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Mono- and polynuclear Cu(II) coordination compounds that contain diazine ligands

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ABSTRACT

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Keywords: Low-dimensional Copper Diazine, coordination polymer Molecular magnet Cu(OTf)₂(2-mepyz)₂(H₂O)₂ (2-mepyz = 2-methylpyrazine; OTf⁻ = CF₃SO₃⁻ = triflate), **1**, and Cu(OTf)₂-(H₂O)₂(pyz) (pyz = pyrazine), **2**, consist of monomeric and polymeric structures, respectively. Both compounds contain octahedral Cu(II) metal centers surrounded by *trans*-coordinated OTf⁻, H₂O, and diazines, either 2-mepyz in the case of **1** or pyz in **2**. In **1**, O–H···O(triflate) hydrogen bonds link CuO₄N₂ monomers into quasi-1D chains which are joined via O–H···N interactions to afford a three-dimensional (3D) network. Pyz ligands in **2** link CuO₄N₂ octahedra into linear chains similar to Cu(NO₃)₂(pyz). Magnetically, neither **1** or **2** show indications for long-range magnetic ordering (LRO) above 2 K. Least-squares fits of the magnetic susceptibility data, $\chi(T)$, to a Bonner–Fisher uniform chain model gave 2*J*/*k*_B = -0.005(1) and -6.0(1) K for compounds **1** and **2**, respectively, indicative of negligible and moderate antiferromagnetic coupling between spin-1/2 Cu(II) ions. Inter-chain magnetic interactions seem to be negligible for both systems.

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1. Introduction

Low-dimensional molecule-based magnets comprised of spin-1/2 ions represent an area of intense research interest [1–8]. Spin-1/2 ions such as Cu(II) have been used extensively owing to the lack of single-ion anisotropy leading to more easily interpretable magnetic behaviors. The single spin involved is also more amenable to theoretical investigations.

From a crystal engineering perspective, there are many ways in which the paramagnetic spin-bearing units can be arranged in the solid state which ultimately depends on the choice of organic synthons. The coordinative properties of the synthons dictate the number of ligands to be used, geometrical constraints, and the number of synthons that will attach to the metal ion. Owing to its good Lewis basicity, pyrazine (pyz) is arguably one of the most successfully utilized synthons in crystal design. As hydrogen atoms in the parent pyz molecule are replaced by alkyl groups (Scheme 1), the basicity decreases due to increased steric hindrance, however, there are numerous compounds known to possess monoor bidentate diazine derivatives that are coordinated to Cu(II) ions. Examples that possess either bridging or mono-coordinate dimethyl-substituted pyrazine ligands include Cu(NCO)₂(2-mepyz)₂ [9], Cu(NO₃)₂(2-mepyz) [10], CuBr₂(2,3-me₂pyz) [11], Cu₂(HCO₂)₄-(2,3-me₂pyz) [12], CuCl₂(2,5-me₂pyz) [13], CuCl₂(2,5-me₂pyz)-(CH₃CN) [14], CuCl₂(2,6-me₂pyz) [13], and [Cu(2,6-me₂pyz)₄]SiF₆ [15].

Structural modification can also be achieved by varying the size, molecular shape and charge of the counter-anion. Excluding halides, numerous anions (including coordinating and weakly-coordinating types) such as ClO_4^- [2,16], BF_4^- [4], NO_3^- [10], PF_6^- [16], SO_4^{2-} [17], $CH_3CO_2^-$ [18], and many others are frequently employed in the design of functional molecule-based solids. In our quest to self-assemble novel magnetic materials comprised of molecular building blocks we have combined triflate anions with pyrazine and 2-mepyz. These efforts lead to new molecular and polymeric structures, namely $Cu(OTf)_2(2-mepyz)_2-(H_2O)_2$ (1) and $Cu(OTf)_2(H_2O)_2(pyz)$ (2), respectively, where mono-coordinate 2-mepyz or bridging pyz ligands are involved. Our continued use of pyz and its various substituted variants is driven by our desire to understand and ultimately control the magnetic behavior of complex magnetic solids.

2. Experimental

2.1. Synthesis

Compound **1** was prepared by slow dropwise addition of 2methylpyrazine (1.52 mmol, 0.1435 g) to a 5-mL CH₃CN solution of Cu(OTf)₂ (0.762 mmol, 0.2758 g) to afford a deep blue solution. Crystalline plates suitable for X-ray structure determination were obtained by slow evaporation of the solvent over a 5-week period. The material was collected by vacuum filtration and gently dried (0.3215 g, 72% yield). Compound **2** was synthesized by dissolving each reactant, Cu(OTf)₂ (0.781 mmol, 0.2846 g) and pyrazine (1.56 mmol, 0.1260 g), in 5 mL of a 50:50 v:v mixture containing





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Scheme 1. Parent pyrazine molecule and its dimethyl-substituted variants.

 H_2O/CH_3CN . The two solutions were gently mixed to give a dark blue solution from which large pale blue crystals of **2** were obtained upon slow evaporation of the solvent over a period of 2 months. The crystals were collected by vacuum filtration and carefully dried to produce 0.3222 g of solid in 86% yield.

2.2. X-ray crystallography

Crystals of compound 1 and 2 were removed from the flask, a suitable crystal was selected of each, attached to a glass fiber and data were collected at 297(2) K using a Bruker/Siemens SMART APEX X-ray diffractometer (Mo K α radiation, λ = 0.71073 Å). Data were measured using omega scans of 0.3° per frame for 5 s, and a partial and full sphere of data was collected. A total of 1324 and 2400 frames were collected with a final resolution of 0.83 and 0.77 Å for 1 and 2, respectively. Cell parameters were retrieved using SMART [19] software and refined using SAINTPLUS [20] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPLUS software. Absorption corrections were applied using sadabs [21]. Structures were solved by direct methods and refined by least-squares method on F^2 using the SHELXTL [22] program package. Analysis of systematic absences led to the solution and refinement of the structures of **1** and **2** in the space groups $P2_1/n$ (#14) and C2/c (#15), respectively. The triflate anion in **1** was found to be disordered in two positions (70:30%) and only the non-carbon and oxygen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically in 2. No decomposition was observed during data collection. De-

Table 1

Crystallographic data and structure refinement parameters

	1	2
Formula	C12H16CuF6N4O8S2	C ₆ H ₈ CuF ₆ N ₂ O ₈ S ₂
Molecular weight	585.95	477.80
Crystal system, space group	monoclinic,	monoclinic, C2/c
	P2(1)/n	
a (Å)	11.5197(10)	13.002(2)
b (Å)	7.5615(6)	6.8016(12)
c (Å)	12.6908(11)	18.261(3)
β(°)	100.288(2)°	105.299(3)
V (Å ³)	1087.67(16)	1557.7(4)
Ζ	2	4
T (K)	297(2)	298(2)
λ (Å)	0.71073	0.71073
ρ_{calc} (Mg/m ³)	1.789	2.037
μ (mm ⁻¹)	1.294	1.779
F(000)	590	948
Crystal size (mm ³)	$0.64 \times 0.54 \times 0.05$	$0.43 \times 0.32 \times 0.09$
θ Range (°)	2.20 to 25.25	2.31 to 27.46
Index ranges	$-13 \leqslant h \leqslant 13$,	$-16\leqslant h\leqslant 16$,
	$-9\leqslant k\leqslant 6$,	$-8 \leqslant k \leqslant 8$,
	$-15 \leqslant l \leqslant 13$	$-23 \leqslant l \leqslant 23$
Number of reflections collected	9024	10551
Number of independent reflections (R_{int})	1965 (0.0245)	1792 (0.0266)
Data/restraints/parameters	1965/20/178	1792/0/115
Goodness-of-fit	1.080	1.042
$R_1^a \left[I > 2\sigma(I) \right]$	0.0652	0.0323
$wR_2^a [I > 2\sigma(I)]$	0.1834	0.0851
Largest difference in peak, hole (e Å ⁻³)	0.824, -0.941	0.532, -0.243

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$.

Selected bond lengths (Å) and bond angles (°) for $Cu(OTf)_2(2-mepyz)_2(H_2O)_2$ (1) and $Cu(OTf)_2(H_2O)_2(pyz)$ (2)

1		2	
Cu(1)-N(1)	2.011(4)	Cu(1)-N(1)	2.024(2)
Cu(1)-O(3)	1.968(3)	Cu(1)-N(4A)	2.024(2)
Cu(1)-O(4A)	2.420(4)	Cu(1)-O(1)	1.966(2)
Cu(1)-O(4B)	2.423(6)	Cu(1)-O(2)	2.402(2)
S(1A)-O(1A)	1.428(8)	S(1)-O(2)	1.434(2)
S(1A)-O(2A)	1.423(8)	S(1)-O(3)	1.425(2)
S(1A)-O(4A)	1.443(6)	S(1)-O(4)	1.422(2)
S(1A)-C(6A)	1.816(9)	S(1)-C(5)	1.821(3)
C(6A)-F(1A)	1.39(1)	C(5)-F(1)	1.323(3)
C(6A)-F(2A)	1.31(1)	C(5)-F(2)	1.306(4)
C(6A)-F(3A)	1.27(1)	C(5)-F(3)	1.315(4)
N(1)-C(2)	1.332(6)	N(1)-C(2)	1.329(2)
C(1)-C(2)	1.382(7)	C(2)-C(3)	1.386(3)
N(1)-Cu(1)-N(1A)	180	N(1)-Cu(1)-N(4A)	180
N(1)-Cu(1)-O(3)	89.5(2)	N(1)-Cu(1)-O(1)	90.68(4)
N(1)-Cu(1)-O(4A)	85.7(2)	O(2)-Cu(1)-O(2A)	178.45(8)
O(3)-Cu(1)-O(3A)	180	N(4A)-Cu(1)-O(1)	89.32(4)
O(4A)-Cu(1)-O(4AA)	180	N(4A)-Cu(1)-O(2)	89.22(4)
O(3)-Cu(1)-O(4A)	84.7(2)	O(1)-Cu(1)-O(1A)	178.63(8)
C(2)-N(1)-Cu(1)	121.1(3)	C(2)-N(1)-Cu(1)	120.9(1)
S(1A)-O(4A)-Cu(1)	151.8(5)	S(1)-O(2)-Cu(1)	134.2(1)
O(2A)-S(1A)-O(4A)	116.4(5)	O(2)-S(1)-O(3)	114.5(1)
F(1A) - C(6A) - F(2A)	101.3(10)	F(1)-C(5)-F(2)	109.0(3)
C(2) - N(1) - C(3)	117.8(4)	C(2)-N(1)-C(2A)	118.2(2)

tails of the data collection and refinement are given in Table 1 and selected bond lengths and angles can be found in Table 2. Further details are provided in the Supplementary data.

2.3. Magnetic properties

A Quantum Design MPMS-5XL ac/dc SQUID magnetometer equipped with an RSO transport was used to measure the temperature-dependence of the magnetization. Appropriate amounts of polycrystalline samples of **1** and **2** were loaded into pharmaceutical gelatin capsules, placed inside a plastic drinking straw and affixed to the end of a carbon fiber rod. Samples were mounted in the magnetometer at 295 K and zero-field cooled to 2 K. The magnetic field was charged to 1-kOe and data collected upon warming to room temperature. All magnetic data were corrected for core diamagnetism using Pascal's constants.

3. Results and discussion

The crystal structures of 1 and 2 were determined by conventional X-ray crystallographic techniques and both Cu(II) coordination spheres are shown in Fig. 1. Both compounds feature identical coordination environments with donor atoms of the same type positioned trans to one another. The Cu(II) ions in both compounds exhibit the usual Jahn-Teller (4+2) distortion with the Cu-O(triflate) bond distances the longest at 2.420(4) and 2.423(6) Å for 1 and 2.402(2) Å for 2. The Cu(II) ion in 1 lies on an inversion center while the metal and ligand atoms N(1) and N(4) occupy the twofold rotation axis in **2**. The CuO₄N₂ octahedron is significantly more distorted in 1 than in 2 with the bond angles O(3)-Cu(1)- $O(4A) = 84.7(2)^{\circ}$ and $O(1)-Cu(1)-O(2) = 88.21(7)^{\circ}$, respectively, exhibiting the greatest deviation from the ideal 90° angle. All observed geometric parameters found for the 2-mepyz and parent pyz ligands in 1 and 2 are in agreement with previously reported structures [2,4,9-15].

The methyl substituents in **1** are distal to the Cu–N coordinate bond which prevents ligation of the second nitrogen atom, thus limiting the lattice dimensionality to molecular. Each molecule is linked to nearest-neighbors through $O(1A) \cdots H(3A) - O(3)$ hydrogen Download English Version:

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