

Anion-Directed Crystallization of Coordination Polymers: Syntheses and Characterization of $\text{Cu}_4(2\text{-pzc})_4(\text{H}_2\text{O})_8(\text{Mo}_8\text{O}_{26})\cdot 2\text{H}_2\text{O}$ and $\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2(\text{V}_{10}\text{O}_{28}\text{H}_4)\cdot 6.5\text{H}_2\text{O}$ (2-pzc = 2-Pyrazinecarboxylate)

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Two new copper 2-pyrazinecarboxylate (2-pzc) coordination polymers incorporating $[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{2-}$ anions were synthesized and structurally characterized: $\text{Cu}_4(2\text{-pzc})_4(\text{H}_2\text{O})_8(\text{Mo}_8\text{O}_{26})\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2(\text{V}_{10}\text{O}_{28}\text{H}_4)\cdot 6.5\text{H}_2\text{O}$ (**2**). Crystal data: **1**, monoclinic, space group $P2_1/n$, $a = 11.1547(5)$ Å, $b = 13.4149(6)$ Å, $c = 15.9633(7)$ Å, $\beta = 90.816(1)^\circ$; **2**, triclinic, space group $P\bar{1}$, $a = 10.5896(10)$ Å, $b = 10.7921(10)$ Å, $c = 13.5168(13)$ Å, $\alpha = 104.689(2)^\circ$, $\beta = 99.103(2)^\circ$, $\gamma = 113.419(2)^\circ$. Compound **1** contains $\{\text{Cu}(2\text{-pzc})(\text{H}_2\text{O})_2\}$ chains charge-balanced by $[\text{Mo}_8\text{O}_{26}]^{4-}$ anions. In compound **2**, layers of $\{\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2\}$ form cavities that are filled with $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{2-}$ anions. The magnetic properties of both compounds are described.

Introduction

Anions are capable of directing the crystallization of some supramolecular entities through either cation–anion interactions or hydrogen-bonding interactions between an organic host and an anionic guest.^{1,2} Recently, a number of inorganic/organic hybrid structures containing polyoxomolybdate or vanadate cluster anions have been reported.³ Examples of cation–anion interactions, hydrogen-bonding interactions, and the direct bonding between cluster anions and coordinated cations are found. Novel materials that have been discovered include the molecular compound $[\text{Cu}(\text{phen})_2]_2\text{Mo}_8\text{O}_{26}$,⁴ the chain compounds $[\text{Cu}(\text{enMe})_2]_3[\text{V}_{15}\text{O}_{36}\text{Cl}]\cdot 2.5\text{H}_2\text{O}$,⁵ $\text{Ni}_2(2,2'\text{-bpy})_4\text{Mo}_8\text{O}_{26}$,⁶ and $[\text{Cu}(4,4'\text{-bpy})]_4\text{Mo}_8\text{O}_{26}$,⁷ the layer compounds $\text{Cs}_{0.5}[\text{Ni}(\text{en})_2]_3[\text{V}_{18}\text{O}_{42}\text{Cl}]\cdot 2\text{en}\cdot 6\text{H}_2\text{O}$ ⁵ and $[\text{Ni}(\text{H}_2\text{O})_2(4,4'\text{-bpy})_2]_2\text{Mo}_8\text{O}_{26}$,⁷ and the three-dimensional compounds $(\text{N}_2\text{H}_5)_2[\text{Zn}_3\text{V}_{18}\text{O}_{42}(\text{SO}_4)(\text{H}_2\text{O})_{12}]\cdot 24\text{H}_2\text{O}$ ⁸ and $[\text{Fe}(\text{tpypor})_3\text{Fe}](\text{Mo}_6\text{O}_{19})_2\cdot x\text{H}_2\text{O}$ ⁹ (tpypor = tetrapyridylporphyrin). The cluster anions in these compounds can be discrete and play a space-filling role, as found in $[\text{Cu}(4,4'\text{-bpy})]_4\text{Mo}_8\text{O}_{26}$ and $[\text{Fe}(\text{tpypor})_3\text{Fe}](\text{Mo}_6\text{O}_{19})_2\cdot x\text{H}_2\text{O}$. More

often, however, they behave as “ligands” and form an integral part of the framework structure.

As a multidentate ligand, the 2-pyrazinecarboxylate anion has the potential to link metal ions into coordination polymers. When 2-pyrazinecarboxylic acid reacts with the Cu(II) ion in aqueous solution, mononuclear compounds $\text{Cu}(2\text{-pzc})_2$ and $\text{Cu}(2\text{-pzc})_2(\text{H}_2\text{O})_{10}$ are isolated. In the presence of Cu^+ or Ag^+ cations, these mononuclear species can act as bridging “ligands” and link the Cu^+ or Ag^+ cations into infinite chains.^{11,12} Anion-directed assembly of $\text{Cu}^{2+}/2\text{-pzc}$ polymers, on the other hand, has not been studied. In this paper, we describe the syntheses, structures, and magnetic properties of a chain compound $\text{Cu}_4(2\text{-pzc})_4(\text{H}_2\text{O})_8(\text{Mo}_8\text{O}_{26})\cdot 2\text{H}_2\text{O}$ (**1**) and a layer compound $\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2(\text{V}_{10}\text{O}_{28}\text{H}_4)\cdot 6.5\text{H}_2\text{O}$ (**2**).

Experimental Section

Materials and Methods. All the starting materials were reagent grade and used as purchased. The infrared spectra were recorded on a Galaxy FTIR 5000 series spectrometer with pressed KBr pellets. Magnetic susceptibility data were obtained on polycrystalline samples (**1**, 71.4 mg; **2**, 22.5 mg) from 2 to 300 K in a magnetic field of 5 kG using a SQUID magnetometer.

Synthesis of $\text{Cu}_4(2\text{-pzc})_4(\text{H}_2\text{O})_8(\text{Mo}_8\text{O}_{26})\cdot 2\text{H}_2\text{O}$, **1.** A solution (2 mL) of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.4 mmol, 0.0990 g) was added to an aqueous solution (20 mL) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.1 mmol, 0.1233 g) and 2-pyrazinecarboxylic acid (0.2 mmol, 0.0255 g). The resulting blue solution was allowed to evaporate slowly at room temperature. Blue crystals were obtained after 1 month. Yield: 95% based on 2-pzc. (Found: C, 10.47; H, 1.41; N, 5.11. Calcd: C, 11.37; H, 1.52; N, 5.31). IR (KBr): 3403s(br), 3106s(br), 1672s, 1640s, 1605s, 1535vw, 1485vw, 1474vw, 1424m, 1385m, 1350m, 1287w, 1184m, 1169m, 1059m, 945s, 909s, 833m, 785w, 706s, 667m, 557w, 525w, 473m, 411w cm^{-1} .

Synthesis of $\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2(\text{V}_{10}\text{O}_{28}\text{H}_4)\cdot 6.5\text{H}_2\text{O}$, **2.** An aqueous solution (10 mL) of NH_4VO_3 (0.5 mmol, 0.0585 g) was added to a

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Table 1. Crystallographic Data

	1	2
chemical formula	C ₂₀ H ₃₂ Cu ₄ Mo ₈ N ₈ O ₄₄	C ₂₀ H ₃₃ Cu ₃ N ₈ O _{44.50} V ₁₀
fw	2110.22	1797.56
cryst syst	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	11.1547(5)	10.5896(10)
<i>b</i> , Å	13.4149(6)	10.7921(10)
<i>c</i> , Å	15.9633(7)	13.5168(13)
α , deg		104.689(2)
β , deg	90.816(1)	99.103(2)
γ , deg		113.419(2)
<i>V</i> , Å ³	2388.5(2)	1311.5(2)
<i>Z</i>	2	1
temp, K	293(2)	293(2)
ρ_c , g cm ⁻³	2.934	2.276
μ (Mo K α), cm ⁻¹	38.98	30.04
R1, wR2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0218, 0.0512	0.0370, 0.1057
R1, wR2 (all data) ^a	0.0301, 0.0534	0.0449, 0.1106

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

solution of Cu(NO₃)₂·3H₂O (0.5 mmol, 0.1227 g) and 2-pyrazinecarboxylic acid (0.35 mmol, 0.0433 g) in 5 mL of H₂O. The resulting green solution was adjusted to pH ~3.5 with 1.5 M HNO₃. The solution was allowed to evaporate slowly at room temperature for 2 months, during which time the byproduct Cu(2-pzc)₂(H₂O)₂ was filtered off. Dark-green crystals were collected and used for physical measurements. Yield: 24% based on pzc. (Found: C, 13.11; H, 1.83; N, 6.80. Calcd: C, 13.29; H, 1.88; N, 6.20). IR (KBr): 3503s(br), 1659s, 1620s, 1591s, 1541vw, 1481w, 1431m, 1383m, 1362m, 1296vw, 1196m, 1182m, 1165m, 1078w, 1061m, 993m, 978s, 841m, 787m, 760m, 718w, 594m, 498m, 465m cm⁻¹.

Crystallographic Studies. Single crystals of dimensions 0.12 mm × 0.10 mm × 0.05 mm for **1** and 0.30 mm × 0.20 mm × 0.03 mm for **2** were used for the structure determinations. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 25 s/frame for **1** and 30 s/frame for **2**. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied on the intensities was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Number of measured, unique, and observed reflections [*I* > 2 σ (*I*)] are 11 028, 3711, 2936 (*R*_{int} = 0.0322) for **1** and 7937, 5548, 4654 (*R*_{int} = 0.0165) for **2**. Empirical absorption and the extinction corrections were applied for both compounds.

The structures were solved by direct methods, and the data were refined on *F*² by full-matrix least squares using SHELXTL.¹³ All non-hydrogen atoms except the O(w) disordered water molecules in **2** were refined with anisotropic displacement parameters. The disordered O(w) and all hydrogen atoms were refined isotropically. The hydrogen atoms of disordered water molecules in **2** were not located. To balance charge, two additional protons are required, which could not be located experimentally. Protonation of the decavanadate cluster appears more reasonable, and for the purpose of discussion V₁₀O₂₈H₄²⁻ is assumed. Crystallographic data of the two compounds are summarized in Table 1 and selected bond lengths and angles in Tables 2 and 3.

Results and Discussion

Crystal Structures. The structure of **1** consists of chains of repeated Cu(2-pzc)(H₂O)₂ units and discrete β -[Mo₈O₂₆]⁴⁻ clusters (Figures 1 and 2). Within the chain, two crystallographically independent copper atoms are found (Figure 1). Each

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**^a

Cu(1)—O(1)	1.937(3)	Cu(1)—O(2w)	1.969(3)
Cu(1)—O(1w)	1.988(3)	Cu(1)—N(1)	2.015(3)
Cu(1)—N(4A)	2.315(3)	Cu(2)—O(3)	1.940(3)
Cu(2)—O(4w)	1.955(3)	Cu(2)—O(3w)	1.984(3)
Cu(2)—N(3)	1.998(3)	Cu(2)—N(2)	2.385(3)
O(1)—Cu(1)—O(2w)	177.62(12)	O(1)—Cu(1)—O(1w)	86.16(12)
O(2w)—Cu(1)—O(1w)	96.14(12)	O(1)—Cu(1)—N(1)	82.55(12)
O(2w)—Cu(1)—N(1)	95.08(13)	O(1w)—Cu(1)—N(1)	160.49(13)
O(1)—Cu(1)—N(4A)	94.87(12)	O(2w)—Cu(1)—N(4A)	85.50(12)
O(1w)—Cu(1)—N(4A)	95.22(12)	N(1)—Cu(1)—N(4A)	101.53(13)
O(3)—Cu(2)—O(4w)	173.12(13)	O(3)—Cu(2)—O(3w)	88.65(13)
O(4w)—Cu(2)—O(3w)	95.3(2)	O(3)—Cu(2)—N(3)	81.55(13)
O(4w)—Cu(2)—N(3)	93.44(14)	O(3w)—Cu(2)—N(3)	164.66(14)
O(3)—Cu(2)—N(2)	92.31(12)	O(4w)—Cu(2)—N(2)	93.49(12)
O(3w)—Cu(2)—N(2)	88.09(12)	N(3)—Cu(2)—N(2)	103.98(12)
C(1)—N(1)—Cu(1)	131.5(3)	C(4)—N(1)—Cu(1)	111.0(3)
C(2)—N(2)—Cu(2)	133.3(3)	C(3)—N(2)—Cu(2)	111.0(3)
C(6)—N(3)—Cu(2)	128.9(3)	C(9)—N(3)—Cu(2)	113.0(3)
C(7)—N(4)—Cu(1B)	118.4(3)	C(8)—N(4)—Cu(1B)	124.7(3)
C(5)—O(1)—Cu(1)	116.3(3)	C(10)—O(3)—Cu(2)	117.6(3)

^a Symmetry transformations used to generate equivalent atoms: (A) *x* − 1, *y*, *z*; (B) *x* + 1, *y*, *z*. The Mo—O distances and O—Mo—O angles in [Mo₈O₂₆]⁴⁻ are typical for this anion.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**^a

Cu(1)—O(1)	1.966(2)	Cu(1)—N(1)	2.008(3)
Cu(2)—O(2)	2.018(2)	Cu(2)—N(4)	2.027(3)
Cu(2)—O(1w)	2.401(4)	Cu(3)—O(3)	1.942(3)
Cu(3)—N(3)	1.991(3)		
O(1)—Cu(1)—O(1A)	180.0	O(1)—Cu(1)—N(1)	83.43(10)
O(1A)—Cu(1)—N(1)	96.57(10)	N(1)—Cu(1)—N(1A)	180.0
O(2B)—Cu(2)—O(2)	180.0	O(2)—Cu(2)—N(4B)	87.59(10)
O(2)—Cu(2)—N(4)	92.41(10)	N(4B)—Cu(2)—N(4)	180.0
O(2B)—Cu(2)—O(1w)	99.99(11)	O(2)—Cu(2)—O(1w)	80.01(11)
N(4B)—Cu(2)—O(1w)	84.85(12)	N(4)—Cu(2)—O(1w)	95.15(12)
O(1w)—Cu(2)—O(1B)	180.0	O(3C)—Cu(3)—O(3)	180.0
O(3C)—Cu(3)—N(3)	95.48(11)	O(3)—Cu(3)—N(3)	84.52(11)
N(3)—Cu(3)—N(3C)	180.0	C(10)—O(3)—Cu(3)	114.4(2)
C(5)—O(1)—Cu(1)	114.8(2)	C(5)—O(2)—Cu(2)	129.3(2)
C(1)—N(1)—Cu(1)	130.7(2)	C(4)—N(1)—Cu(1)	111.2(2)
C(9)—N(3)—Cu(3)	110.5(2)	C(6)—N(3)—Cu(3)	130.3(2)
C(8)—N(4)—Cu(2)	120.3(2)	C(7)—N(4)—Cu(2)	121.3(2)

^a Symmetry transformations used to generate equivalent atoms: (A) −*x*, −*y*, −*z*; (B) −*x* + 1, −*y*, −*z*; (C) −*x* + 1, −*y*, −*z* + 1. The V—O distances and O—V—O angles in [V₁₀O₂₈H₂]⁴⁻ are typical for this anion.

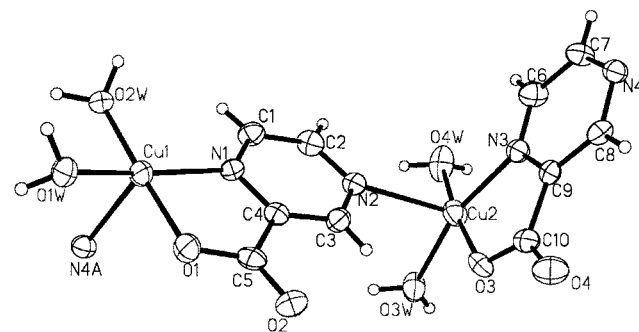


Figure 1. Fragment of the {Cu(2-pzc)(H₂O)₂} chain in structure **1** with the atomic labeling scheme (thermal ellipsoids are shown at 50% probability).

has a square pyramidal environment. The basal plane of the {CuN₂O₃} square pyramid is defined by N(1), O(1), O(1w), and O(2w) for Cu(1) and by N(3), O(3), O(3w) and O(4w) for Cu(2). The largest deviations from the basal plane are 0.1503 Å at O(1) and 0.0666 Å at O(3). The Cu(1) and Cu(2) atoms lie above their basal planes by 0.1397 and 0.1500 Å. The apical positions of the Cu(1) and Cu(2) square pyramids are occupied by the N(4) and N(2) atoms, respectively. The Cu—O [mean

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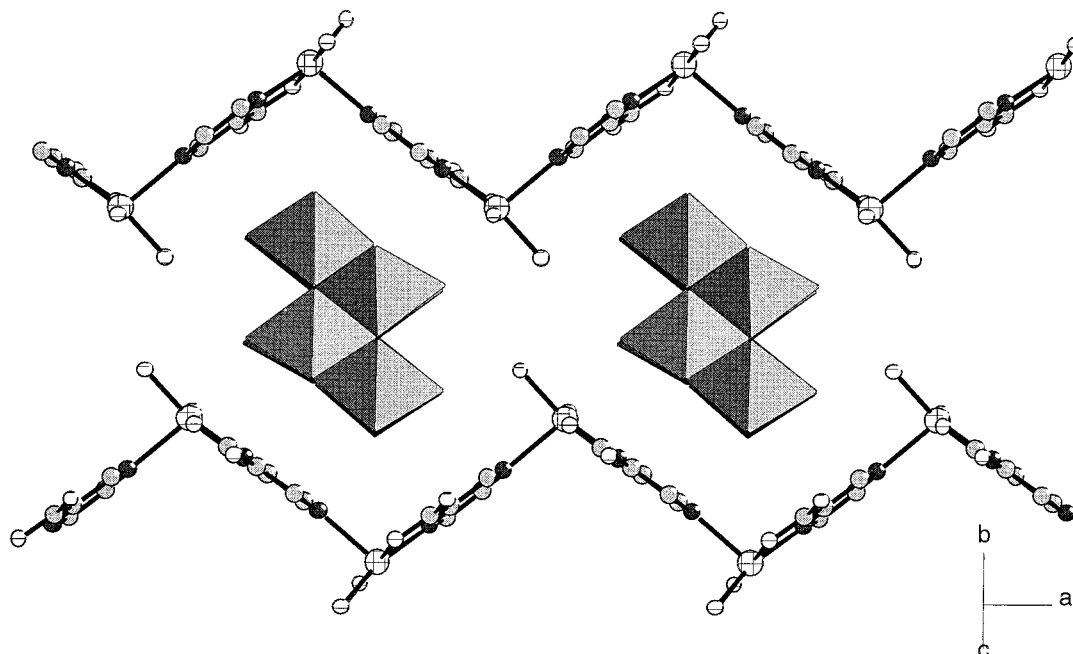


Figure 2. Part of structure **1** viewed along [011], emphasizing the encapsulation of $[\text{Mo}_8\text{O}_{26}]^{4-}$ anions between the $\{\text{Cu}(\text{2-pzc})(\text{H}_2\text{O})_2\}$ chains. All H atoms are omitted for clarity.

1.962(3) Å] and equatorial Cu–N [mean 2.007(3) Å] distances in **1** are comparable to those in $\alpha,\beta\text{-}[\text{Cu}_2\text{X}(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_n]$ (X = Cl, Br),¹¹ $[\text{KCu}_2(\text{2-pzc})(\text{N}_3)_4]_n$,¹⁴ $\text{Cu}(\text{2-pzc})_2$, and $\text{Cu}(\text{2-pzc})_2(\text{H}_2\text{O})_{10}$ [Cu–O, 1.94–1.98 Å; Cu–N, 2.00–2.022 Å]. However, the axial Cu(1)–N(4A) [2.315(3) Å] and Cu(2)–N(2) [2.385(3) Å] bond lengths are significantly longer, as expected for d^9 cations in square pyramidal geometry. The 2-pzc group serves as a tridentate bridging ligand, using one carboxylate O and two pyrazine N atoms to link the Cu atoms into infinite zigzag chains (Figure 2). The Cu(1)⋯Cu(2) distances across the two 2-pzc ligands within the chain are 7.102 and 7.059 Å, respectively. The shortest Cu⋯Cu distance between the chains is 5.281 Å. The lattice water molecules are located between the chains.

The presence of carboxylate oxygen atoms and coordinated and lattice water molecules allows extensive hydrogen bonding between the chains. The three shortest contacts between neighboring chains are O(2w)⋯O(2) 2.698(4) Å, O(1w)⋯O(3) 2.819(4) Å, and O(3w)⋯O(1w) 2.838(4) Å. Linear rows of $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters are surrounded by four polymeric coordination chains connected through these hydrogen-bonding interactions (Figure 3). Hydrogen bonds are also observed between the cation chains and the anionic clusters: O(1w)⋯O(13), 2.697(4) Å, and O(3w)⋯O(10), 2.952(4) Å.

Compound **2** crystallizes in space group $P\bar{1}$ and contains layers of $\{\text{Cu}_3(\text{2-pzc})_4(\text{H}_2\text{O})_2\}^{2+}$ and protonated decavanadate anions. Figure 4 shows a fragment of the $\{\text{Cu}_3(\text{2-pzc})_4(\text{H}_2\text{O})_2\}^{2+}$ layer with the atomic labeling scheme. The crystallographic asymmetric unit contains three independent Cu atoms, each on an inversion center. Both Cu(1) and Cu(3) have square planar coordination environments, each chelated by two N and two O atoms from two equivalent 2-pzc groups forming $\text{Cu}(\text{2-pzc})_2$ building units. The Cu–N [mean 2.000(3) Å] and Cu–O [mean 1.954(2) Å] bond lengths are comparable with those found in $\text{Cu}(\text{2-pzc})_2$ [Cu–N, 1.98(1) Å; Cu–O, 1.93(1) Å].¹⁰ The Cu(2) atom has an axially elongated octahedral coordination

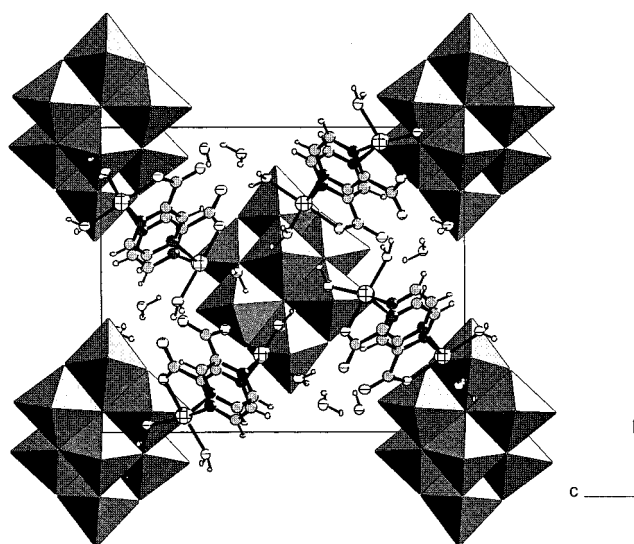


Figure 3. Packing of the structure of **1** viewed along [100].

geometry, with the equatorial plane formed by two pyrazine N atoms and two carboxylate O atoms, both trans to their own kind. The two axial positions are occupied by weakly bound water molecules [Cu–O(1w), 2.401(4) Å]. A two-dimensional coordination layer in the *ac* plane is formed by alternating Cu ions and 2-pzc molecules (Figure 5). This coordination layer contains cross-linked infinite –Cu(2)–OCO–Cu(1)–OCO– and –Cu(2)–pz–Cu(3)–pz– chains, both of which provide pathways for magnetic interactions. The shortest Cu(1)⋯Cu(2) and Cu(2)⋯Cu(3) distances are 5.295 and 6.758 Å, respectively. The protonated $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{2-}$ clusters act as charge-compensating anions and reside in the cavities bounded by the square planar Cu atoms (Figure 6). Water molecules fill the interlayer spaces, and hydrogen bonds are observed: within the layers O(1w)⋯O(1), 2.942 Å; between the cation layers and the anionic clusters O(3w)⋯O(4), 2.705, 2.802 Å; and between the anionic clusters and interlayer water molecules O(1w)⋯O(12), 2.841 Å; O(2w)⋯O(5), 3.003 Å; O(3w)⋯O(8), 2.694 Å.

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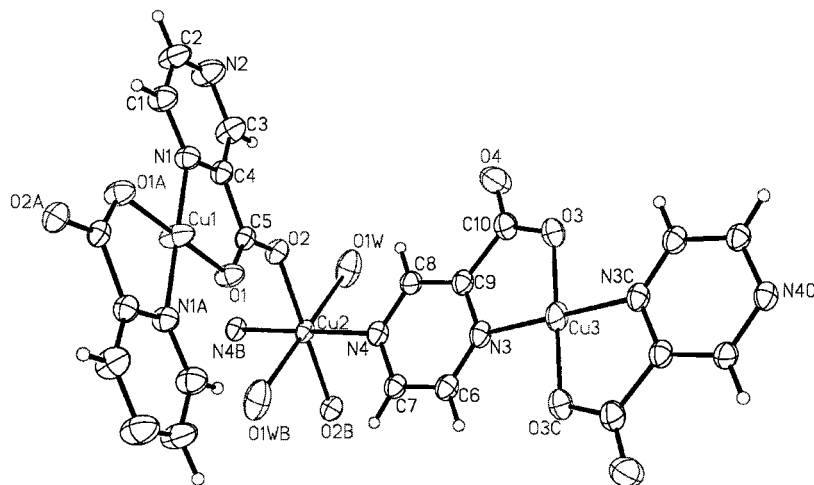


Figure 4. Fragment of the $\{\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2\}$ layer in structure **2** with the atomic labeling scheme (thermal ellipsoids are shown at 50% probability).

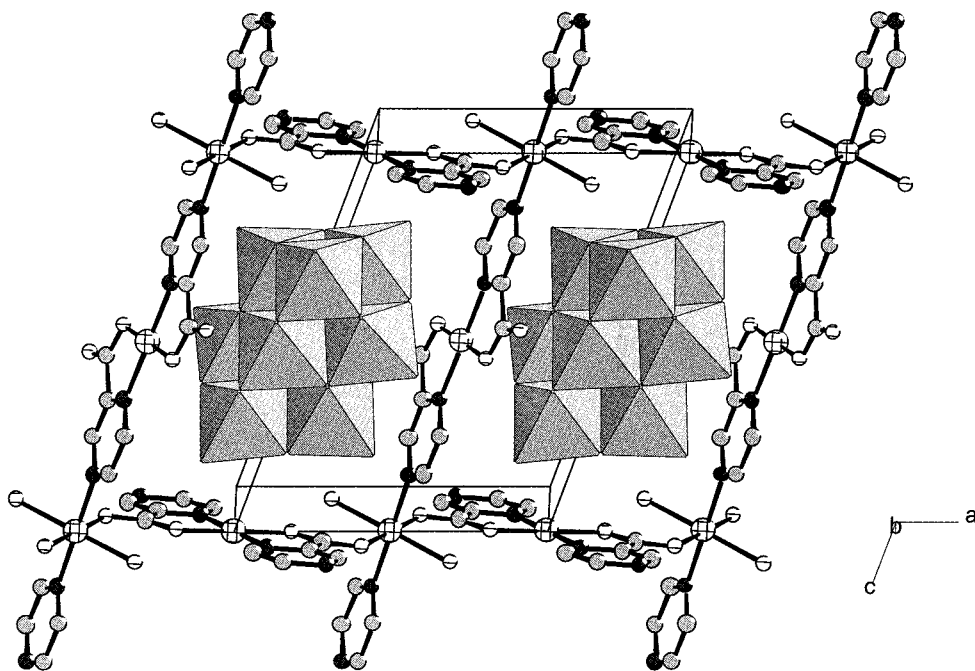


Figure 5. One layer of the structure of **2** in the ac plane.

The isolation of compounds **1** and **2** depends on the presence of $[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{2-}$ cluster anions. Without these cluster anions, the mononuclear compound $\text{Cu}(2\text{-pzc})_2(\text{H}_2\text{O})_2$ is precipitated under similar experimental conditions. Presumably, the preference of $[\text{Mo}_8\text{O}_{26}]^{4-}$ to direct crystallization of a one-dimensional $\{\text{Cu}(2\text{-pzc})(\text{H}_2\text{O})_2\}_n$ chain and $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{2-}$ of a two-dimensional $\{\text{Cu}_3(2\text{-pzc})_4(\text{H}_2\text{O})_2\}_n$ layer is related to the difference in size and shape of these anions.

Magnetic Properties. The temperature-dependent magnetic susceptibilities of **1** and **2** have been measured in the range 300–2 K. Both follow the Curie–Weiss law at high temperature. Between 60 and 300 K, the susceptibility data of **1** were fit by the equation

$$\chi_m = \frac{Ng^2\beta^2}{4K(T - \theta)} + N_\alpha \quad (1)$$

where θ is the Weiss constant and N_α accounts for the diamagnetic contribution, leading to parameters $g = 2.17$, $\theta = -5.15$ K, and $N_\alpha = -0.000726 \text{ cm}^3 \text{ mol}^{-1}$. The negative θ value suggests an antiferromagnetic interaction. This antifer-

romagnetic interaction is confirmed by the continuous decrease of $\chi_m T$ upon cooling (Figure 7). As already mentioned, structure **1** contains infinite chains of $\{\text{Cu}(2\text{-pzc})(\text{H}_2\text{O})_2\}$ separated by diamagnetic $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters. The antiferromagnetic interaction is attributed to the superexchange couplings between the copper(II) centers within the chain. Considering that the $\text{Cu}(1) \cdots \text{Cu}(2)$ distances across the two 2-pzc bridging ligands within the chain are 7.102 and 7.059 Å, the susceptibility data were analyzed by an exchange expression derived for chains of equally spaced $S = 1/2$ centers.¹⁵ A good fit is obtained with $g = 2.12$, $J = -2.12 \text{ cm}^{-1}$, $r^2 = 0.9440$. The inclusion of an interchain interaction does not improve the theoretical fitting. The small exchange coupling constant is as expected and agrees with that of other pyrazine-bridged copper compounds.^{16,17}

The magnetic behavior of **2** is different from that of **1**. In the temperature range 60–300 K, a fit of the data to eq 1 gives g

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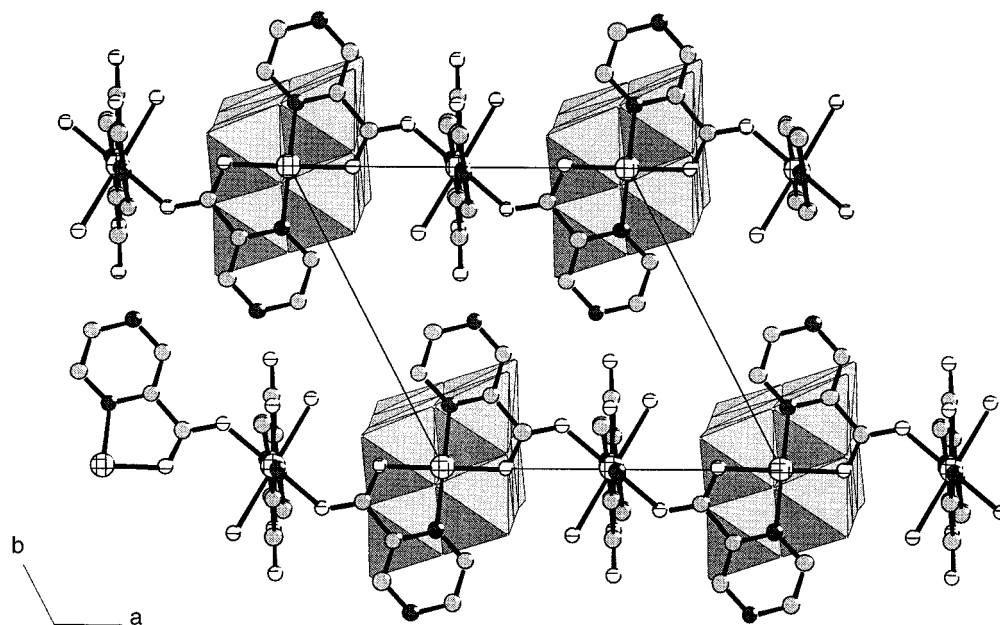


Figure 6. Packing of the structure of **2** viewed along [001].

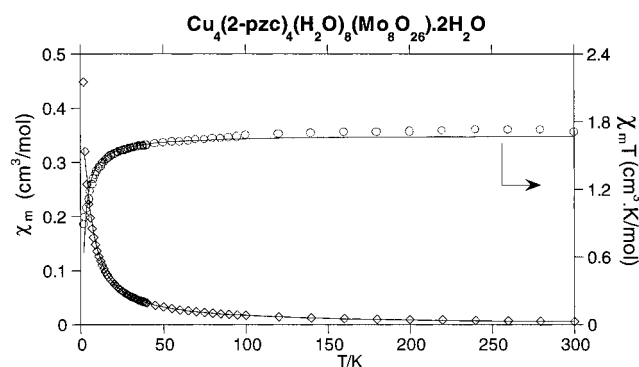


Figure 7. χ_m and $\chi_m T$ vs T plots for **1**.

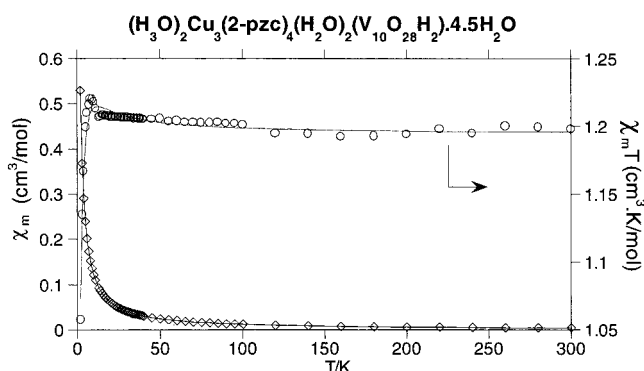


Figure 8. χ_m and $\chi_m T$ vs T plots for **2**.

$= 2.06$, $\theta = +0.61$ K, and $N_A = -0.000\,990\,33$ cm³ mol⁻¹. In this case, the positive θ value indicates a very weak ferromagnetic interaction between the magnetic centers. The temperature-dependent susceptibilities of **2**, after diamagnetic correction, are shown in Figure 8 in the forms of χ_m and $\chi_m T$ vs T plots. At 300 K, $\chi_m T$ is equal to 1.198 cm³ K mol⁻¹, as expected for three magnetically isolated Cu(II) ions. Below 100 K, the $\chi_m T$ value increases gradually upon cooling, reaching a maximum (1.220 cm³ K mol⁻¹) at 8 K. Then it decreases abruptly down to 2 K (1.06 cm³ K mol⁻¹). This behavior corresponds to a very weak ferromagnetic coupling with antiferromagnetic interactions dominant at very low temperature.

Examination of structure **2** reveals that the {Cu₃(2-pzC)₄-

(H₂O)₂} layer contains anti-syn carboxylato-bridged Cu(1)-OCO-Cu(2) chains that are cross-linked by pyrazine-bridged Cu(2)-pz-Cu(3) chains. It has been found that weak ferromagnetic interactions are propagated in the carboxylate-bridged copper(II) compounds in which the carboxylate adopts the anti-syn conformation and the Cu-O-C-O-Cu skeleton deviates from planarity.¹⁸⁻²⁰ The pyrazine bridge, on the other hand, is well-known for transmitting weak antiferromagnetic interactions.^{16,17} Because the Cu(1)···Cu(2) distance over the carboxylate bridge (5.295 Å) is much shorter than the Cu(2)···Cu(3) distance over the pyrazine bridge (6.758 Å), the exchange through the carboxylate bridges is dominant, in agreement with the experimental observation. The magnetic data were analyzed by Baker's series expansion²¹ for the $S = 1/2$ Heisenberg ferromagnetic linear chain. θ' is included to account for the interchain interactions. The theoretical fit results in the solid line as shown in Figure 8 with parameters $g = 2.06$, $J = +3.51$ cm⁻¹, $\theta' = -2.97$ K, $r^2 = 0.9529$. The J value is comparable to that of the chain compound [Cu(H₂O)₃][Cu(mal)₂(H₂O)]¹⁸ (mal = malonic acid) where J is 3.0 cm⁻¹. The small θ' value suggests that the antiferromagnetic coupling through the pyrazine bridge is also weak and is about the same order of magnitude as the ferromagnetic coupling over the carboxylate bridge. This result is consistent with that of compound **1** as well as with data for other pyrazine-bridged copper compounds.

Summary

Two new Cu(II)/2-pzC coordination compounds containing cluster anions have been obtained. The compound Cu₄(2-pzC)₄(H₂O)₈(Mo₈O₂₆)·2H₂O (**1**) has a zigzag chain structure bridged by the 2-pzC ligands, with discrete [Mo₈O₂₆]⁴⁻ clusters encapsulated by four H-bonded chains. The compound Cu₃(2-pzC)₄(H₂O)₂(V₁₀O₂₈H₄)·6.5H₂O (**2**) has a layer structure with win-

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dows generated by cross-linked infinite chains of Cu—OCO—Cu— and Cu—pz—Cu—. The $[V_{10}O_{28}H_4]^{2-}$ clusters reside in these windows. Weak antiferromagnetic and ferromagnetic interactions are observed in **1** and **2**, respectively. We anticipate that with the incorporation of different anions other Cu(II)/2-pzc compounds with one- to three-dimensional structures and tunable magnetic properties could be created.

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

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