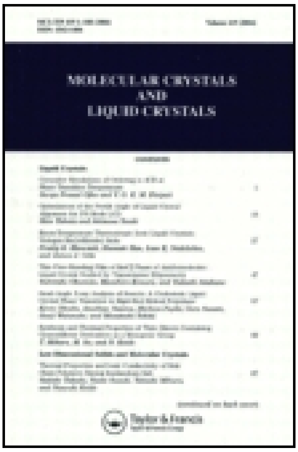

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New One-dimensional Chain Compounds of [M (pdz) $Cl_2]_n$(M=Cu(II), Fe(II), Mn(II); pdz = pyridazine and Their Magnetic Properties

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Three novel one-dimensional coordination polymers with pyridazine (pdz), [M (pdz) $Cl_2]_n$ (M = Cu (II) (**1**), Fe (II) (**2**), Mn (II) (**3**)), were synthesized and characterized. All the compounds have one-dimensional zigzag chain structures. The copper ion in compound **1** has a planer coordination sphere with two bridging pdz ligands and two Cl^- anions, while the metal ions in the other compounds have a distorted octahedral environment with pdz and Cl^- groups both acting as bridges. The magnetic data of these compounds show antiferromagnetic interaction between the magnetic centers within the chains.

Keywords: pyridazine, the first-transition metal ion, one-dimensional structure, and antiferromagnetic interaction

INTRODUCTION

The use of small molecules to bridge magnetic centers has recently gained much interest because of the discovery of molecular magnetic materials based on metal-cyano and metal-oxo bridges. [1-2] Heterocyclic diazine group, such as pyrazine, pyrimidine, pyridazine, and their adducts are one of the most useful bridging ligands to form multinuclear and polymer complexes. [3, 4] In comparison with pyrazine and pyrimidine, pyridazine could afford a compact structure with strong electronic or magnetic interaction between metal ions because of the short exchange pathway. However, few polymer complexes directly bridged by pyridazine ligand are reported. To our knowledge, only two crystal structures of polymer compounds $[CuCl_2(pdz)]_n$ and $\{[Cu(\mu\text{-pdz})(\mu\text{-OH})(\mu\text{-}O_2NO)]_2Cu\}\cdot 4ClO_4\cdot 2MeOH$ were obtained. [3] This manuscript describes the structures and magnetic behavior of three novel one-dimensional compounds with pyridazine linkage.

EXPERIMENT

Synthesis

Single crystals of compounds **1-4** are obtained by layered method with methanol solution of MCl_2 and chloroform solution of pdz. Anal. Calcd for $C_4H_4Cl_2CuN_2$ (**1**): N, 13.05; C, 22.38; H: 1.87, Found: N, 13.08; C, 22.52; H, 1.97. IR (KBr, cm^{-1}) for **1**: 3416 (br, m), 3106 (m), 3092 (m), 1576 (m), 1458 (w), 1406 (s), 1074 (w), 1008 (w), 767 (s), 679 (w), 425 (w). Anal. Calcd for $C_4H_4Cl_2FeN_2$ (**2**): N, 13.54; C, 23.20; H: 1.93, Found: N, 13.31; C, 23.39; H, 2.32. IR (KBr, cm^{-1}) for **2**: 3388 (br, m), 3106 (sh, w), 3091 (m), 1576 (m), 1455 (m), 1416 (s), 1398 (sh, m), 1070 (m), 991 (s), 763 (s), 680 (m), 405 (m). Anal. Calcd for $C_4H_4Cl_2MnN_2$ (**3**): N, 13.59; C, 23.31; H: 1.94, Found: N, 13.48; C, 23.45; H, 2.14. IR (KBr, cm^{-1}) for **3**: 3423 (br, m), 3158 (sh, m), 3092 (m), 1577 (m), 1456 (w), 1415 (s), 1396 (m), 1223 (m), 1069 (m), 989 (s), 767 (s), 677 (m), 397 (w).

X-ray structure analysis

The X-ray diffraction data of the single crystals of **1-3** were collected on the Rigaku Mercury CCD system using graphite monchromated Mo-Kα radiation (λ = 0.71069Å) with the sample-to-detector distance of 35mm. The data were collected at room temperature using ω scan technique. All the structures were solved by direct methods and expanded using Fourier techniques. The refinements were performed using least-square method of the teXsan crystallographic software package of Molecular Structure Corporation.[5] Non-hydrogen atoms were refined anisotropically. Crystallographic data for compounds **1**, **2** and **3** is listed in Table 1.

TABLE 1 Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
formula	*$C_4H_4Cl_2CuN_2$	$C_4H_4Cl_2FeN_2$	$C_4H_4Cl_2MnN_2$
FW	214.54	206.84	205.93
crystal system	triclinic	orthorhombic	orthorhombic
space group	*P*-1	*Imma*	*Imma*
a (Å)	6.763 (5)	6.750 (4)	6.877 (3)
b (Å)	7.395 (6)	7.377 (1)	7.429 (1)
c (Å)	7.781 (6)	12.949 (2)	13.023 (1)
α (°)	114.99 (3)		
β (°)	112.03 (3)		
γ (°)	97.07 (4)		
V (Å^3)	308.1 (4)	644.8 (4)	665.4 (3)
Z value	2	4	4
ρ^{cal} (g/cm^3)	2.313	2.131	2.056
residuals: ^aR, ^bRw	0.033, 0.057	0.035, 0.05	0.026, 0.047
GoF	2.92	2.59	1.99

$^aR = \Sigma||F_{obsv}| - |F_{calc}|| / \Sigma|F_{obsv}|$ for $I > 3.0\sigma(I)$ data

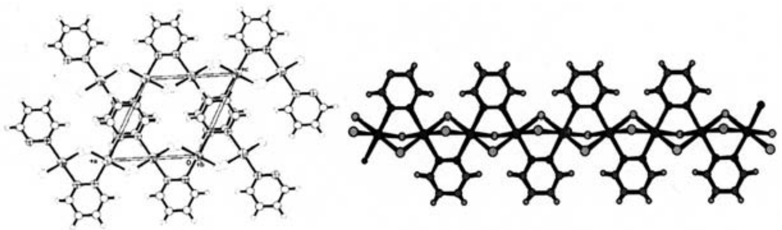
$^bRw = [\ \Sigma w\ (|F_{obsv}| - |F_{calc}|)^2 / \Sigma w\ Fo^2\ ]^{1/2}$ $(\ w = 1 / [\ \sigma_c^2\ (F_o) + p^2 / 4F_o^2\ ]\ )$

*The monoclinic phase of compound **1** which obtained by gel technique (See ref.[4]) $a = 9.383$, $b = 12.429$, $c = 6.757$ Å, $\beta = 128.48°$

RESULTS AND DISCUSSION

Crystal Structures

All the three compounds **1, 2** and **3** (Fig. 1) have one dimensional zigzag chain structures connected by μ-pdz ligand. The bond distances of M-N for these compounds are 2.033(4) (M = Cu), 2.195(5) (M = Fe) and 2.275(2) Å (M = Mn), respectively. The difference between compound **1** and **2** (or **3**) is appeared in the coordination mode of Cl^- group. In the later two compounds, the two Cl^- anions act as the bridges



Cu (1)-Cl (1): 2.295(1) Å
Cu (2)-Cl (2): 2.294(1) Å
Cu (1)-N (1): 2.038(4) Å
Cu (2)-N (2): 2.027(4) Å

M (1)-Cl (1): 2.495(2) (Fe), 2.544(1) Å (Mn)
M (1)-N (1): 2.195(5) (Fe), 2.275(2) Å (Mn)
Cl (1)-M (1)-Cl (1): 84.06(7) (Fe), 83.67(3)° (Mn)
Cl (1)-M (1)-Cl (1)$: 95.94(7)(Fe), 96.33(3) ° (Mn)
M (1)-Cl (1)-M (1)#: 85.12(6)(Fe), 85.03(3) ° (Mn)
Symmetry: $: -0.5+*x*, *y*, 0.5-*z*, #: 1-*x*, *y*, *z*

FIGURE 1 1-D zigzag chain structures of compounds **1** (left), **2** and **3** (right)

2.495(2) (M = Fe) and 2.544(1) Å (M = Mn), respectively. The M-Cl-M angles of the adjacent metal ions through bridged Cl^- are 85.12(6) and 85.03(3)Å for compounds **2** and **3**, respectively. In compound **1,** two Cl^- anions terminally coordinate to the copper atom with bond distances of 2.295(1) and 2.294(1) Å, shorter than the bridging ones in compounds **2** and **3,** and weakly link to adjacent copper atom with distance of 2.801(2) Å. The Fe (II) and Mn (II) atoms in compounds **2** and **3** have distorted octahedral coordination environments, while in **1** the unsymmetrical coordination mode of Cl^- anions and Jahn-Teller distortion make the coordination sphere of the copper atom deviate from octahedral symmetry into a planar distorted ones. The nearest intrachain distances of the metal ions are 3.38, 3.38 and 3.44 Å for compound **1**, **2** and **3**, respectively. There are weak π…π interaction between pdz ligands of adjacent chains in these compounds, the distance between the nearest neighbor pdz planes being 3.6~3.7 Å

Magnetic properties

Magnetic susceptibilities for **1-3** were measured on a SQUID magnetometer in the temperature range of 2-300K. Corrections for diamagnetism were applied by using Pascal's constants. The magnetic data for **1** and **3** have a Heisenberg 1D chain behavior. Even at room temperature, the $\chi_M T$ values for **1** and **3** (0.33 and 3.75 cm^3 K mol^{-1}, respectively) are smaller than spin-only value for noninteracting copper ion of $S = 1/2$ (0.375 cm^3 K mol^{-1}) and manganese ion of $S = 5/2$ (4.377 cm^3 K mol^{-1}), respectively (Fig. 2). These values of the two compounds continuously decrease upon cooling to reach to 0 and 0.1 cm^3 K mol^{-1} at 2 K, respectively, showing an antiferromagnetic interaction within the chain. The data for compound **1** is fitted by Bonner-Fisher equation for the chain structure giving $g = 2.05$ and $J = -78.9$ cm^{-1}. The $\chi_M T$ value of **2** at room temperature is 3.13 cm^3 K mol^{-1}, a little higher than what is expected for noninteracting single ion of $S = 2$ (3 cm^3 K mol^{-1}). This value remains practically unchanged down to 20 K and decreases quickly to 0.87 cm^3 K mol^{-1} at 2K under the magnetic field of 1T. The data above 20K for **2** can be fitted with Curie-Weiss equation giving $C = 3.19$ cm^3mol^{-1} and $\theta = -4.1$K. The rapid decreasing of the $\chi_M T$ value for compounds **2** could be due to weak antiferromagnetic coupling, zero-field splitting or both. The χ_M data in very low temperature for all the compounds indicates a paramagnetic impurity.

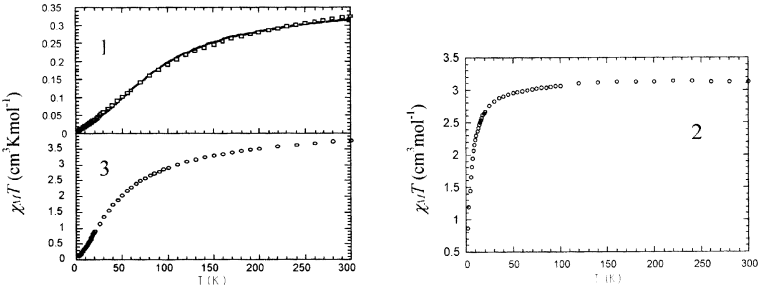


FIGURE 2 Thermal variation of $\chi_M T$ for compounds **1** and **3** (right) at magnetic field of 0.1T and **2** at magnetic field of 1 T. The dot line shows the fitting curve of $\chi_M T$ using Bonner - Fisher's equation

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