

New Types of Metal Squarato-phosphonates: Condensation of Aminodiphosphonate with Squaric Acid under Hydrothermal Conditions

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The syntheses and crystal structures of the first copper(I) phosphonate, $\text{Cu}_2(\text{H}_3\text{L})(\text{bipy})_2 \cdot 2\text{H}_2\text{O}$ **1** ($\text{H}_5\text{L} = \text{C}_4\text{HO}_3\text{N}(\text{CH}_2\text{-PO}_3\text{H}_2)_2$), which is also the first example of metal phosphonates formed by a type of organic reaction, and a novel luminescent Mn(II) squarate diphosphonate, $\{\text{Mn}[\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)]_2(\text{H}_2\text{O})_2\}_2\{\text{Mn}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_4\} \cdot (\text{C}_4\text{H}_2\text{O}_4)$ **2**, have been reported. The structure of **1** features a layer architecture in which the Cu(I) centers are three coordinated, and the newly formed ligand acts as a bidentate metal linker. Compound **2** is composed of 1D chains of $\text{Mn}[\text{NH}(\text{CH}_2\text{-PO}_3\text{H}_2)]_2(\text{H}_2\text{O})_2$, 1D chains of $\{\text{Mn}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_4\}$, as well as the neutral squaric acid molecules. These three types of building units are interconnected via hydrogen bonding.

Introduction

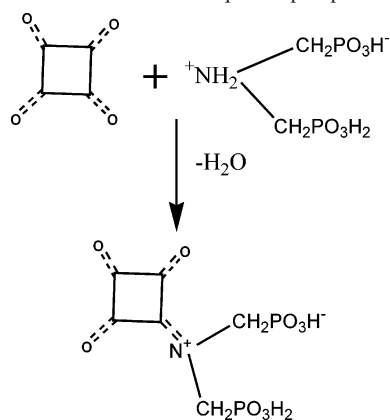
Recently, a lot of research effort has been devoted to the synthesis and designing of metal phosphonates with novel open-framework or microporous structures due to their potential applications in electrooptical, ion-exchange, catalysis, and sensors.¹ The strategy of attaching functional groups such as crown ether, amine, hydroxyl, and carboxylate groups to the phosphonic acid has proven to be effective for the isolation of a variety of metal phosphonates with open-framework and microporous architectures.^{2–7} Another useful synthetic strategy for the open frameworks based on metal phosphonates involves a second ligand such as 4,4'-bipyridine (bipy) or a carboxylic acid. The use of bidentate metal

linkers such as 1,10-phenanthroline, 2,2'-bipyridine, piperazine, and 4,4'-bipyridine has been successful for building mixed-metal hybrid structures of V and Mo as well as other transition metal hybrid compounds with 1D, 2D, and 3D structures.⁷ Metal phosphonates containing additional oxalate, 1,3,5-benzenetricarboxylate, carboxylate-sulfonate ligands have been reported by us and others.^{2,8,9} Our exploration of novel transition metal aminodiphosphonates with squaric acid as the second metal linker afforded a new layered copper(I) phosphonate, $\text{Cu}_2(\text{H}_3\text{L})(\text{bipy})_2 \cdot 2\text{H}_2\text{O}$ **1**, in which a new multifunctional squarato-imino-diphosphonate ligand (H_5L) was formed by the condensation reaction between one C=O group of the squaric acid and the amino group of NH-

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Scheme 1. Formation of the New Squarato-phosphonic Ligand, H₅L**Table 1.** Summary of Crystal Data and Refinements for **1** and **2**

	1	2
formula	C ₂₆ H ₂₆ Cu ₂ N ₅ O ₁₁ P ₂	C ₁₂ H ₃₂ Mn ₃ N ₂ O ₂₈ P ₄
fw	773.54	941.09
temp, K	293(2)	293(2)
space group	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)
<i>a</i> , Å	11.7680(4)	7.6267(1)
<i>b</i> , Å	12.1790(4)	8.1689(1)
<i>c</i> , Å	12.6422(4)	12.8587(4)
α /deg	77.886(1)	95.724(2)
β /deg	65.213(1)	103.905(2)
γ /deg	63.538(1)	90.657(2)
<i>V</i> , Å ³	1472.05(8)	773.24(3)
<i>Z</i>	2	1
<i>D</i> _{calc} , g cm ⁻³	1.745	2.021
μ , mm ⁻¹	1.624	1.527
GOF	1.069	1.114
R1, wR2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0441, 0.1107	0.0669, 0.1491
R1, wR2 (all data)	0.0498, 0.1172	0.0882, 0.1672

$$^a R1 = \sum(|F_o| - |F_c|) / \sum |F_o|, wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

(CH₂PO₃H₂)₂ (Scheme 1), and a new luminescent mixed-ligand Mn(II) squarate diphosphonate, {Mn[NH(CH₂PO₃H₂)₂](H₂O)₂}₂{Mn(C₄O₄)(H₂O)₄}·(C₄H₂O₄) **2**. Herein, we report their syntheses, physical properties, and crystal structures.

Experimental Section

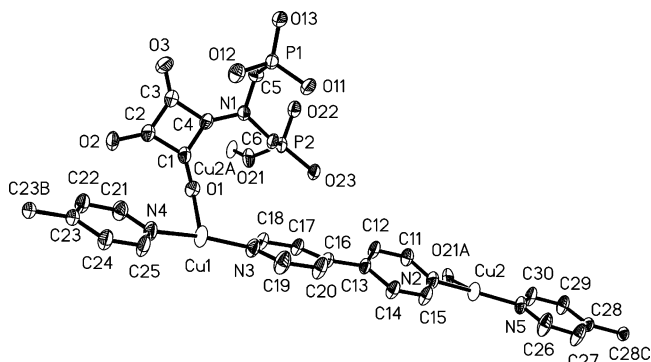
Materials and Instrumentations. All chemicals were from commercial sources and were used as received and without further purification. Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm⁻¹. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. X-ray powder diffraction (XRD) patterns (Cu K α) were collected in a sealed glass capillary on a XPERT-MPD θ -2 θ diffractometer. Magnetic susceptibility measurements for compounds **1** and **2** were carried out on a Quantum Design PPMS at a magnetic field of 1000 G in the range of 2–300 K. The raw data were corrected for the susceptibility of the container and the diamagnetic contributions of the sample using Pascal's constants.

Synthesis of Cu₂(4,4'-bipy)₂(H₅L)·2H₂O (1**).** A mixture of copper(II) acetate (0.5 mmol), HN(CH₂PO₃H₂)₂ (0.5 mmol), squaric acid (0.25 mmol), 4,4'-bipyridine (0.25 mmol), and distilled water (10 mL) with an initial pH = 2 was put into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 5 days. Brown brick-shaped crystals of **1** were collected in ca. 35% yield based on copper. Its purity was also confirmed by XRD powder diffraction. Anal. Calcd for C₂₆H₂₆Cu₂N₅O₁₁P₂ (Mr = 773.54): C, 40.37; H,

Table 2. Selected Bond Lengths (Å) for Compounds **1**^a and **2**^b

1			
Cu(1)–N(3)	1.891(3)	Cu(2)–N(2)	1.917(3)
Cu(1)–N(4)	1.891(3)	Cu(2)–N(5)	1.926(3)
Cu(1)–O(1)	2.423(3)	Cu(2)–O(21)#1	2.392(3)
Hydrogen Bonds			
O(12)···O(2)#2	2.524(4)	O(12)–H(12b)···O(2)#2	175.6
O(23)···O(13)#3	2.583(3)	O(23)–H(23a)···O(13)#3	179.3
O(11)···O(22)#3	2.443(3)		
2			
Mn(1)–O(22)#1	2.100(5)	Mn(2)–O(2)#3	2.119(5)
Mn(1)–O(23)	2.169(5)	Mn(2)–O(2)	2.119(5)
Mn(1)–O(2W)	2.193(5)	Mn(2)–O(4W)#3	2.201(6)
Mn(1)–O(13)	2.199(5)	Mn(2)–O(4W)	2.201(6)
Mn(1)–O(12)#2	2.201(5)	Mn(2)–O(3W)	2.254(5)
Mn(1)–O(1W)	2.266(5)	Mn(2)–O(3W)#3	2.254(5)
Hydrogen Bonds			
O(11)···O(3)	2.588(7)	O(11)–H(11a)···O(3)	169.3
O(1)···O(3W)#5	2.678(7)	O(4)···O(2W)#5	2.645(7)
O(4)···O(4W)	2.752(8)		

^a Symmetry codes for **1**: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 3, -y, -z$; #3 $-x + 2, -y + 1, -z$. ^b Symmetry codes for **2**: #1 $-x, -y + 1, -z + 2$; #2 $-x + 1, -y + 1, -z + 2$; #3 $-x + 1, -y + 1, -z + 1$; #4 $x, y + 1, z$; #5 $x + 1, y, z + 1$.

**Figure 1.** ORTEP representation of the selected unit of **1**. The thermal ellipsoids are drawn at 50% probability. The lattice water molecules have been omitted for clarity.

3.39; N, 9.05. Found: C, 40.45; H, 3.22; N, 9.03. IR data (cm⁻¹): 3456 (m), 3049 (w), 1788 (w), 1610 (m), 1527 (s), 1408 (m), 1298 (m), 1225 (m), 1153 (m), 1061 (m), 926 (m), 820 (m), 725 (m), 519 (m).

Synthesis of {Mn[NH(CH₂PO₃H₂)₂](H₂O)₂}₂{Mn(C₄O₄)(H₂O)₄}·C₄H₂O₄ (2**).** A mixture of manganese(II) sulfate (0.75 mmol), HN(CH₂PO₃H₂)₂ (H₅L) (0.5 mmol), squaric acid (0.5 mmol), and distilled water (10 mL) with the pH value adjusted to 3 by addition of 1 M NaOH solution was put into a Teflon-lined autoclave (23 mL) and then heated at 180 °C for 5 days. Colorless prismatic crystals of compound **2** were obtained as a single-phase product. Yield: 54% based on Mn. Compound **2** can also be prepared by using 2,2'-bipyridine instead of sodium hydroxide in the above reaction mixture in a much lower yield (33%). Its purity is also confirmed by XRD powder diffraction. Anal. Calcd for C₁₂H₃₂Mn₃N₂O₂₈P₄ (Mr = 941.09): C, 15.32; H, 3.43; N, 2.98. Found: C, 15.26; H, 3.25; N, 3.07. IR data (cm⁻¹): 3600–2300 (br), 1538 (s), 1326 (m), 1274 (s), 1194 (s), 1094 (s), 1048 (s), 934 (s), 907 (s), 718 (m), 559 (m).

Single-Crystal Structure Determination. Single crystals of compounds **1** and **2** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for

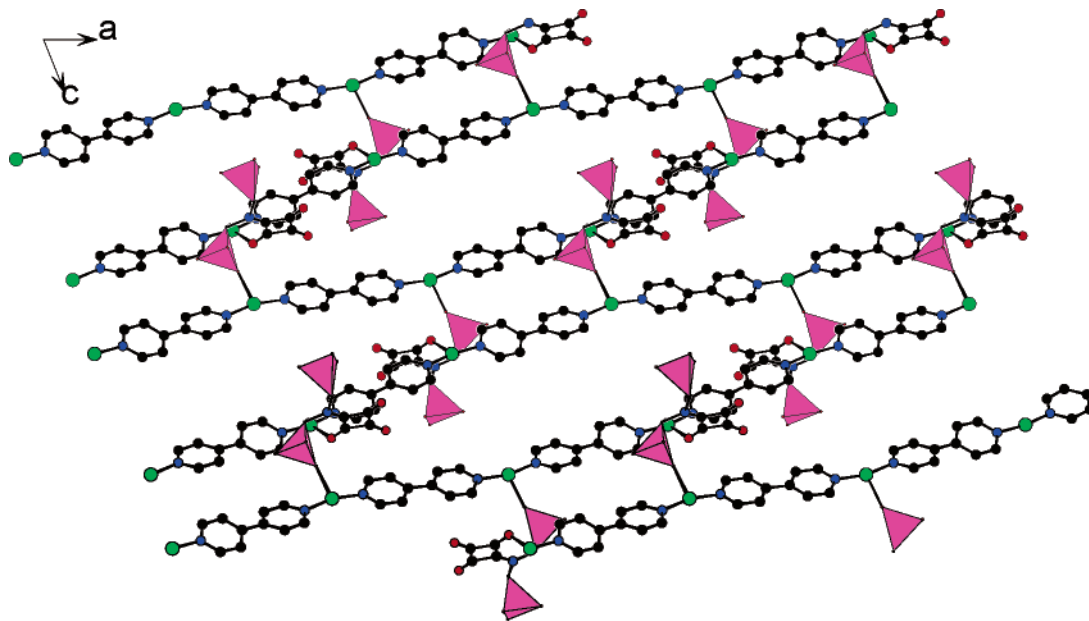


Figure 2. A 2D layer of $\text{Cu}_2(\text{H}_3\text{L})(\text{bipy})_2$ in **1**. The CPO_3 groups are represented by pink tetrahedra. Cu, N, O, and C atoms are drawn as green, blue, red, and black circles, respectively.

Lorentz and polarization factors as well as for absorption by SADABS program.¹⁰ Both structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.¹⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and structural refinements for compounds **1** and **2** are summarized in Table 1. Important bond lengths and angles are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

Results and Discussion

The hydrothermal reactions of the divalent transition metal ions with squaric acid and aminodiphosphonic acid ($\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)_2$) lead to two new metal diphosphonates with different structures. In $\text{Cu}_2(\text{H}_3\text{L})(\text{bipy})_2 \cdot 2\text{H}_2\text{O}$, the above two types of ligands form a new multifunctional phosphonate ligand (H_3L) through condensation reaction (Scheme 1); furthermore, the Cu^{2+} ion has been reduced to Cu^+ ion. In $\{\text{Mn}[\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)]_2(\text{H}_2\text{O})_2\}_2\{\text{Mn}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_4\} \cdot (\text{C}_4\text{H}_2\text{O}_4)$ **2**, each type of ligand forms a 1D chain with Mn(II) ions. The structures of the above two compounds are different from Cu(II), Co(II), and Mn(II) complexes of $\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ without squaric acid as the second metal linker.¹¹

The structure of $\text{Cu}_2(\text{H}_3\text{L})(\text{bipy})_2 \cdot 2\text{H}_2\text{O}$ features a new layered architecture. The asymmetric unit of $\text{Cu}_2(\text{H}_3\text{L})$

$(\text{bipy})_2 \cdot 2\text{H}_2\text{O}$ contains two Cu(I) ions, two 4,4'-bipy ligands, one squarato-phosphonate dianion, as well as two lattice water molecules (Figure 1). Both Cu(I) ions are three coordinated by two N atoms from two bipy ligands and one oxygen atom from the squarato-phosphonate ligand (O(1) for Cu(1) and O(21) for Cu(2)). The Cu–N distances range from 1.891(3) to 1.926(3) Å. The Cu–O bonds are rather weak with bond distances ranging from 2.392(3) to 2.423(3) Å. These bond distances are comparable to those reported for Cu(I) centers in the Cu(I)–Cu(II) mixed-valence phosphonates.¹² The assignments of oxidation state of +1 for copper ions are also supported by the total bond valence calculations (1.044 and 0.977 for Cu(1) and Cu(2), respectively.)¹³ The squarato-phosphonate ligand is bidentate in a cis fashion and bridges with two Cu(I) centers. The protonation of the squarato-phosphonate ligand merits special attention. The neutral squarato-phosphonic acid ligand contains five protons, two in the squarate moiety and the remaining three in the phosphonate moiety. Upon its complexation with two Cu(I) ions, the squarato-phosphonate dianion (2– in charge) has three protons remained. Based on the P–O distances, two phosphonate oxygen atoms (O(12) and O(23)) are protonated. The third proton is expected to be on one of the squarato oxygen atoms. However, it is impossible to locate that proton due to the delocalization of all of the C–O bonds. The N(1)–C(4) bond connecting the squarate with the aminodiphosphonate moiety is significantly shorter than the N–C bonds in the aminophosphonate moiety and is slightly shorter than those of the bipy ligands, indicating its nature of a C=N double bond, which is also supported by related C–N–C bond angles (close to 120°).

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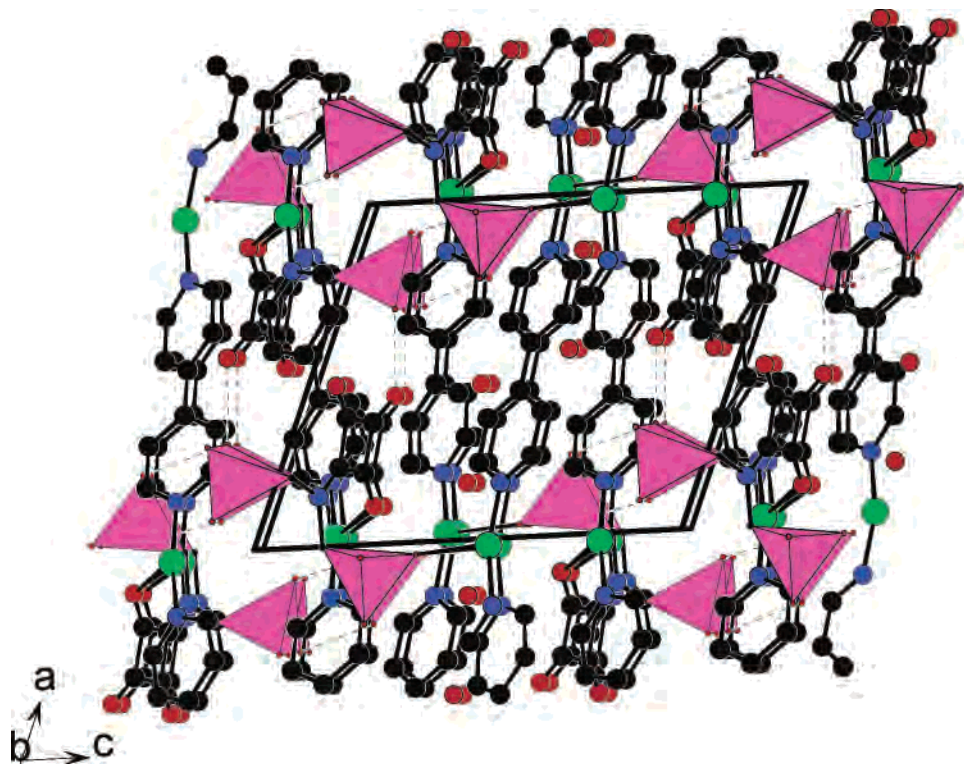


Figure 3. View of the structure of **1** along the *b* axis. The CPO₃ groups are represented by pink tetrahedra. Cu, N, O, and C atoms are drawn as green, blue, red, and black circles, respectively. Hydrogen bonds are drawn as dotted lines.

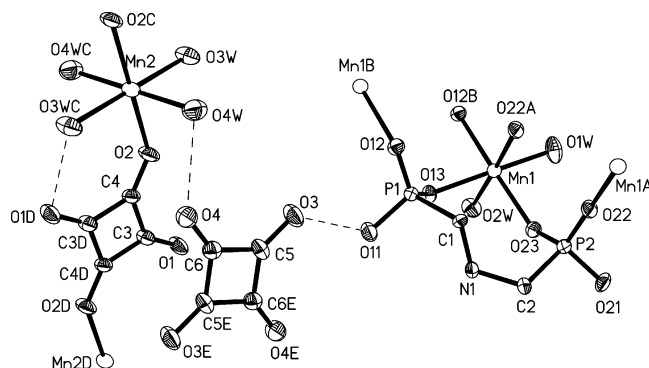


Figure 4. ORTEP representation of the selected unit in compound **2**. The thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are drawn as dotted lines.

The Cu(I) centers are interconnected via bidentate bridging bipy and $\{H_3L\}^{2-}$ dianions to form a new layered architecture (Figure 2). The $\{H_3L\}^{2-}$ dianions also act as pendant groups below and above the 2D layer. Neighboring 2D layers are further interlinked by strong hydrogen bonds among non-coordination squarate and phosphonate oxygen atoms as well as lattice water molecules (Figure 3, Table 2).

No condensation reaction occurred when Mn^{2+} was used instead of Cu^{2+} ion. Compound **2** is composed of two $\{Mn-[NH(CH_2PO_3H)_2](H_2O)_2\}$'s, one $\{Mn(C_4O_4)(H_2O)_4\}$, and a neutral squaric acid (Figure 4). The Mn^{2+} ion in the diphosphonate chain is octahedrally coordinated by four phosphonate oxygen atoms and two aqua ligands, whereas the one in the squarate chain is octahedrally coordinated by two squarate oxygen atoms and four aqua ligands (Figure 4). All Mn–O distances are within the normal range. The aminodiphosphonate anion is tetradentate; it chelates with a

Mn(II) ion by using two phosphonate oxygen atoms and also bridges with two other Mn(II) centers. The coordinated squarate ligand is bidentate bridging. The bridging of diphosphonate and squarate dianions with Mn(II) centers lead to two types of 1D chains, a 1D chain of manganese(II) diphosphonate along the *a* axis (Figure 5a) and a 1D chain of manganese(II) squarate along the *b* axis (Figure 5b). These two types of chains are bridged by the neutral squaric acid molecules via hydrogen bonds into a 3D network (Figure 6, Table 2).

The formation of compound **1** is of special interest. The squarato-phosphonate ligand differs significantly from other carboxylato-phosphonate ligands. Unlike the normal carboxylate group attached to the carboxylato-phosphonate ligands, the squarato moiety in our new ligand has a unique four-member aromatic rigid ring that may adopt a number of coordination modes due to its three oxygen atoms. Such type of ligand may also form metal complexes with unusual physical properties. The Cu(I) ions are probably resulted from the reduction of copper(II) ions by reducing 4,4'-bipy ligand. A few transition metal and lanthanide complexes of amino-monosubstituted squarates have been reported,¹⁴ in which the monosubstituted derivatives were synthesized directly by reaction of squaric acid and amines. Our attempts to synthesize H_3L ligand by the direct reaction of $NH(CH_2PO_3H)_2$ and squaric acid under hydrothermal conditions at

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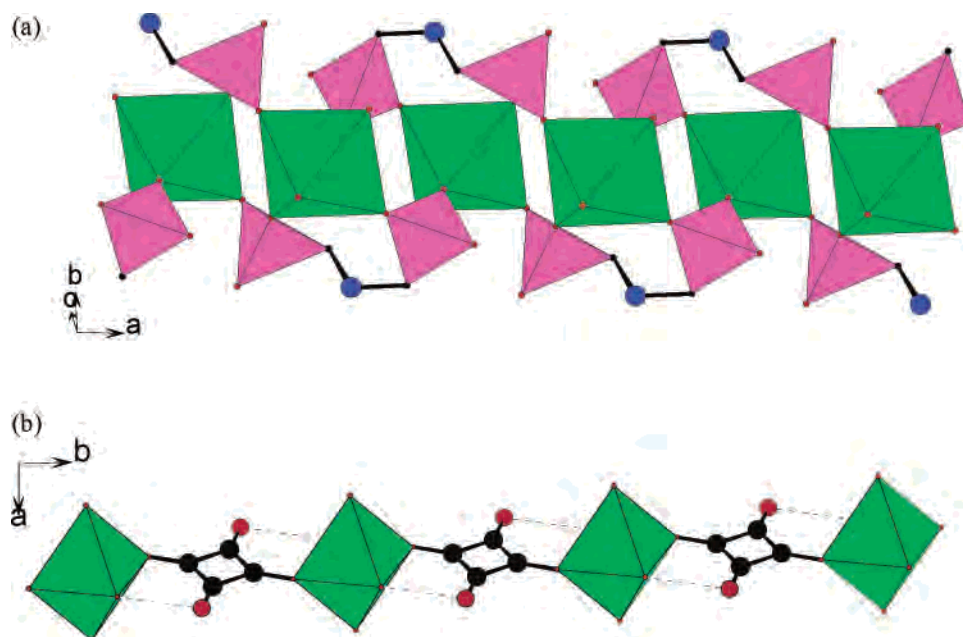


Figure 5. A 1D manganese(II) phosphonate chain along the a axis (a) and a 1D manganese(II) squarate chain along the b axis (b). The CPO_3 tetrahedra and MnO_6 octahedra are shaded in pink and green, respectively. N, O, and C atoms are drawn as blue, red, and black circles, respectively. Hydrogen bonds are drawn as dotted lines.

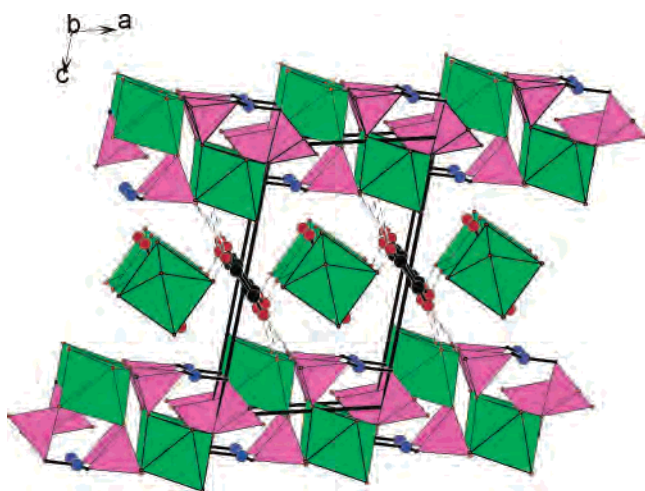


Figure 6. View of the structure of compound **2** along the b axis. The CPO_3 tetrahedra and MnO_6 octahedra are shaded in pink and green, respectively. N, O, and C atoms are drawn as blue, red, and black circles, respectively. Hydrogen bonds are drawn as dotted lines.

140 °C or under solution reaction upon refluxing at 110 °C in absence of copper(II) ion were unsuccessful, and also direct usage of copper(I) source for the preparation of **1** was also in vain, thus we deem that the squarato-phosphonate ligand is probably stabilized by its coordination with Cu(I) ions. When Mn(II) ion was applied, a different mixed-ligand Mn(II) complex (compound **2**) was obtained, and the bipy ligand acts only as pH adjustor.

The squaric acid and aminodiphosphonate ligands as well as **1** show no solid-state emission band at room temperature. The solid-state luminescent spectrum of **2** at room temperature exhibits a very broad emission band over the range of 380–680 nm (two main peaks at 534 and 468 nm, and a shoulder peak at 604 nm) upon excitation at 348 nm (Figure 7). This emission band can be assigned to the ${}^4\text{T}_1({}^4\text{G}) \rightarrow$

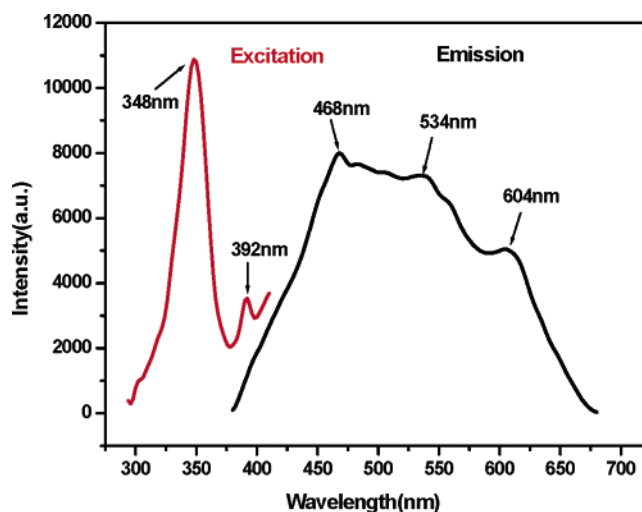


Figure 7. Excitation ($\lambda_{\text{em}} = 470$ nm) and emission spectra ($\lambda_{\text{exc}} = 348$ nm) of compound **2** at 298 K.

${}^6\text{A}_1$ transition of Mn^{2+} ion.¹⁵ The broadening of the emission band is probably due to several overlapping split bands caused by two different types of Mn(II) ions located at positions with C1 and $\bar{1}$ symmetry. It is reported that manganese(II) complexes may emit photoluminescence at low temperature, but their luminescent properties at room temperature are rarely studied.¹⁵

Compound **1** is diamagnetic with a molar susceptibility of -1.6×10^{-4} emu/mol at 300 K, which is in good agreement with the assignment of the oxidation state of Cu(I) based on X-ray structural analysis. For compound **2**, the effective magnetic moment of $10.4 \mu_{\text{B}}$ at 300 K corresponds

(15) (a) Fei, B.-L.; Sun, W.-Y.; Zhang, Y.-A.; Yu, K.-B.; Tang, W.-X. *J. Chem. Soc., Dalton Trans.* **2000**, 2345. (b) Fender, N. S.; Fronczek, F. R.; John, V.; Kahwa, I. A.; McPherson, G. L. *Inorg. Chem.* **1997**, *36*, 5539.

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to three high-spin Mn^{2+} ions ($S = 5/2$) in an octahedral environment. Compound **2** obeys the Curie–Weiss law almost over the whole temperature range with a Weiss constant of $\theta = -1.4$ K, indicating very weak antiferromagnetic interaction between Mn(II) centers.

In conclusion, we have isolated the first example of the Cu(I) phosphonate in which the condensation reaction between two organic ligands leads to a new multifunctional squarato-imino-diphosphonate ligand. The mixed-ligand

manganese(II) squarate aminodiphosphonate exhibits an interesting luminescent behavior.

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Supporting Information Available: X-ray crystallographic files for compounds **1** and **2** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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