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Article

Structure and Magnetic Properties of the Hybrid System Copper(II) μ_2-2,2′-Bipyridine-3-carboxylate-*N*,*N*′:*O*-μ_2-phosphate-*O*,*O*′

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The title compound $[Cu(PO_4H_2)(C_{11}H_7N_2O_2)]_n$ presents antiferromagnetic behavior. It has a polymeric one-dimensional structure in which the elemental links are tetranuclear units and the doubly protonated phosphates and the bipyridinemonocarboxylates act in a bridging mode. The magnetic behavior is described using an alternating chain model, with $J = -3.32$ cm^{-1}, $\alpha = 0.7$, and $g = 2.05$.

Introduction

The search for materials with specific magnetic properties has evidenced the need to produce and structurally explore paramagnetic complexes with as many ligand environments as possible, in order to find superexchange pathways adequate for the needs required. This need, in turn, has boosted the development of new, imaginative synthetic techniques, far away from the traditional synthetic routes.

In this respect, hydrothermal synthesis has become one of the most popular nonstandard methods, quite successful in the production of hybrid solids, viz., compounds in which a metallic cation combines both with multifunctional organic ligands (e.g. complex carboxylates, etc.) as well as with inorganic molecules (e.g., phosphates, etc.),[1–5] often resulting in open frameworks with applications as catalysts, molecular sieves, magnets, etc.[6] In these constructions, metal−carboxylate structures tend to become the elemental bricks and the use of inorganic spacers, such as phosphate, points in turn toward the intercoordination and expansion of the structures. Among the multifunctional organic ligands commonly used, carboxylated aromatic amines appear as primary class ligands in view of their versatility, their wide range of coordination modes, and their ability to mediate magnetic exchange through the polymeric structure as they can bridge the paramagnetic centers.

Among the magnetic materials attainable through these methods, the simpler molecular systems with $S = {}^1/_2$ are by far the most amenable for an adequate understanding and modeling of their magnetic interactions.[7,8] Thus, in pursuing our interest in these latter systems, we report herein on the synthesis and magnetic behavior of the hybrid $[Cu(PO_4H_2)(C_{11}H_7N_2O_2)]_n$, (**1**), where a bipyridine unit with a carboxylate function has been used as the organic ligand and a bridging phosphate as the inorganic link between the magnetic copper centers. The resulting chain structure presents two well-differentiated distances between metal centers: a shorter one, through the phosphate bridge, and a longer one, through the bipyridine-3-carboxylate ligand (bpy-COO).

Experimental Section

The starting organic ligand, 2,2′-bipyridine-3,3′-dicarboxylic acid, was purchased from Aldrich Chemical Co. and used as received, without further purification.

The complex has been obtained after soft hydrothermal treatments, mixing 1.5 mmol (366 mg) of the latter organic ligand, 0.25 mmol (46 mg) of V_2O_5, 0.5 mmol (121 mg) of $Cu(NO_3)_2 \cdot 3H_2O$,

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Table 1. Data Collection Details

Bruker CCD area detector diffractometer	2660 indep rflns
ψ and ω scans	1942 rflns with $I > 2\sigma(I)$
abs cor: multiscan SADABS (Sheldrick, 2001)	$R_{\mathrm{int}} = 0.055$
$T_{\mathrm{min}} = 0.721$, $T_{\mathrm{max}} = 0.800$	$\theta_{\mathrm{max}} = 28.0°$
5195 measd rflns	

Table 2. Crystal Data

$PO_4H_2 \cdot C_{11}H_7N_2O_2 \cdot Cu$	$V = 612.3(4)$ Å^3
$M_r = 359.71$	$Z = 2$
triclinic, $P\bar{1}$	$D_{\mathrm{exptl}} = 1.951$ Mg m^{-3}
$a = 8.239(3)$ Å	Mo Kα radiation
$b = 8.805\ (3)$ Å	$\mu = 1.95$ mm^{-1}
$c = 9.558(3)$ Å	$T = 275(2)$ K
$\alpha = 104.645(6)°$	blocks, green
$\beta = 106.000(6)°$	$0.18 \times 0.14 \times 0.12$ mm
$\gamma = 102.841(6)°$	

3.0 mmol (295 mg) of H_3PO_4, and 10 mL of distilled water. The reaction mixture was held at 165 °C over 3 days in a Teflon-sealed reactor. After slow cooling to room temperature, small blue crystals of the title compound were obtained. Anal. Found: C, 36.8; H, 2.5; N, 7.8. Calcd: C, 36.7; H, 2.5; N, 7.7.

It is perhaps interesting to insist on the fact that the product finally obtained differs from the initially intended one (a mixed binuclear complex containing copper and vanadium as metal centers and 2,2′-bipyridine-3,3′-dicarboxylic acid as a ligand), confirming that hydrothermal processes are still not too well understood on an “ab initio” basis, though it is possible to have a reasonable explanation of the final outcome. The noninsertion of the vanadate in the structure was very probably due to a problem with the solubility of V_2O_5. On the other hand, the in situ decarboxylation of the 2,2′-bipyridine-3,3′-dicarboxylic acid, resulting in the monocarboxylate as the final product, was probably favored by the high temperature and acidic conditions of the synthesis; in addition, the two carboxylic functions in the original 2,2′-bipyridine-4,4′-dicarboxylic acid appear rather near to each other, eventually promoting some kind of a steric problem.[9,10]

In order to understand if the decarboxylation is due to any effect of this particular reaction, we have carried out the reaction of the organic ligand, 2,2′-bipyridine-4,4′-dicarboxylic acid, with phosphate acid under identical experimental conditions (without copper or vanadium ions). In this experiment the organic ligand lost one carboxylate group; therefore, the same effect as in the original reaction was obtained. The decarboxylation was probed through comparison of ^1H and ^{13}C NMR spectra (Bruker AC-250P spectrometer) of the organic ligand, before and after reaction.

The hybrid compound was characterized by infrared spectroscopy (Magna Nicolet IR-550 spectrophotometer) and thermogravimetric analyses (40–1000 °C; Mettler Toledo TGA/SDTA851 thermobalance). With these analyses it is possible to determine the coordination of the copper ion. There is an intense absorption band at 1595 cm^{-1} that corresponds to the carboxylate group (the band for the free organic ligand is about 1700 cm^{-1}). Moreover, the infrared spectra exhibit a band at 1071 cm^{-1} due to the phosphate group.

The thermal analysis of this compound exhibits a mass loss of 24% centered at 346 °C, due to the loss of the $P_2O_7^{4-}$ group (this is characteristic of the presence of PO_3^{4-}).

X-ray studies were made at room temperature on a single crystal glued on a glass fiber. The diffraction data were recorded using a Brucker SMART diffractometer according to the experimental conditions given in Table 1, while Tables 2−5 show details of the crystal, refinement, and structural data.

Table 3. Refinement Details

refinement on F^2
$R(F^2 > 2\sigma(F^2)) = 0.069$
$R_w(F^2) = 0.190$
$S = 0.92$
2660 rflns
198 params
H atoms treated by a mixture of indep and constrained refinement
$w = 1/[119\sigma^2(F_o^2) + (0.0981P)^2 + 3.2299P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\mathrm{max}} = 0.001$
$\Delta\rho_{\mathrm{max}} = 1.16$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -0.67$ e Å^{-3}
extinction cor: none

Table 4. Selected Geometric Parameters (Å)[a]

Cu1−O2$^{\mathrm{i}}$	1.910(5)	P1−O1	1.507(5)
Cu1−O1	1.915(4)	P1−O4	1.561(6)
Cu1−N1	1.983(6)	P1−O3	1.563(6)
Cu1−N2	1.991(6)	O5−C11	1.247(9)
Cu1−O5$^{\mathrm{ii}}$	2.382(6)	O6−C11	1.245(9)
P1−O2	1.497(5)		

[a] Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y + 2, -z + 2$.

Table 5. Hydrogen-Bond Geometry (Distances in Å and Angles in deg)[a]

D−H···A	D−H	H···A	D···A	D−H···A
O3−H3A···O5$^{\mathrm{iii}}$	0.85(4)	1.98(7)	2.637(8)	133(9)
O4−H4A···O6$^{\mathrm{iv}}$	0.85(5)	1.74(5)	2.571(8)	167(12)

[a] Symmetry codes: (iii) $x, y - 1, z - 1$; (iv) $-x + 2, -y + 2, -z + 2$.

The magnetic susceptibilities were measured using a Quantum Design MPMS XL5 SQUID magnetometer at an applied field of 0.2 T in the temperature range 2–300 K. Powder samples were placed and compacted inside a gelatin capsule. The magnetic susceptibilities were corrected for background signal of the sample holder and for the diamagnetism. The magnetic measurements were performed on finely powdered samples, and the data are given herein on a per mole copper basis.

Results and Discussion

Structure. Solid compounds containing carboxylate aromatic amines are common, as confirmed by a search in the CSD (November 2006 release and updates[11–15]) where a large number of such complexes are present, in particular many containing 2,2′-bipyridine dicarboxylate groups, in any of their variants (COO at 3,3′, 4,4′, 5,5′ or 6,6′) and displaying a large variety of coordination modes.

The first structure with a single carboxylate group at site 6 (a species we shall refer to as bpy-COO) could be surveyed.

The copper complex presented herein appears as the first example of such a structure. The compound $[Cu(PO_4H_2)(C_{11}H_7N_2O_2)]_n$ (**1**) is a polymeric one-dimensional structure, the elemental link of the chain being a tetranuclear unit containing two different embedded symmetry centers, as shown in Figure 1. The asymmetric unit (one-fourth of the preceding elemental link) consists of a copper cation in a square-pyramidal arrangement, the base defined by the two nitrogen atoms (N1 and N2) of a chelating bpy-COO unit,

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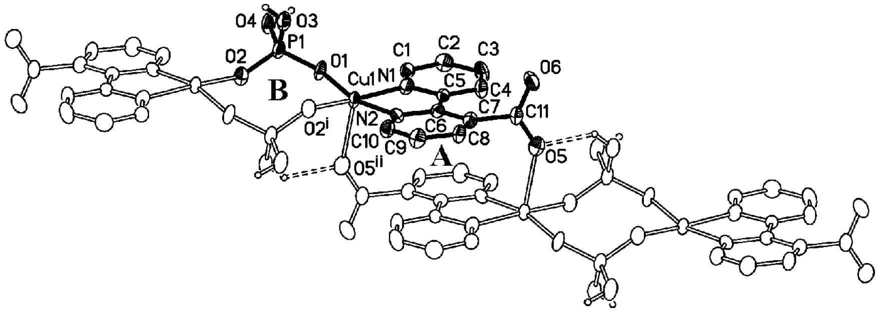


Figure 1. Molecular diagram of **1**, showing the numbering scheme used. The bridging modes for phosphate and bpy-COO groups take place around two different symmetry centers, defining two loops in the structure (labeled A and B). For clarity, only the asymmetric unit has been labeled, the labeling of the other atoms can be obtained by a simple symmetry operation.

and two oxygen atoms (O1 and O2^{i}; (i) $1 - x$, $1 - y$, $1 - z$) from two bridging phosphates (Table 4). The shape of this square arrangement is that of a squashed tetrahedron, with atoms departing alternatively at both sides of the mean plane by 0.06(1) Å, leaving the cation 0.18(1) Å aside toward the axial position. This axial site is occupied by one of the carboxylato oxygen atoms (O5^{ii}; (ii) $1 - x$, $2 - y$, $2 - z$) from a symmetry-related bpy-COO unit, with the Cu---O5^{ii} vector subtending an angle of 5.2(1)° to the plane.

The phosphate unit binds in a bridging mode, linking cations around a symmetry center. The anion is doubly protonated at the sites which are not involved in coordination (O3---H3 and O4---H4), and the effect is clearly visible in their P---O distances, some 4% longer than the coordinated distances (Table 4). The bpy-COO group also acts in a bridging fashion, one of its branches being the chelating N,N′ and the other the coordinated carboxylato oxygen O5. The group is unexceptional regarding bond distances and angles, and its sole distinctive feature is the planar carboxylato group standing upright at 82.1(1)° to the bipy mean plane. In spite of their asymmetry in coordination, the two C---O lengths are identical, suggesting a resonant double bond.

These bridging modes for phosphate and bpy-COO groups, which take place around two different symmetry centers, end up defining two loops in the structure (labeled A and B in Figure 1): a smaller, eight-membered loop defined by the phosphate molecule, containing Cu1---O1---P1---O2− plus its (i) symmetry-related counterpart, (where the path through covalent bonds joining metal centers amounts to 6.83 Å, leading to a Cu1···Cu1^{i} distance of 5.08 Å) and a much larger twelve-member loop through the bpy-COO, consisting of Cu1---N2---C6---C7---C11---O5 and its equivalent half, generated through the (ii) symmetry operation (with a bond pathway of 9.88 Å leading to a Cu1···Cu1^{ii} distance of 6.55 Å).

Table 5 presents the hydrogen bonds that stabilize the structure, in which both phosphato H atoms are involved, as shown in Figures 1 and 2. While H3 makes an intramolecular bond to a neighboring coordinated carboxylato oxygen (given by double broken lines in Figure 2), thus contributing to the chain stability, the bond involving H4 (given by a single broken line) makes a [100] interconnection of the chains running along the [011] direction, thus defining H-bonded layers parallel to (01–1) (shown in projection in Figure 2).

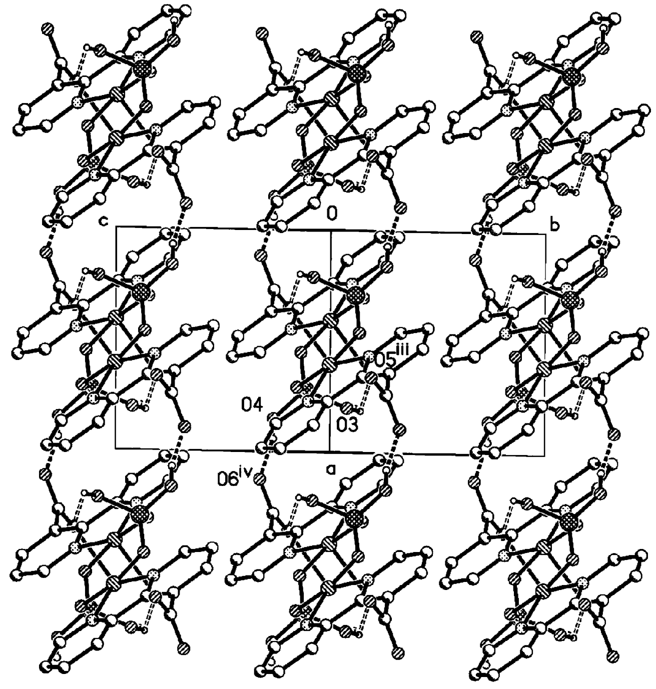


Figure 2. Packing view of **1**, showing the hydrogen bonds that stabilize the structure.

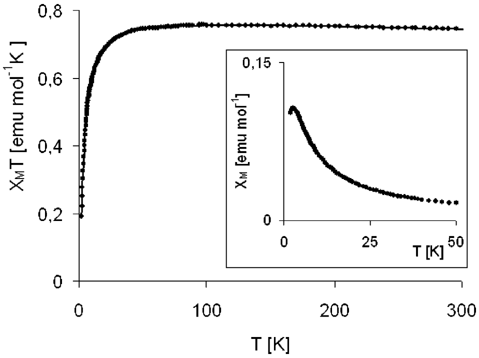
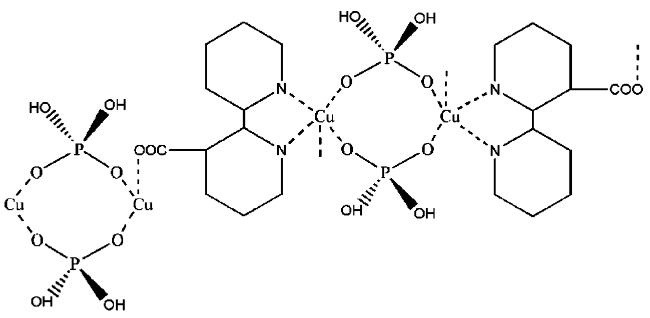


Figure 3. Product of molar susceptibility by temperature versus temperature (2–300 K). The solid line is the best fit of the Heisenberg alternating linear chain with $J = -3.32$ cm^{-1}, $\alpha = 0.7$, and $g = 2.05$. Insert: molar susceptibility versus temperature (2–50 K).

Magnetism. Figure 3 presents the product of molar susceptibility by temperature versus temperature, from which an antiferromagnetic interaction can be readily inferred. The graphic of molar susceptibility versus temperature (insert in Figure 3), shows a maximum of the susceptibility at 3 K. The high-temperature linear regression of the inverse susceptibility yields an effective moment of 1.79 μ_B and a

Scheme 1



Curie–Weiss temperature Θ of −2.1 K.

There are two possible magnetic exchange pathways in the structure, both of them via centrosymmetric bridges (A and B in Figure 1). The longest path is across a bridging bpy-COO unit, while the shortest path goes along a phosphate spacer. It was in principle reasonable to associate the second path with the stronger interactions, for which we tried a Bleaney–Bowers model[16] with a single intradimer interaction (the one along the phosphates), neglecting in turn the interaction between dimers (via the bpy-COO). Such a model turned out to be not appropriate to describe the experimental data, for which an interdimer interaction along the chain had to be included (that is, the longest path across the bridging bpy-COO unit).

Chain Model. In the general case of a chain such as that in **1** two different situations may occur: either the Cu centers are situated at a constant distance along the same magnetic pathway or they may alternate along two different magnetic pathways, presenting alternatively short and long intermetallic spacings.

The chain in **1** clearly falls into the second, alternating case (Scheme 1).

Such a situation can be schematized as

$$-A_{2i-1}\overset{J}{-}A_{2i}\overset{\alpha J}{-}A_{2i+1}-$$

for which the Hamiltonian could be written as

$$H = -J\sum_{i=1}^{n/2}\left[\hat{S}_{A_{2i}}\cdot\hat{S}_{A_{2i-1}} + \alpha\hat{S}_{A_{2i}}\cdot\hat{S}_{A_{2i+1}}\right]$$

In these expressions J is the exchange integral between a spin and its nearest neighbor within the same dimer (short distance) and αJ is the exchange integral between a spin and its neighbor situated in a nearby dimer (long distance); α is the alternation parameter ≤ 1. For $\alpha = 0$, this model corresponds to a dimer situation with pairwise interactions; for $\alpha = 1$, the model reduces to the regular, equally spaced linear-chain model. In our case, α is intermediate between 0 and 1 ($0 \leq \alpha \leq 1$) and the exchange interaction J is negative: that is, of antiferromagnetic type ($J < 0$). This model has been studied in detail by Duffy and Barr, Bonner and Friedberg, and Diederix et al.[17–19]

The analytical expression of the magnetic susceptibility for a 10-membered ring, which should be a reasonable approximation for an infinite system, is

$$X = \frac{Ng^2\beta^2}{kT}\cdot\frac{A+Bx+Cx^2}{1+Dx+Ex^2+Fx^3}$$

where $x = |J|/kT$, and the coefficients $A-F$ are functions of α.[9,20]

The best fit of the experimental data was for $\alpha = 0.7$, leading to $-3.33\ \text{cm}^{-1} \leq J \leq -3.31\ \text{cm}^{-1}$ and $2.00 \leq g \leq 2.10$ with the best value for $-3.32\ \text{cm}^{-1}$ and 2.05, respectively. The results of our calculations are in agreement with those previously reported by ter Harr and Hatfield for the alternating chain compound $\text{LiCuCl}_3\cdot 2\text{H}_2\text{O}$ ($J = -3.7\ \text{cm}^{-1}$, $g = 2.14$, and $\alpha = 0.89$[21]); although the bonding groups are different, the models of alternating chains are similar.

The product of molar susceptibility by temperature is displayed as a function of temperature in Figure 3, together with the best fit by an alternating Heisenberg linear chain (solid line).

The importance of H-bonding in magnetic interactions is well-known because of its structural role in holding oxygen atoms, which in turn, are directly linked to the copper atoms.[22] However, in our case, such an indirect magnetic pathway (Cu−carboxylato•••H−phosphate−Cu), although including one H-bond, can be neglected because of the quite large distances involved.

Conclusion

The polymeric compound $[\text{Cu}(\text{PO}_4\text{H}_2)(\text{C}_{11}\text{H}_7\text{N}_2\text{O}_2)]_n$ was synthesized by hydrothermal techniques, and its structure was refined. It consists of an infinite chain where the copper units are bonded to double-protonated phosphate groups and to bipyridinemonocarboxylate ligands. The magnetic behavior was analyzed by an alternating Heisenberg-chain model where the magnetic exchange pathway is assured through the phosphate bridge. The magnetic susceptibility data were analyzed in terms of an exchange coupling constant J between copper spins within a dimer, modulated (αJ) by an alternation parameter α for copper spins situated in neighboring dimers. Numerical values ($\alpha = 0.7$, $J = -3.32\ \text{cm}^{-1}$, $g = 2.05$) were obtained.

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Supporting Information Available: A CIF file giving crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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