of coordination geometries and connectivities are exhibited by the previously described series of Fig. 2

Packing diagrams for a) [Cu₂(phen)₂(H₂O)₂(H₂PO₄)₂][NO₃]₂·2H₂O (1), b) [Cu₂(bipy)₂(V₂O₇)(PO₄)₂(HPO₄)(H₂P₂O₇)]ₙ·nH₂O (2) and c) [Cu(dpa)₂(V₂P₂O₁₂)]ₙ (4).
bridged by phosphonate and/or pyrophosphate and/or vanadyl bridges to define dimer (1) or dimer chains (2–4).

### Table 2

Selected bond lengths (Å) and angles (°) for [Cu(phen)3(H2O)2(H2PO4)2](NO3)2·2H2O (1), [Cu(bipy)2(V2O4)2(HPO4)2(H2PO4)3] (2), [Cu(bipy)2(VO2)2(PO4)2](H2O)2 (3) and [(Cu(dpa))2(V2P2O12)] (4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O4P</td>
<td>1.941(2)</td>
<td>Cu-O3Pb 1.920(2)</td>
</tr>
<tr>
<td>Cu-N1</td>
<td>2.019(2)</td>
<td>Cu-N2 2.021(2)</td>
</tr>
<tr>
<td>Cu-O1W</td>
<td>2.308(2)</td>
<td>Cu-O1w 1.971(8)</td>
</tr>
<tr>
<td>O4P-Cu-N1</td>
<td>94.17(8)</td>
<td>O4P-Cu-N2 174.54(8)</td>
</tr>
<tr>
<td>N1-Cu-N2</td>
<td>81.51(8)</td>
<td>O4P-Cu-O1w 92.7(1)</td>
</tr>
<tr>
<td>N1-Cu-O1W</td>
<td>97.7(1)</td>
<td>N2-Cu-O1w 91.2(1)</td>
</tr>
</tbody>
</table>

### b) Magnetic behaviour

As commented in the structural section, compounds 1–4 contain one unpaired electron Cu(n) (3d3, S = ½) centre in a distorted-square (4) or square pyramidal environment (1–3),

- **Table 2** Shows the bond lengths (Å) and angles (°) for [Cu(phen)3(H2O)2(H2PO4)2](NO3)2·2H2O (1), [Cu(bipy)2(V2O4)2(HPO4)2(H2PO4)3] (2), [Cu(bipy)2(VO2)2(PO4)2](H2O)2 (3) and [(Cu(dpa))2(V2P2O12)] (4).

**Table 3** Temperature dependence of the corrected molar susceptibility of compounds a) [Cu(phen)3(H2O)(H2PO4)(NO3)2·2H2O (1), b) [Cu(bipy)2(V2O4)2(HPO4)(H2P2O7)] (2), c) [Cu(bipy)2(VO2)2(PO4)2](H2O)2 (3) and d) [(Cu(dpa))2(V2P2O12)] (4).
Conclusions

New 0D and 1D compounds were synthesised by the hydrothermal method. Even though a reducing medium was used (Zn), all the isolated species were copper(II) and vanadium(V) compounds. We herein report a new example of a vanadium(V) species in which both PO₄ and P₂O₇ groups coexist. All the studied compounds with copper(II) atoms in a square pyramidal geometry present antiferromagnetic behavior. In compounds 2 and 3, the two PO₄ bridges are part of one P₂O₇ unit, determining a boat-like conformation for the Cu–O–P–O–Cu–O–P–O unit, while a chair-like conformation is found in 1. There is no obvious relationship between the value of the bridging angles and the observed magnitude of the antiferromagnetic coupling through this anion. Oxovanadium groups have been reported to act as a pathway for magnetic coupling.

Table 3 Summary of the structural and magnetic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cu(ii) Geom.</th>
<th>Dihedral angles/°</th>
<th>Bond angles/°</th>
<th>( d_{\text{Cu-C}}/\text{Å} )</th>
<th>( \mu/\text{BM} )</th>
<th>( \theta/\text{K} )</th>
<th>( T_{\text{max}}/\text{K} )</th>
<th>( J/\text{cm}^{-1} )</th>
<th>g</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu₂(bipy)₂(H₂PO₄)]²⁺</td>
<td>S-P</td>
<td>52.3 150.8 121.2</td>
<td>Cu-O-P 135.1</td>
<td>5.01</td>
<td>1.82</td>
<td>-7.2</td>
<td>8</td>
<td>-8.0</td>
<td>2.00</td>
<td>0.01</td>
</tr>
<tr>
<td>[Cu₂(bipy)₂(P₂O₇)]²⁺</td>
<td>S-P</td>
<td>84.3 48.6 89.1</td>
<td>O-P-O 93.3/94.97</td>
<td>4.647</td>
<td>—</td>
<td>—</td>
<td>19</td>
<td>-20.0</td>
<td>2.09</td>
<td>—</td>
</tr>
<tr>
<td>[(Cu₂(bipy)₂)(V₄O₈)(H₂P₂O₇)] · nH₂O</td>
<td>S-P</td>
<td>74.1 43.4 53.6</td>
<td>Cu-O-P 132.0</td>
<td>4.481</td>
<td>1.97</td>
<td>-19.8</td>
<td>25</td>
<td>-28.8</td>
<td>2.25</td>
<td>0.025</td>
</tr>
<tr>
<td>[Cu₂(bipy)₂(V₂PO₄)]²⁺</td>
<td>S-P</td>
<td>63.3 14.8 70.0</td>
<td>O-P-O 139.3/124.8</td>
<td>5.06</td>
<td>1.88</td>
<td>-19.0</td>
<td>26</td>
<td>-29.0</td>
<td>2.12</td>
<td>0.023</td>
</tr>
<tr>
<td>[(Cu(bpy)₂)₂(V₂P₂O₇)]n</td>
<td>S-P</td>
<td>89.6 21.0 68.7</td>
<td>Cu-O-P 120.0/148.0</td>
<td>5.03</td>
<td>1.79</td>
<td>-23.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

S-P: square pyramidal; D-SP: distorted square planar; CC: chair conformation; BC: boat conformation; J, g and \( \rho \): dimer model.
illustrates how far geometry can modify magnetic coupling between Cu(II) centres bridged by O–P–O groups. They also suggest that the ability of these fragments to transmit magnetic exchange can be modified by oxovanadium centres connected to them.

Acknowledgements

The authors acknowledge financial support from FONDAP (grant 11980002), CNRS/CONICYT (programs 10071 and 11952) and PICS 922. We are also grateful to Fundacion Andes for supporting the purchase of the SMART APEX system currently operating at the University of Chile.

References