



Copper Phosphonates

The Dimeric Pyramidal Cu₂O₆(H₂O)₂ Unit – A Structural Invariant of a Homologous Series of Copper-Layered Phosphonates

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Abstract: Two new layered copper hybrid materials, namely, the copper thiophene-2,5-diphosphonate $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ (*Pnma*; a = 7.525 Å, b = 18.292 Å, c = 7.520 Å) and the copper 3-fluorophenylphosphonate Cu(H₂O)PO₃-C₆H₄F (*P*2₁/*c*; a = 14.305 Å, b = 7.550 Å, c = 7.479 Å, $\beta = 92.32^{\circ}$), have been synthesized. These compounds belong to the large homologous Cu(H₂O)PO₃R/[Cu₂(H₂O)₂(O₃P-R-PO₃)] series, the structure of which is dictated by the presence of isolated dimeric pyramidal Cu₂O₆(H₂O)₂ units. The role of the Cu/H₂O mo-

lar ratio of 1 in the stabilization of such a structure is discussed in connection with the Jahn–Teller effect of the copper cation. The study of the magnetic behavior of polycrystalline samples of the two compounds has revealed antiferromagnetic coupling between the copper ions. The interactions within the dimeric unit were estimated by the Bleaney–Bowers law with the spin Hamiltonian $H = -JS_{Cu1}S_{Cu2} + g\beta HS$: J = -6.27 cm⁻¹ for $[Cu(H_2O)PO_3]_2C_4H_2S$, and J = -6.07 cm⁻¹ for Cu(H_2O)PO_3-C₆H₄F.

Introduction

Transition-metal layered phosphonates^[1,2] are an important class of hybrid inorganic-organic materials that have been investigated for various applications such as catalysis,^[3,4] protonic conductivity,^[5,6] sorption and ionic exchange,^[7–9] and magnetism.^[10–14] Recently, a layered copper (bromothienyl)phosphonate was shown to exhibit exfoliation properties, which allowed remarkably enhanced adsorption of Pb^{II} ions in aqueous solution compared with that of the bulk material.^[15] In this way, such hybrid offers a new route to the adsorption of toxic heavymetal ions in a more efficient way. The scarcity of this phenomenon suggests that the nature of the inorganic nanosheets plays a crucial role in the generation of these properties and raises the issue of the influence of the nature of the organic ligands upon the structure and chemical composition of the inorganic layers. In the present study, we have synthesized two new copper layered phosphonates, [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and Cu(H₂O)PO₃-C₆H₄F, from thiophene-2,5-diphosphonic acid (TPdP) and (3-fluorophenyl)phosphonic acid (FPP). We show that the structures of these hybrids consist of very

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Results and Discussion

The organic precursors thiophene-2,5-diphosphonic acid^[13] (Scheme 1, a) and 3-fluorophenylphosphonic acid^[17] (Scheme 1, b) were obtained by phosphonation of bromoaromatic precursors by adapted Tav^[18] methods.^[19]



Scheme 1. Chemical structures of the organic ligands used for the synthesis of hybrid materials: (a) TPdP and (b) FPP.

These phosphonic acid precursors were chosen because of their rigid structures, which result from the direct linkage of the phosphonic acid groups with a rigid aromatic ring. This rigidity favors the production of crystalline materials, as we and others have shown previously.^[20] More specifically, the thiophene-2,5-diphosphonic acid unit was also selected for comparison with the manganese compound obtained by Rueff et al.^[13] The (3-

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fluorophenyl)phosphonic acid unit was chosen for two additional reasons. First, this molecule presents one strong inductive withdrawing fluorine atom that decreases the two pK_a values of the phosphonic acid function.^[17] This increase of acidity should favor the formation of hybrid materials. However, the impact of this strong electron-withdrawing atom on the topology and properties of the final hybrid material was difficult to anticipate and constitutes one of the reasons of this study. The second reason for the choice of (3-fluorophenyl)phosphonic acid is its low symmetry, for instance, compared with (4-fluorophenyl)phosphonic acid. We have shown previously that the use of low-symmetry organic precursors can produce unexpected homochiral hybrid materials.^[21]

With these two organic precursors, two new hybrid materials were obtained as single crystals and polycrystalline pure phases by hydrothermal synthesis, namely, the copper thiophene-2,5diphosphonate [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and the copper (3fluorophenyl)phosphonate $Cu(H_2O)PO_3-C_6H_4F$ (the crystallographic data are presented in Table 1; for the positional and thermal parameters, see Supporting Information). In spite of their different symmetries, orthorhombic Pnma and monoclinic $P2_1/c$ space groups, respectively (Table 1), these phosphonatebased hybrids exhibit closely related frameworks. The views of the structure along a for [Cu₂(H₂O)₂(O₃P–C₄H₂S–PO₃)] (Figures 1 and S1-1) and along c for Cu(H₂O)PO₃-C₆H₄F (Figures 2 and S2-2) show that they both consist of inorganic "CuH₂OPO₃C" layers interleaved with "C4H2S" and "C6H4F" organic layers, respectively. In [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)], the (010) inorganic layers are interconnected by the PO₃C-C₂H₂S-CPO₃ diphosphonate groups along b, whereas the (100) inorganic layers in Cu(H₂O)PO₃-C₆H₄F are stacked with double organic PO₃C- C_6H_4F ···· $H_4FC_6PO_3C$ layers, which form F····H hydrogen bonds along a (H···F 2.52–2.98 Å; C–H···F 128.84–136.40°).^[22] The structure of the inorganic layers is practically the same in both phosphonates (Figure 3), as expected from the very close values of the lattice parameters (Table 1). The "CuH2OPO3C" layers are built up of isolated dimeric "Cu₂O₆(H₂O)₂" units. Each unit consists of two edge-sharing CuO₄(H₂O) pyramids; two free apices

Table 1. Crystallographic data of the "dimeric" copper phosphonates $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ and $Cu(H_2O)PO_3-C_6H_4F$ recorded at 150 K.

Formula	C ₄ H ₆ Cu ₂ O ₈ P ₂ S	C ₆ H ₆ CuO ₄ PF	
FW	403.17	255.62	
Space group	Pnma	P2 ₁ /c	
a [Å]	7.525(3)	14.3050(6)	
b [Å]	18.292(9)	7.5504(3)	
c [Å]	7.520(3)	7.4799(3)	
α, β, γ [°]	90, 90, 90	90, 92.3227(19), 90	
Z	4	4	
V [ų]	1035.11(80)	807.23(6)	
d _{calcd.} [g/cm ³]	2.587	2.103	
$\mu [{\rm mm}^{-1}]$	4.646	2.90	
Radiation source λ [Å]	Mo- <i>K</i> _α 0.71073	Mo- <i>K</i> _α 0.71073	
Pattern range 2θ [°]	5.84-73.92	5.70-66.34	
Reflections	34090	20434	
Soft constraints	0	0	
R _{wp}	0.0603	0.1746	
R _p	0.0231	0.0617	
R _F	0.0394	0.0409	
χ	1.087	1.084	

are occupied by H_2O molecules, and the six other apices are shared with six PO₃C tetrahedra.



Figure 1. Projection of the structure of $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ along the *a* axis.



Figure 2. Projection of the structure of $Cu(H_2O)PO_3-C_6H_4F$ along the *c* axis.

The analysis of the literature on hybrid inorganic–organic copper phosphonates shows that the TPdP- and FPP-based hybrids belong to a homologous series of compounds with the generic formulas $Cu(H_2O)PO_3R$ for the single phosphonates and $[Cu_2(H_2O)_2(O_3P-R-PO_3)]$ for the diphosphonates. In addition to the two compounds described here, and to the best of our knowledge, eleven other phosphonates have been found previously to exhibit this type of formula with a closely related structure. The crystallographic data of these 13 compounds is listed in Table 2 and shows that they exhibit inorganic CuH_2OPO_3C layers isostructural to that described above, i.e., they are characterized by the same 2D orthogonal lattice of approx. 7.5 \times 7.5 Å.





Figure 3. Projection of the structure of the inorganic layers in $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ and $Cu(H_2O)PO_3-C_6H_4F$.

In the single phosphonates Cu(H₂O)PO₃R, this arrangement of the inorganic layers is indeed observed for a large variety of organic groups, namely, 3-fluorophenyl (present work), 5-(2-bromothienyl),^[15] methyl,^[23,24] ethyl,^[25] propyl,^[26] bromoethyl,^[25] benzyl,^[24] 2-carboxyethyl,^[25] cyclohexene,^[27] and fluorene.^[28] The number of [Cu₂(H₂O)₂(O₃P–R–PO₃)] diphosphonates is quite limited; in addition to the thiophenyl phase R = C₄H₂S obtained in the present work, only two copper diphosphonates corresponding to this generic formulation with the same arrangement of the inorganic layers have been synthesized previously for R = C₂H₄^[29,30] and *p*-C₆H₄.^[31]



Thus, the Cu(H₂O)PO₃R and [Cu₂(H₂O)₂(O₃P-R-PO₃)] phosphonates form a large homologous series; the structures of these phosphonates differ by the nature and thickness of the organic layers, which induces a possible translation of the inorganic layers with respect to each other. Remarkably, the nature of the organic ligand does not affect the framework of the inorganic layers significantly. The interatomic distances of these compounds (Table S4-1) show that the geometry of the $CuO_4(H_2O)$ pyramid is practically the same whatever the organic ligand: the four equatorial Cu–O distances range from 1.91 to 1.99 Å, and the apical distance is between 2.31 and 2.40 Å. The condensed nature of the dimeric Cu₂ species with Cu-Cu distances ranging from 3.04 to 3.15 Å is also not affected by the organic ligands. As expected, the PO₃C tetrahedra are very similar; the three P-O bonds range from 1.525 to 1.537 Å, and the P-C bond length is between 1.782 and 1.799 Å.

The cell parameters that characterize the 2D orthogonal lattice (Table 2) are between 7.32 and 7.65 Å and also vary only slightly; this confirms that the arrangement of the copper pyramids and PO₃C tetrahedra is practically not influenced by the nature of the organic ligand. The above observations show that the dimeric pyramidal $Cu_2O_6(H_2O)_2$ unit is a structural invariant of this homologous series and imposes a particularly rigid geometry of the inorganic layers of these hydrated copper phosphonates.

To the best of our knowledge, only two other phosphonates with the Cu(H₂O)PO₃R formulation exhibit a different structure of their inorganic layers. The first exception concerns the 4-(3bromothienyl)phosphonate Cu(H₂O)PO₃-C₄H₂BrS.^[31] Though it shows some similarity with the 5-(2-bromothienyl)phosphonate in the lattice parameters (Table 2), the structure of its inorganic layers is completely different and consists of dimeric units of edge-sharing CuO₆ octahedra. This difference is explained by the fact that the Br atom is at the α position with respect to the C atom of the PO₃C group; this is in contrast to the 5-(2bromothienyl)phosphonate and leads to a very close proximity

Table 2. Crystallographic data of isostructural inorganic layers made of dimeric copper phosphonates.

Chemical formula	Space group	Cell parameters		Reference
		a, b, c [Å]	α, β, γ [°]	
[Cu ₂ (H ₂ O) ₂ PO ₃ -C ₄ H ₂ S-PO ₃]	Pnma	7.525, 18.292, 7.520	90, 90, 90	this work
$Cu(H_2O)PO_3-C_6H_4F$	P21/c	14.305, 7.550, 7.4479	90, 92.32, 90	this work
β -Cu(H ₂ O)PO ₃ -C ₄ H ₂ BrS	P21/c	15.899, 7.627, 7.344	90, 100.07, 90	[15]
$Cu(H_2O)PO_3-CH_3$	P21/c	8.530, 7.602, 7.321	90, 90.11, 90	[22]
Cu(H ₂ O)PO ₃ -CH ₃	P2 ₁ /c	8.495, 7.580, 7.289	90, 90.08, 90	[24]
$Cu(H_2O)PO_3-C_6H_5$	Pbca	7.555, 7.448, 27.982	90, 90, 90	[24]
$Cu(H_2O)PO_3-CH_2-CH_3$	unknown	7.47, 9.94, 7.51	90, 93.1, 90	[25]
Cu(H ₂ O)PO ₃ (CH ₂) ₂ CO ₂ H	unknown	7.39, 12.54, 7.55	90, 93.3, 90	[25]
$Cu(H_2O)PO_3(CH_2)_2Br$	unknown	7.65, 11.26, 7.67	90, 89.5, 90	[25]
$Cu(H_2O)PO_3-C_3H_7$	P2 ₁ /a	7.437, 7.611, 12.011	90, 97.78, 90	[26]
$Cu(H_2O)PO_3 - C_6H_9$	P21/c	14.415, 7.612, 7.529	90, 92.12, 90	[27]
$Cu(H_2O)PO_3 - C_{13}H_9$	$P2_1/a$	7.497, 7.547, 22.370	90, 97.79, 90	[28]
$[Cu(H_2O)(O_3P-p-C_6H_4-CO_2H)]$	P21/c	8.076, 7.587, 7.410	90, 116.32, 90	[29]
$[Cu_2(H_2O)_2(O_3P-p-C_6H_4-CO_2H)]$	$P2_1/c$	8.075, 7.587, 7.399	90, 116.32, 90	[30]
$[Cu_2(H_2O)_2(O_3P-p-C_6H_4-CO_2H)]$	C2/c	18.889, 7.622, 7.464	90, 90.4, 90	[31]
Exceptions				
α -Cu(H ₂ O)PO ₃ -C ₄ H ₂ BrS	P2 ₁ /c	13.578, 7.587, 7.956	90, 99.8, 90	[32]
$Cu(H_2O)PO_3-m-C_6H_4-CO_2H$	P2 ₁ /m	4.841, 32.557, 5.784	90, 96.02, 90	[21]



of the Br atom and the inorganic layer. The second exception deals with the (carboxyphenyl)phosphonate Cu(H₂O)PO₃-m-C₆H₄-COOH,^[21] whose layered structure consists of copper octahedra that form a pseudo-perovskite 2D lattice. This different behavior might be due to the experimental conditions, as the pH was shown to play a crucial role in the selectivity of various compounds during the synthesis. The review of all the copper phosphonates shows that the formation of such dimeric pyramidal units is unique and only suited to the Cu(H₂O)PO₃R/ [Cu₂(H₂O)₂(O₃P-R-PO₃)] series, and the Cu/H₂O molar ratio must be equal to 1. It is indeed remarkable that anhydrous copper phosphonates such as CuPO₃R with $R = CH_3$, C_2H_5 , C_6H_5 , and CH₂C₆H₅ or other hydrated copper phosphonates such as $Cu_2[(O_3PC_4H_8PO_3)(H_2O)_2]\cdot 2H_2O_1$ $Cu_3O(CH_3PO_3)_2 \cdot 2H_2O_1$ and $Cu_{2}[(O_{3}PC_{5}H_{10}PO_{3})(H_{2}O)_{2}]$

 $2{\centerdot}8H_2O^{[33-35]}$ do not exhibit such pyramidal Cu_2O_8 or $Cu_2O_6(H_2O)_2$ units.

The evolution of the magnetic susceptibility (χ) and the product of the susceptibility and temperature (χT) versus temperature for [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and Cu(H₂O)PO₃- C_6H_4F are presented in Figures 4 and 5, respectively. For the TPdP and FPP hybrids, the susceptibilities increase continuously from 0.00162 and 0.00159 emu/mol, respectively, at 280 K to reach maximum values of 0.03995 and 0.03994 emu/mol at 5 K. Below this temperature, χ decreases to 0.02568 and 0.02453 emu/mol at 2 K for [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and Cu(H₂O)PO₃-C₆H₄F, respectively. These χ curves are typical of antiferromagnetic behavior. For χT , the curves present plateaus from 280–70 K with corresponding χT values of 0.45027 and 0.4377 emu K/mol for [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and Cu(H₂O)PO₃-C₆H₄F, respectively. Below 70 K, χT decreases to reach values of 0.05136 and 0.04906 emu K/mol at 2 K. The χ = f(T) and $\gamma T = f(T)$ curves were fit simultaneously with the Bleaney–Bowers law^[16] with the spin Hamiltonian H = $-JS_{Cu1}S_{Cu2} + g\beta HS$; all of the parameters have their usual meaning, and the spin operator is defined as $S = S_{Cu1} + S_{Cu2}$.



Figure 4. Variation of χ (open black circles) and χT (open black squares) with temperature for $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ under 1000 Oe. The red full line corresponds to the best fit of the experimental data to the Bleaney–Bowers law. Inset: $1/\chi$ versus *T* and Curie–Weiss fit (performed between 150 and 280 K) leading to *C* = 0.45 emu K/mol.

For the TPdP hybrid, the fit leads to J = -6.27(4) cm⁻¹, g = 2.21(1); and that for the FPP hybrid leads to J = -6.07(3) cm⁻¹, g = 2.18(1). Note that the interdimer exchange coupling was neglected on the basis of our previous results for Cu^{II} *n*-alkyl-phosphonates.^[26]





Figure 5. Variation of χ (open black circles) and χT (open black squares) with temperature for Cu(H₂O)PO₃–C₆H₄F under 1000 Oe. The red full line corresponds to the best fit of the experimental data to the Bleaney–Bowers law. Inset: $1/\chi$ versus *T* and Curie–Weiss fit (performed between 150 and 280 K) leading *C* = 0.44 emu K/mol.

Conclusions

Two new members of the homologous series of layered copper phosphonates Cu(H₂O)PO₃R/[Cu₂(H₂O)₂(O₃P-R-PO₃)] have been synthesized. A comparative study of the 13 known members of the whole series shows that the crystal chemistry of these compounds is dominated by the formation of unique dimeric $Cu_2O_6(H_2O)_2$ pyramidal units. The stability of such strongly condensed units, in which two pyramids share one edge, is rather rare. Beyond the fact that the Cu²⁺ ion favors the pyramidal coordination owing to the Jahn-Teller effect, the presence of one water molecule per copper ion apparently plays a crucial role in the stabilization of such units by decreasing significantly the negative charge and, consequently, electronic repulsions around the Cu-Cu dimer relative to those for an eventual Cu₂O₈ unit. The antiferromagnetic behaviors of both compounds were fitted by the Bleaney-Bowers law, which led to exchange constants of ca. -6 cm⁻¹ for both compounds.

Experimental Section

General: Thiophene-2,5-diphosphonic acid was synthesized by following the reported procedures.^[13]

All compounds were characterized by NMR spectroscopy [Bruker AC 300, Avance DRX 400, or Avance DRX 500 spectrometers were used to record the NMR spectroscopic data (¹H: 500, 400, or 300 MHz; ³¹P: 162 or 121.5 MHz; ¹³C: 125.8 or 75.5 MHz)]. The chemical shifts are in ppm. Coupling constants *J* are given in Hz. The following abbreviations are used: s singlet, d doublet, t triplet, q quadruplet, qt quintuplet, m multiplet, and dt doublet of triplets. The ESI mass spectra were recorded with a Shimadzu LCMS-2020 instrument with samples in MeOH. The IR spectra of the organic compounds were recorded with a Nicolet Nexus FTIR spectrometer working in the transmittance mode in the $\tilde{\gamma} = 200-4000 \text{ cm}^{-1}$ range. 3-Bromofluorobenzene was purchased from TCI, and 2,5-dibromothiophene was purchased from Acros and used without further purification. For both hybrid materials, inorganic reagents were purchased from Sigma–Aldrich.

The thermogravimetric analysis (TGA) of polycrystalline samples was performed with a SETARAM TAG 92 apparatus under a nitrogen atmosphere for $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ and an air atmosphere for $Cu(H_2O)PO_3-C_6H_4F$ at a heating rate of 3 °C/min from room temperature to 1000 °C. The scanning electron microscopy (SEM) characterization was performed with a Carl Zeiss SUPRA 55 instru-





ment with raw samples with gold metallization. The magnetic susceptibilities were recorded versus temperature with a Quantum Design superconducting quantum interference device (SQUID) magnetometer operating in the temperature range 2–300 K under zero-field cooling (ZFC) and field cooling (FC) conditions with an applied magnetic field of 0.1 T. The data were corrected for the sample holder, and diamagnetism was estimated from Pascal constants.

Diethyl 3-Fluorophenylphosphonate: To a solution of NiBr₂ (1.87 g, 8.57 mmol; 6 %) suspended in mesitylene (25 mL) and 3bromofluorobenzene (25 g, 142.86 mmol) under nitrogen at 165 °C for activation was added triethyl phosphite (27 mL, 157.14 mmol, 1.1 equiv.) by slow and discontinuous dropwise addition (this addition must be achieved with care). At the end of the addition, the reaction mixture was stirred at 165 °C overnight. After the reaction mixture cooled, the excess triethyl phosphite and mesitylene were removed by distillation under reduced pressure (ca. 0.1 mbar). The resulting mixture was dissolved in dichloromethane (250 mL), and water (250 mL) was added. The heterogeneous solution was stirred at room temperature for 6 h. The two layers were separated, and the organic layer was washed with water (250 mL). The aqueous phase was extracted with dichloromethane (2×250 mL). The organic layers were combined, dried with MgSO₄, and evaporated under reduced pressure to yield a clear oil. The crude product was purified by silica gel column chromatography (CH₂Cl₂) to yield a clear oil (24.0 g, 72 %). R_f (CH₂Cl₂/MeOH: 98:2): 0.3. ¹H NMR (CDCl₃, 500 MHz): δ = 1.33 (t, ³J = 7.5 Hz, 6 H, CH₃), 4.05–4.21 (m, 4 H, CH₂), 7.19–7.25 (td, ${}^{3}J$ = 9.0 Hz, ${}^{4}J$ = 2.5 Hz, 1 H, H_{Ar4}), 7.39–7.52 (m, 2 H, H_{Ar2+5}), 7.54–7.56 (ddm, J = 7.5, 12.9 Hz, 1 H, H_{Ar6}) ppm. ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ = 17.1 (d, ⁴J_{P,F} = 8.8 Hz) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ = 16.2 (d, ${}^{3}J_{P,C}$ = 6.4 Hz, CH₃), 62.3 (d, ${}^{2}J_{C,P}$ = 5.4 Hz, CH₂), 118.5 (dd, ³J = 10.4 Hz, ³J = 10.4 Hz, CH_{Ar2}), 119.5 (dd, ${}^{2}J_{C,F} = 21.1 \text{ Hz}, {}^{4}J_{C,P} = 2.5 \text{ Hz}, \text{ CH}_{Ar4}$, 127.4 (dd, ${}^{2}J_{C,P} = 9.0 \text{ Hz}, {}^{4}J_{C,F} =$ 2.7 Hz, CH_{Ar6}), 130.4 (dd, ³J = 7.4, 7.3 Hz, CH_{Ar5}), 131.0 (dd, ¹J_{C,P} = 189.0 Hz, ${}^{3}J_{C,F}$ = 6.0 Hz, C_{q1}), 162.3 (dd, ${}^{1}J_{C,F}$ = 249.0 Hz, ${}^{3}J_{C,P}$ = 21.4 Hz, C_{q3}) ppm. ¹⁹F {¹H} NMR (CDCl₃, 282 MHz): δ = -112.1 (d, ${}^{4}J_{F,P} = 8.8 \text{ Hz}$ ppm. MS: $m/z = 233.00 \text{ [M + H]}^{+}$, 265.00 [M + Na]⁺, 465.10 $[2M + H]^+$, 488.15 $[2M + H + Na]^+$. IR: $\tilde{v} = 961$ (C–O), 1015 (P-O), 1224 (P=O), 1426 (C-F), 2984 (C-H) cm⁻¹.

3-Fluorophenylphosphonic Acid: Diethyl 3-fluorophenylphosphonate (20 g, 86.1 mmol) was dissolved in concentrated hydrochloric acid (125 mL). The solution was stirred under reflux overnight. The HCl and water were evaporated under reduced pressure to give a white powder (14.0 g, 93 %). ¹H NMR (D₂O, 400 MHz): δ = 7.28 (t, ${}^{3}J$ = 8.4 Hz, 1 H, H_{Ar}), 7.42–7.56 (m, 3 H, H_{Ar}) ppm. ${}^{31}P{}^{1}H$ NMR (D₂O, 162 MHz): δ = 14.0 (d, ⁴J_{P,F} = 7.9 Hz) ppm. ¹³C{¹H} NMR (D₂O, 125 MHz): δ = 119.7 (dd, ³J = 10.9, 10.9 Hz, CH_{Ar2}), 121.4 (dd, ${}^{2}J_{C,F} = 21.2 \text{ Hz}, {}^{4}J_{C,P} = 2.6 \text{ Hz}, \text{ CH}_{Ar4}$), 129.0 (dd, ${}^{2}J_{C,P} = 9.5 \text{ Hz}, {}^{4}J_{C,F} =$ 2.7 Hz, CH_{Ar6}), 133.5 (dd, ³J = 7.8, 7.8 Hz, CH_{Ar5}), 137.0 (dd, ¹J_{C,P} = 181.7 Hz, ${}^{3}J_{C,F}$ = 6.1 Hz, C_{q1}), 164.9 (dd, ${}^{1}J_{C,F}$ = 246.2 Hz, ${}^{3}J_{C,P}$ = 21.0 Hz, C_{q3}) ppm. ¹⁹F{¹H} NMR (D₂O, 282 MHz): $\delta = -113.1$ (d, ⁴ $J_{P,F} =$ 8.5 Hz) ppm. MS: m/z = 177.00 [M + H]⁺, 218.05 [M + H + CH₃CN]⁺, 259.00 [M + H + 2CH₃CN]⁺, 353.00 [2M + H]⁺, 394.00 [2M + H + CH_3CN ⁺, 529.05 [3M + H]⁺. IR: \tilde{v} = 1001 (P–O), 1231 (P=O), 1425 (C–F), 2000–3000 (O–H) cm⁻¹. UV/Vis (MeOH): $\lambda_{max} = 216$ nm.

Single-Crystal X-ray Diffraction: For both compounds, suitable single crystals were selected, and X-ray diffraction experiments were performed at 150 K with a Bruker-Nonius Kappa CCD area detector diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). SHELXL-2014 was used to refine the structure.

CCDC 1478143 {for $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ } and 1478142 [for $Cu(H_2O)PO_3-C_6H_4F$] contain the supplementary crystallographic

data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

The homogeneity of both phases was confirmed by powder X-ray diffraction (Supporting Information).

[**Cu₂(H₂O)₂(O₃P–C**₄H₂S–**PO**₃)]: A mixture of Cu(NO₃)₂·3H₂O (0.409 mmol, 0.0990 g, 2 equiv.) and tetraethyl thiophene-2,5-diphosphonate (0.205 mmol, 0.0502 g, 1 equiv.) was placed in a 50 mL polytetrafluoroethylene (PTFE) liner (Scheme 1, a). To these reagents, urea (0.409 mmol, 0.0247 g, 1 equiv.) was added, and then all precursors were dissolved in distilled water (10 mL). The liner was transferred into a Berghof DAB-2 pressure digestion vessel, and the mixture was heated from room temperature to 140 °C over 25 h, kept at 140 °C for 35 h, and a cooled to room temperature over 25 h. The final product, obtained as green platelets, was collected by filtration, washed with distilled water, rinsed with ethanol, and then dried in air. Cu₂C₄H₆P₂O₈S (403.17): calcd. C 11.92, H 1.50; found C 11.65, H 1.78.

Cu(H₂O)PO₃-C₆H₄F: Cu(H₂O)PO₃-C₆H₄F (Scheme 1, b) was obtained by the same process as described previously from Cu(NO₃)₂·3H₂O (0.0687 g, 0.284 mmol), (3-fluorophenyl)phosphonic acid (0.0501 g, 0.284 mmol), and urea (NH₂)₂CO (0.017 g, 0.203 mmol) in distilled water (15 mL). The heating cycle was as follows: room temperature to 140 °C over 20 h, 30 h at 140 °C, and room temperature over 20 h. CuC₆H₆PO₄F (255.62): calcd. C 28.19 H 2.37; found C 27.96, H 2.79.

Thermogravimetric Analysis: The TGA curves for polycrystalline samples of [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and Cu(H₂O)PO₃-C₆H₄F are presented in Figure 6. Both compounds exhibited thermal stability from room temperature to 140 °C, in agreement with the presence of a first plateau in the curves. The first weight losses, from 140-200 °C, indicate the departure of the water molecules linked to the Cu centers and correspond to two and one H₂O molecule per formula for the TPdP and FPP hybrids, respectively. For the TPdP hybrid, the experimental value of 8.40 % is in good agreement with the calculated value of 8.96 % expected for the departure of two water molecules, and the loss of 6.77 % for the FPP hybrid corresponds to a theoretical value of 7.05 % for the departure of one water molecule. From 200-300 °C, a second plateau provides evidence of the thermal stability of the dehydrated compounds [Cu-PO₃]₂-C₄H₂S and CuPO₃-C₆H₄F. Beyond 300 °C, the last weight losses can be attributed to the decomposition of the organic moieties and to the transformation of the dehydrated compounds into Cu₂P₂O₇ at 830 °C for [Cu₂(H₂O)₂(O₃P-C₄H₂S-PO₃)] and at 560 °C for $Cu(H_2O)PO_3-C_6H_4F$. The copper pyrophosphate was identified by powder X-ray diffraction with the TGA residues.



Figure 6. TGA curves of $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ (full line) and $Cu(H_2O)PO_3-C_6H_4F$ (dashed line) recorded under nitrogen and air, respectively.





Scanning Electron Microscopy: The homogeneous batches of $[Cu_2(H_2O)_2(O_3P-C_4H_2S-PO_3)]$ were identified as platelets with an average length of 34.3 µm, width of 25.7 µm, and an average thickness of 2 µm (see Supporting Information).

Cu(PO₃–C₆H₄F)·H₂O also consists of platelets with lengths of 85.7–108.6 μ m, widths of 51.4–100 μ m, and an average thickness of 1.6 μ m (see Supporting Information).

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Copper Phosphonates

The Dimeric Pyramidal Cu₂O₆(H₂O)₂ Unit – A Structural Invariant of a Homologous Series of Copper-Layered Phosphonates



The layered copper phosphonates $Cu(H_2O)PO_3R$ and $[Cu_2(H_2O)_2(O_3P-R-PO_3)]$ form a large structural family characterized by the presence of condensed dimeric pyramidal $Cu_2O_6(H_2O)_2$ units. Two new members of this family with $R = C_6H_4F$ and C_4H_4S are synthesized. These hybrids exhibit antiferromagnetic interactions between the copper ions that obey the Bleaney–Bowers law.

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