Catena–(bis((1,10-phenanthroline-N,N')-copper(II)) hydroxy-bis (phosphato)-tris(dioxo-vanadium(v))): A polymorphic phase driven by disorder

Cristian Silva-Galaz, Marianela Saldías, Eleonora Freire, Ricardo Baggio, E. Le Fur, Evgenia Spodine, Diego Venegas-Yazigi

*Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, Santiago, Chile
bCEDENNA, Santiago, Chile
cFacultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile
dGerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
eEscuela de Ciencia y Tecnología, Universidad Nacional General San Martín, Buenos Aires, Argentina
fENSCR, CNRS, UMR 6226, Rennes, France
gUniversité Européenne de Bretagne, UMR 6226, France
hFacultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile
iUniversidad de Santiago de Chile, USACH, Santiago, Chile

**HIGHLIGHTS**

- A crystallographic study of \([\text{Cu}_6(\text{phen})_6(\text{VO}_2)_6(\text{PO}_4)_6(\text{V}^\text{V}_2\text{O}_7\text{H}_2\text{O})_2]\).
- The crystal structure analysis suggests that this can be one of a large number of polymorphic states with structural differences.
- The pseudo symmetry problem defining the polymorphic states is discussed.
- A magnetic characterization of \((1a)\) was performed, showing that the compound is antiferromagnetic.

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**ABSTRACT**

In the present paper a copper(II) phosphovanadate is presented and formulated as \([\text{Cu}_6(\text{phen})_6(\text{VO}_2)_6(\text{PO}_4)_6(\text{V}^\text{V}_2\text{O}_7\text{H}_2\text{O})_2]\) \((1a)\). This compound was obtained by hydrothermal synthesis and crystallizes in the triclinic group \(P\bar{1}\), with \(a = 10.6290(5), b = 17.4275(8), c = 23.6151(11)\ \AA\); \(\alpha = 92.888(4)^\circ\), \(\beta = 98.910(4)^\circ\) and \(\gamma = 91.995(4)^\circ\). The \(\text{leimotif}\) in \((1a)\) is almost identical to some previously reported ones, viz., \([\text{Cu}(\text{phen})(\text{VO}_2)(\text{PO}_4)(\text{V}^\text{V}_2\text{O}_7\text{H}_2\text{O})_2]\) except for the fact that the small cells found in \((2)\)–\((3)\) are tripled in \((1a)\). The reasons driving to these differences are subtle, and reside in the way in which the disorder in some vanadate groups takes place, viz., completely at random in \((2)\)–\((3)\) thus leading to a small “average” cell, while keeping some systematics in \((1a)\) thus needing for a larger \(\text{leimotif}\) to take account of its repetition scheme in the crystal. The magnetic unit in the structure of \((1a)\) is defined by a dinuclear system of \(\text{Cu}^\text{II}\) bonded by a \(\text{Cu}^{2+}\text{PO}_4\text{H}_2\text{O}\) bridge. A fit of the corresponding magnetic data of \((1a)\) was done, using the van Vleck equation for two \(S = \frac{1}{2}\) centres \((H = -J S_x\ S_x)\). The parameters obtained by the fit of the experimental data were \(g = 2.1\) and \(J = -3.5\ \text{cm}^{-1}\).

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**1. Introduction**

Phosphovanadates (VPO) constitute a well explored type of compounds, which in spite of their long term studies persist in driving the attention of structural chemists due to their unpredictable structural diversity. This is the result of the variety of geometric surroundings, which the vanadium cation can adopt in its different oxidation states, as well as the way in which it can condense with the phosphate anion \([1]\). Besides the fact that functionalization of these oxides with transition metal complexes allows the generation of quite different structures and dimensionalities, like chains, lamellar or heavily interconnected three-dimensional arrays \([2–10]\). A final, non-minor ingredient in this structural “Pandora’s box” is the finding that slight differences in synthetic conditions might derive in
either subtle or important structural differences in the final products.

In this work an interesting example of the former case is presented. A detailed structural analysis of an organo-inorganic hybrid compound is discussed, corresponding to an inorganic VPO framework functionalized with a CuII complex having 1,10-phenanthroline (phen) as ligand, \([\text{Cu}_6\text{(phen)}_6\text{(PO}_4\text{)}_6\text{(VO}_2\text{HO)}_3]\) (1a) (Scheme 1) that was obtained by the hydrothermal method. Almost exact replicas of this structure had already been reported by Finn and Zubieta [4] and Zhang et al. [5], but as we shall discuss below, with some subtle differences setting them apart as different polymorphic structures.

The magnetic characterization shows that compound (1a) presents an antiferromagnetic behaviour due to the super-exchange interaction existing between CuII and CuIII (3.262(3) Å).

2. Materials and methods

2.1. Synthesis

A mixture of NaVO3 (0.156 g, 1.2 mmol), H3PO4 (0.098 g, 1.0 mmol), Cu(NO3)2 3H2O (0.290 g, 1.2 mmol), 1,10-phenanthroline (phen) was obtained by the hydrothermal method. Almost exact replicas of this structure had already been reported by Finn and Zubieta [4] and Zhang et al. [5], but as we shall discuss below, with some subtle differences setting them apart as different polymorphic structures.

The magnetic characterization shows that compound (1a) presents an antiferromagnetic behaviour due to the super-exchange interaction existing between CuII and CuIII (3.262(3) Å).

2.2. X-ray diffraction

Infrared spectrum of the powder sample was recorded in the 4000–4000 cm\(^{-1}\) range at room temperature on a Perkin Elmer FTIR spectrophotometer, model BX II, using KBr pellets. The principal bands are (cm\(^{-1}\)): 898 (s), 987 (s) corresponding to terminal V=O and O−V−O bridge stretching modes; 1114 (s), 1164 (s) assigned to P=O and P−O groups; 1392 (m) and 1443 (m) assigned to C=C and C=N groups of the organic ligand (phen).

2.4. FTIR

Single crystal data were collected on an Oxford Diffraction Gemini diffractometer, Mo Kα radiation, and the following software was used in different stages of the crystal structure analysis process: Data collection: CrysAlis PRO (Oxford Diffraction, 2009) [11]; cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SHELXS97 [12]; program(s) used to refine structure: SHELXL97 [12]; molecular graphics: SHELXTL [12]; software used to prepare material for publication: SHELXL97, PLATON [13]. All H atoms were identified in a difference Fourier map, and further idealized and allowed to ride (C−H: 0.93 Å, O−H: 0.85 Å, U(H)iso = 1.2 × U(host).

The structure presents an important pseudo translation symmetry, broken by a differentiated splitting in a few, otherwise equivalent, vanadyl V=O’s. The latter groups were refined with similar restraints (SADI and DELU in SHELXL), and their

![Scheme 1. Basic unit of (1a).](image)

Table 1

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<th>(1b)</th>
<th>(2)</th>
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<tr>
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na: not-available info.

* Cell axes transformed to facilitate comparison with those in (1b).
Hydrogen-bond geometry for (1a) (Å).

Table 2

Selected bond lengths for (1a) (Å).

Table 3

Hydrogen-bond geometry for (1a) (Å, °).

2.5. Magnetic measurements

The magnetization was measured over the temperature range of 2–300 K for (1a). Measurements were performed on 73.7 mg at 1 kOe, using a Quantum Design SQUID magnetometer (MPMS-XL5). Diamagnetic corrections of the constituent atoms were estimated from Pascal constants [14]. The validity of the fitting procedure for the used model in this work was done using the agreement factor, defined as:

\[ R = \frac{\sum (\chi_M(T)_{exp} - \chi_M(T)_{calc})^2}{\sum (\chi_M(T)_{exp})^2} \]

The molar magnetic data of (1a) were obtained using the formula weight determined by crystallography, that is, with six spin carriers per mole.

3. Results and discussion

Fig. 1 presents an ellipsoid plot of the compound. The complexity of the structure (apparent from inspection) is the result of a frustrated threefold translation symmetry along the \((1/3, -1/3, -1/6)\) vector which makes the asymmetric unit three times as

![Fig. 1. Molecular view of (1a) with displacement ellipsoids at a 30% level. Carbon atoms in the phen groups “B” to “F” are not labelled in the figure, but repeat the labelling scheme as those in the “A” moiety. Aromatic H atoms omitted. Symmetry codes: (i) \(-x + 2, y - 1, -z\); (ii) \(-x, y + 2, z + 1\); (iii) \(x - 1, y, z\); and (iv) \(x + 1, y, z\).](image)

![Fig. 2. The inorganic 2D structure in a view normal to (011) (phenligands and H atoms removed, for clarity). Line codes: full heavy lines: \(\text{O}_{\text{vanadyl}}, \text{O}_{\text{phosphate}}\) Covalent bonds; full weak lines: \(\text{O}_{\text{vanadyl}}, \text{O}_{\text{phosphate}}\) Coordination bonds; strong broken lines: \(\text{O}_{\text{hydroxy}}\) Coordination bonds.](image)

Table 1 (first column) presents the crystal data and structure refinement parameters for (1a). Further information on structural details on the structure can be found in Table 2 (coordination distances) and Table 3 (H-bonding interactions).
large as it would be if the proper symmetry were in force. This means that, in a first order approximation the structure of \( \text{(1a)} \) can be considered as a triple leitmotiv with very minor variations from one another, and in other words and from a purely crystallographic point of view, \( \text{(1a)} \) is approximately \( \{[\text{Cu}_2(\text{phen})_2][\text{PO}_4]_2\} \left\{[\text{VO}_2][\text{VOH}]\right\}_2 \). (See below for a thorough discussion on this pseudo symmetry.) The pseudo “elemental” unit is highlighted in Fig. 2, where a schematic view of the resulting 2D structure is presented with the phenligands removed, for clarity.

As can be observed from both Figs. 1 and 2, each “elemental” unit is formed by two copper \( \text{Cu}^\text{II} \) and three vanadyl \( \text{V}^{\text{IV}} \) groups, charge balanced by two phosphate \( \text{PO}_4^\text{3-} \) and one hydroxyl \( \text{OH}^- \) groups. The relevant atoms characterizing each group in the three moieties are in an ordered sequence: \{Cu1, Cu2, V1, V2, V3; P1, P2, O72\}; \{Cu3, Cu4, V4, V5, V6; P3, P4, O75\} and \{Cu5, Cu6, V7, V8, P5, P6, O78\} with Cu1 being the “quasi equivalent” to Cu3 and Cu5, and so on.

Both copper cations in each unit have a similar square pyramidal geometry, and both are chelated by the phen ligands, through the corresponding N atoms (N1,N2) A,B, to (N1,N2) E,F with Cu-N distances of 1.984 (3)–2.019 (3) (Table 2). The oxygen atoms that bind the copper centres correspond to two phosphate and one vanadyl group (Cu1, Cu3 and Cu5). The apical bond corresponds to one of the vanadyl oxygen atoms (Cu-Oapical: 2.226 (3)–2.351 (3) Å) with basal Cu-Ophosphate, Cu-Ovanadyl being shorter and very similar, spanning the tight range 1.957 (3)–1.972 (3) Å. A hydroxyl group replaces the vanadyl oxygen in Cu2, Cu4 and Cu6.

There are two different coordination types within the vanadium cations in each group: the outermost ones V1, V3; V4, V6; V7, V9 are similar to each other with a fourfold, deformed tetrahedral coordination, fulfilled by its two intrinsic vanadyl plus two phosphate oxygen atoms. Both groups of bonds are similar in the three “pseudo equivalent” units, but different from each other (V-Ovanadyl: 1.603 (3)–1.613 (3) Å, V-Ophosphate: 1.856 (3)–1.866 (3) Å). The central vanadium cations, V2, V5 and V8, present instead a fivefold coordination by inclusion of a hydroxyl group, which completes a deformed square pyramidal arrangement where vanadyl bonds are also shorter than the phosphate/hydroxyl ones. In all cases, their internal spread is larger than in the previous group (V-Ovanadyl range: 1.596(3)–1.711(3) Å, V-Orest: 1.910(3)–2.044(3) Å). It is important to note for future reference, that the V2–O62, V8–O68 groups appear as slightly disordered, through splitting at both sides of the basal plane of the corresponding pyramidal, with a local change of chirality.

Occupation factors were independently refined for both groups, and converged to very similar final values (V2/O62: 0.8432 (14/0.1568 (14), V8/O68: 0.8525 (14), 0.1475 (14)). On the other hand, the V5–O65 group did not show any appreciable splitting. The PO42− groups are featureless, with an even span of P-O distances (1.514 (3)–1.555 (3) Å) for the six independent moieties.

The planar inorganic 2D structure evolves parallel to \( (0–11) \) (Fig. 2). The network presents five different kind of loops of general type \( (M–O)_n \), where M stands for either Cu, V or P, two of them with \( n = 3 \) (A, A’ in Fig. 2) and three with \( n = 2, 4 \) and \( 10, (B, C \text{ and } D, \text{ respectively).} \) The phenanthroline ligands decorate the planar arrays stretching outwards, either above or below the narrow 2D inorganic structures. By interdigitation of these protruding phen ligands of neighbouring planes, the 2D structures finally link into a 3D one (Fig. 3). The process, however, takes place in an unexpected way since the “gluing” agent is not, as usual in this type of arrangement, the \( \pi \cdots \pi \) stacking interaction between adjacent phen groups but a number of non-conventional C–H·O contacts instead, (Table 3) having phen C–H’s as acceptors and (mainly) Ovanadyl (entries 1–10 in Table 3) or Ophosphate (entries 11–13 in Table 3) as donors.

3.1. The pseudo symmetry problem

The presence of eventual pseudo symmetry was something foreseeable “ab initio” from a careful observation of the diffraction data, which present an evident intensity systematics. Finding the law which describes these systematics, what would correspond to a reciprocal space approach to the problem, appeared however as non-trivial. The solution of the structure was attempted instead, looking for some noticeable pseudo symmetry aspects in the resulting model. This “direct space approach” proved to be successful, and the expected singularity prompted out as the threefold translational pseudo symmetry along the \( (1/3, 1/3, –1/6) \) vector.

The pseudo operation was accurate for most of the structure including the phen molecules. The main deviation from a perfect match corresponded to the V2–O62, V5–O65 and V8–O68 groups, some of them disordered, which by the pseudo translation mixed up and loosed their otherwise well defined “identity” (V2->V5; V5->V8; V8->V2).

In order to further investigate the degree of matching a transformation matrix leading to a “single motive cell” was used and this was found to be \( M: (100; 010; 1/3, –1/3, –1/6) \). This transformed the original cell into a rather deformed primitive one with \( V' = 718.66 \) (6) Å3 = 1/6 V, and \( a' = b' = c' = 17.4275 \) (8) Å; \( \alpha' = 91.995 \) (4)°; \( \beta' = 95.737 \) (4)°; \( \gamma' = 91.995 \) (4)°. In this way, the \( hkl \) data set, consisting of the reflections which indices transformed into a set of integers, reduced to \( 1/3 \) of the original one. The other \( 2/3 \) of the total reflections, showed a much weaker intensity on average, but large enough as to confirm the original triple cell as the correct one, describing the structure under study.

The transformed model could be treated and refined in P-1 (1b), with inversion centres at the midpoint of all type B loops (Fig 2); loops A and A’ being equivalent through disorder. In this description, the pair V2/V2’ also appeared related by the inversion centre.
The net result was a reduction of the number of parameters by ca. 1/6, without jeopardizing the refinement performance (Table 1). Through all the procedure, the R indices and residual densities dropped appreciably. However, the model so refined suffered from a severe over simplification, showing only one type of disordered vanadyl group, now split into equally populated halves at both sides of an inversion centre.

Analysis of the results in Table 1 leads to the conclusion that the centrosymmetric sixfold cell is the proper one to correctly describe the “superstructure” in (1a), and this is confirmed in the differentiated disorder shown by the central V2, V5 and V8 atoms. However, if this effect is considered second order and accordingly disregarded, the system could be described by a much smaller cell, \( V = 1/6 \) V, with only half of a motive as the independent part and no substantial differences in its structural main features, but with loss of the finer details introduced by the “ordered” disorder scheme.

3.2. Comparison with related structures

Finn and Zubieta reported a structural study for a compound formulated as \([\text{Cu}(\text{phen})\{\text{V}^0\text{O}_2\}(_2\text{PO}_4\})\] \((2)\) [4], matching exactly the formulation of (1b). This compound was reported to crystallize in a triclinic cell, with half of a “single motive” (in the sense described so far in this paper) in the asymmetric unit. Unfortunately, no structural data seems to be available in the crystallographic data base (CSD) beyond the description in the asymmetric unit, as to make any further comparison. On the other hand, a subsequent paper by Zhang et al. [5] describes what claimed to be an isostructural compound of \( \text{Cu}(\text{phen})\{\text{V}^0\text{O}_2\}(_2\text{PO}_4\})\] \((2)\) of slightly different formulation, \([\text{Cu}(\text{phen})\{\text{V}^0\text{O}_2\}(_2\text{PO}_4\})\] \((3)\). Since structural data of this latter compound is available in the CSD, a comparison was in principle possible: the transformation \( M = (1 - 1, 1, 110, 0, 010)\) drives the cell vectors of (2) and (3) into those in (1b), and the transformed model of (3) fits almost exactly onto (1b). Thus, it should be concluded that structures (2) and (3) coincide with the “average” description of (1a), and what we have called (1b).

Considering that both structures (2) and (3) appear as fairly accurate the possibility of a coincidental artefact in both, such as the overlooking of a large number of weak reflections must be considered as highly improbable, and consequently the models presented for (2) and (3) should be taken as basically correct.

The conclusion seems to be that \([\text{Cu}(\text{phen})\{\text{V}^0\text{O}_2\}(_2\text{PO}_4\})\] \((2)\) can present some very subtle polymorphic states, of which (1a) and (2) are perhaps two out of a larger number, where the way in which a particular site is disordered allows it to “command” the long range order. This situation resembles the classic case of the Cu3Au alloy which, when in its ordered phase, is simple cubic (P), with Au at \((000)\) and Cu at \((1/2,1/2,1/2)\), but face centred cubic (FCC) when completely disordered, with an “atom-per-site” of average composition 1/4(3Cu + Au) [15]. In the case of (1a) and (2), an evenly disordered state, which means a non-systematic distribution in space of the central VO3polyhedra with opposite chirality, would lead to a small cell as in (2) and a unique 50%/50% split for the central V atom. Instead a partially ordered state, meaning some more systematic distribution in space of the central VO3polyhedra with opposite chirality, can lead to much larger cells (sixfold in the case of (1a)). As stated before, intermediate situations cannot be disregarded from scratch.

3.3. Magnetic studies

The temperature dependence of \( \chi T \) observed for (1a) is displayed in Fig 4, already corrected for diamagnetism and TIP, which was estimated to be \( 3 \times 10^{-5} \) emu mol\(^{-1}\). The \( \chi T \) value at 300 K is 2.52 emu mol\(^{-1}\) K, which corresponds to six \( S = 1/2 \) centres with \( \mu_{\text{eff}} \) 1.83. This value is consistent with the spin only value of 1.73 \( \mu_{\text{B}} \) for an isolated Cu\(^{2+}\) centre. At low temperatures the \( \chi T \) product decreases sharply; this phenomenon being explained as due to the presence of antiferromagnetic interactions. The low temperature limit for the \( \chi T \) value at 5 K is 1.84 emu mol\(^{-1}\) K. The inverse susceptibility in the high temperature range follows the Curie–Weiss law, with a Weiss constant \( \theta \) of \(-0.7\) K. The negative value of the Weiss constant makes evident the bulk antiferromagnetic interactions present at low temperatures in the studied 2D system.

Compound (1a) presents the shortest Cu···Cu distance of 3.262 Å between Cu2 and Cu3 (Cu4 and Cu5). Taking into account that the other distances between the spin carriers are larger, the most relevant intramolecular super exchange interaction was defined between Cu2 and Cu3. This magnetic unit can be treated as a dinuclear system of Cu\(^{2+}\) atoms bridged by \( \mu_2\eta_1\)-PO4 groups (Scheme 2).

A fit of the corresponding magnetic data of (1a) was done, using the van Vleck equation for two \( S = 1/2 \) centres, \( \langle H = -J S_1 \cdot S_2 \rangle \) with the analytical expression given below:

\[
\chi = \frac{2N g^2 \beta^2}{kT} \frac{e^{\beta}}{1 + 3e^{\beta}}
\]

where \( N \) is Avogadro’s number, \( \beta \) is the Bohr magneton and \( k \) the Boltzmann constant.

The parameters obtained by the fit of the experimental data using the above expression are \( g = 2.1 \) and \( J = -3.51\) cm\(^{-1}\) (\( K = 5 \times 10^{-4}\)). The full line (red in the web, grey in print) in Fig 4 shows the fit of the experimental data, using these parameters. The obtained \( J \) value can be related to antiferromagnetic coupling, and suggests a weak transmission of the magnetic phenomenon.
through the $\mu_2,\eta^1$-PO$_4$ bridges. The bonds between both Cu$^{II}$ centres occur through an equatorial–apical coordination mode. Since both copper centres present $d_{x^2-y^2}$ magnetic orbitals, the coordination mode does not allow a more effective overlap, and therefore a more intense antiferromagnetic exchange phenomenon.

The low value of $J$ obtained for (1a) can be compared with that of [Cu$_2$(bipy)$_2$($\mu_2,\eta^1$-HPO$_4$)$_2$($\mu_2,\eta^1$-H$_2$PO$_4$)($\mu_2,\eta^2$-H$_2$PO$_4$)]$_n$ [16], where the two metal centres also have a square pyramidal geometry and are bridged by phosphate groups, with a Cu···Cu distance of 3.22 Å, forming a dinuclear system. Although, both experimental magnetic data were fitted using different analytical models, the obtained values of $J$ are similar. For [Cu$_2$(bipy)$_2$($\mu_2,\eta^1$-HPO$_4$)($\mu_2,\eta^1$-H$_2$PO$_4$)($\mu_2,\eta^2$-H$_2$PO$_4$)]$_n$, $J = -5.3$ cm$^{-1}$, a value which also indicates a weak antiferromagnetic behaviour produced by the same connectivity mode (equatorial–apical positions) between the metallic centres as in (1a). Only a few magnetic studies of phosphate-bridged Cu$^{II}$ complexes are available in the literature. The work of Ainscough et al. shows that a $\mu_2,\eta^1$-PO$_4$ bridge in an equatorial–axial coordination fashion between copper centres producing weak antiferromagnetism [17].

3.4. Conclusions

In the present work the studied compound [Cu$_6$(phen)$_6$($V^{IV}$O$_2$)$_6$(PO$_4$)$_6$($V^{IV}$O$_2$)$_3$O$_3$] (1a) was obtained by the hydrothermal method. The main conclusion is that [Cu(phen)($V^{IV}$O$_2$)$_2$(PO$_4$)$_2$]$_2$ ($V^{IV}$O$_2$O$_3$) motif can present some subtle polymorphic states, of which (1a) is perhaps one out of a larger number of related structures. In the present case the presence of a small vanadate disorder gives rise to a threefold translational pseudo symmetry, as the basis of this subtle superstructure difference. Even though there is a short Cu–Cu distance (3.262(3) Å), the apical-equatorial coordination mode of the bridging $\mu_2,\eta^1$-PO$_4$ groups leads to a poor overlap of the magnetic orbitals and therefore to a weak antiferromagnetic phenomenon.

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Appendix A. Supplementary material

CCDC 924170 contains a Crystallographic Information File (CIF) for this structure. This file can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.08.005.

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