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Synthesis, Structure and Magnetic Properties of a Two- Dimensional Nickel(II) Coordination Polymer, $\{[Ni(pzdc)(pyz)].2H_2O\}_n$ (H_2pzdc = pyrazine-23-dicarboxylic acid; pyz = pyrazine)

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SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF A TWO-DIMENSIONAL NICKEL(II) COORDINATION POLYMER, $\{[Ni(pzdc)(pyz)]\cdot 2H_2O\}_n$ (H_2pzdc = pyrazine-2,3-dicarboxylic acid; pyz = pyrazine)

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Abstract A title compound has been synthesized and characterized. The complex crystallizes in the orthorhombic space group *Cmcm* with a = 7.004(2) Å, b = 12.748(2) Å, c = 13.665(2) Å, V = 1220.1(3) Å^3 and Z = 4. The complex consists of two-dimensional square arrays of nickel(II) ions bridged by $pzdc^{2-}$ and pyz ligands. Each nickel ion has a slightly distorted octahedral coordination with N_4O_2 chromopher. The magnetic susceptibility data over a range of 2 - 300 K were fitted by using an Heisenberg antiferromagnet with a mean field approximation. The obtained J and zJ' values are -1.70 cm^{-1} and -0.70 cm^{-1}, respectively.

INTRODUCTION

Recent studies on transition metal compounds have been devoted to the synthesis of coordination polymers towards molecular based materials.[1-6] However, the well-characterized compounds have still been limited because of the difficulty of crystallization of coordination polymers. Therefore, development of rational synthetic routes to designed coordination polymers is one of urgent problems. To succeed in the synthesis, the use of bridging ligands such as oxocarbons,[7-14] diazenes,[15-20] cyanide[4, 5, 21] and azide[22-26] would be one of the effective methods. Especially, pyrazine (pyz) is well-known to act as a bridging ligand to give low-dimensional compounds. Several one- or two-dimensional coordination polymers bridged by pyz derivatives have been structurally and magnetically characterized.[15-19, 27, 28] However, two-dimensional Ni(II) polymers bridged by pyz derivatives have not been reported. We have succeeded in the crystallization of a novel Ni(II) coordination polymer containing pyz and pyrazine-2,3-dicarboxylate ($pzdc^{2-}$) as bridging ligands. This manuscript presents the structural and magnetic characterization of a Ni(II) two-dimensional polymer,

$\{[Ni(pzdc)(pyz)]\bullet 2H_2O\}_n$.

EXPERIMENTAL

Synthesis of $\{[Ni(pzdc)(pyz)]\bullet 2H_2O\}_n$

Nickel(II) sulfate hexahydrate (0.526 g, 2 mmol), Na_2pzdc (0.212 g, 1 mmol) and pyz (0.32 g, 4 mmol) were dissolved in water (20 mL). Plate shaped yellow single crystals suitable for the X-ray diffraction study were obtained after several days. Anal. Calcd for $Ni(C_6H_2N_2O_4)(C_4H_4N_2)(H_2O)_2$: C, 35.2; H, 3.0; N, 16.4. Found: C, 35.9; H, 2.1; N, 17.1.

Magnetic Measurements

Magnetic measurements were carried out on polycrystalline samples of this complex with a SQUID susceptometer (Quantum Design, San Diego, CA) interfaced with an HP Vectra computer system in the 300-2 K range. The magnetic field was approximately 10000 G. Diamagnetic corrections were estimated from the Pascal tables.

RESULTS AND DISCUSSION

Description of the Structure

X-ray crystallography reveals that the asymmetric unit consists of one nickel ion, one $pzdc^{2-}$ ligand, one pyz ligand and two water molecules (Figure 1).[29] Each nickel ion has slightly distorted octahedral environment; the equatorial plane comprises of the two nitrogen atoms and two oxygen atoms from bisbidentate chelating ligands, $pzdc^{2-}$, and the axial coordination sites are occupied by two nitrogen atoms of bridging pyz groups. The bond distances of Ni-N(1), Ni-O(1) and Ni-N(2) are 2.066(7)Å, 2.035(5)Å and 2.120(6)Å, respectively. The equatorial Ni-N(1) and the axial Ni-N(2) bond distances are longer than the Ni-N distance (Ni-N = 1.855Å) of a Ni(II) complex, $[Ni(dmpz)Br_2]_n$[28] which is only one nickel polymer bridged by pyrazine derivative and has one-dimensional chain structure. In $[Ni(dmpz)Br_2]_n$ each nickel ion has a square planer coordination.

$\{[Ni(pzdc)(pyz)]\bullet 2H_2O\}_n$ has a 2-D sheet structure parallel to *ac*-plane which

is composed of the infinite square arrays of [Ni(μ-pyz)(μ-pzdc)] motifs. In this 2-D sheet the Ni-Ni separations through the $pzdc^{2-}$ and pyz ligands are 6.83 and 7.00Å, respectively. The distance between the nearest-neighbor sheets is 6.374 Å. In the related complexes, $[Fe(pyz)_2(NCS)_2]_n$[18], $[Cu(pyz)_2(CH_3SO_3)_2]_n$,[16] and $[Cu(pyz)_2(ClO_4)_2]_n$,[17] which have 2-D sheet structures bridged by pyz ligands, the distances between the 2-D sheets are 6.278Å, 6.565Å and 7.012Å, respectively.

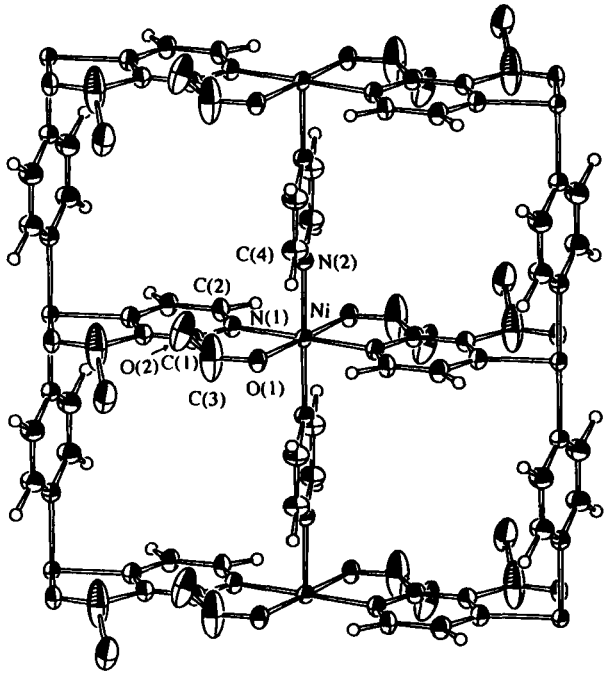

FIGURE 1 Crystal structure for $\{[Ni(pzdc)(pyz)]\cdot 2H_2O\}_n$. Selected bond distances (Å) and angles (°) are as follows: Ni-O(1) 2.035(5), Ni-N(1) 2.066(7), Ni-N(2) 2.120(6), N(1)-C(1) 1.35(1), N(1)-C(2) 1.325(10), C(1)-C(3) 1.51(1), C(3)-O(1) 1.24(1), C(3)-O(2) 1.44(1), N(2)-C(4) 1.338(5), N(1)-Ni-N(2) 90.0, O(1)-Ni-N(1) 81.4(2), O(1)-Ni-N(2) 90.0. The O(2) atom is disordered about the crystallographic mirror with exactly 50% occupancy of each site.

Magnetic Properties

Magnetic susceptibilities of $\{[Ni(pzdc)(pyz)]\cdot 2H_2O\}_n$ were measured from 300 to 2 K and the molar magnetic susceptibilities χ_M and $\chi_M T$ versus temperature is shown in Figure 2. The χ_M value increases with decreasing temperature, reaching a maximum of 0.113 emu•mol^{-1} at 3.0 K, and then rapidly decreases. The $\chi_M T$ value decreases from 1.151 emu•K•mol^{-1} (300 K) to 0.211 emu•K•mol^{-1} (2 K), indicating the existence of antiferromagnetic interaction in this compound.

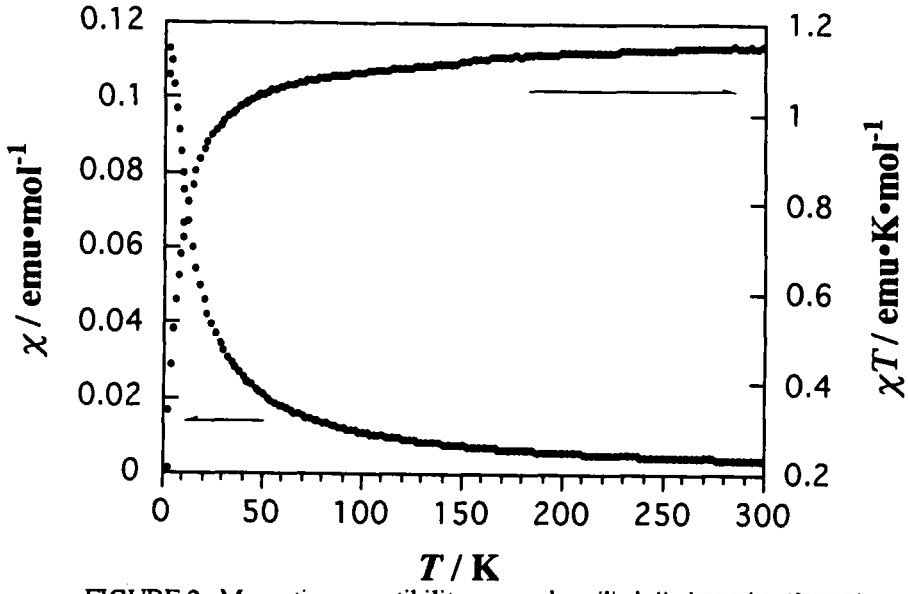

FIGURE 2 Magnetic susceptibility χ_M and $\chi_M T$ plotted as a function of temperature from 2 to 300 K.

The 2-D sheet structure in Figure 1 shows that there are two pathways for antiferromagnetic interaction between the Ni ions, Ni-pyz-Ni and N-pzdc-Ni, within the sheet. In order to analyze the observed χ_M values equations (1)-(3) are used, assuming that either of the two pathways is effective more than the other. This is supported by good fit mentioned below.

$$\chi_{chain} = (N\beta^2 g^2/kT)(A+Bx+Cx^2)/(3+Dx+Ex^2+Fx^3) \quad (1)$$

$$\chi_M = \chi_{chain}/(1-2zJ'\chi_{chain}/(Ng^2\beta^2)) \quad (2)$$

$$\chi_{obs} = \chi_M(1-\rho)+2Ng^2\beta^2\rho/3kT+\mathrm{TIP} \quad (3)$$

where $x = |J|/kT$, A = 2, B = 0.0194, C = 0.777, D = 4.346, E = 3.232 and F = 5.834. Eq (1) is a expression in a chain based on the spin Hamiltonian $H = -J\Sigma S_i S_{i+1}$.[30] χ_{chain} is the susceptibility of an infinite isotropic Heisenberg chain of S=1 spins. The single-ion ground term of high-spin nickel(II) ion (S = 1) in a pseudooctahedral environment is $^3A_2$ and hence has no orbital momentum of the first order. In eq (2) the effect of the weaker exchange interaction through another pathway is considered as a molecular field correction.[31] The observed susceptibilities were corrected according to eq (3), which contains the contribution of the paramagnetic

impurity and temperature independent paramagnetism as $2N\beta^2g^2/3kT$ and TIP, respectively.

The obtained parameters for fitting the experimental data were $J = -1.70cm^{-1}$, $zJ' = -0.70cm^{-1}$, $g = 2.14$ and $\rho = 0.02$. The agreement factor R defined by $\Sigma(\chi_{obsd}-\chi_{calcd})^2/\Sigma\chi_{obsd}^2$ is equal to 5.8×10^{-7}. From the crystal structure it is estimated that the z value equals 2. There have so far been no magnetic studies of the Ni(II) polymers bridged by pyz or $pzdc^{2-}$. However, in copper complexes, several one- and two-dimensional polymers bridged by pyz derivatives have been synthesized and studied from the viewpoint of magnetic properties. The J value of a copper(II) polymer bridged by $pzdc^{2-}$, $\{[Cu(pzdc)(H_2O)_2]\cdot 2H_2O\}_n$, is $-1.24\ cm^{-1}$, smaller than those of Cu(II)-pyz complexes; $J = -7.5\ cm^{-1}$, $-7.6\ cm^{-1}$ and $-5.3\ cm^{-1}$ for $[Cu(pyz)(NO_3)_2]_n$,[15] $[Cu(pyz)(CF_3SO_3)_2]_n$[32] and $[Cu(pyz)_2(ClO_4)_2]_n$,[17] respectively. This is possibly because the overlap integral between the magnetic orbital of the copper ion and the σ ligand orbital decreases from pyz to $pzdc^{2-}$. On the basis of the copper complexes, the larger J value of $-1.70\ cm^{-1}$ is ascribed to the Ni-pyz-Ni pathway, while the smaller J' value of $-0.35\ cm^{-1}$ is that of the $pzdc^{2-}$ ligand.

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