Spin Frustrated Double Chain $\{[Fe(PZDA)H_2O)_2]\bullet 2H_2O\}_n$ (H_2PZDA=2,3-Pyrazinedicarboxylic Acid)

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A novel compound $\{[Fe(PZDA)(H_2O)_2]\cdot 2H_2O\}_n$ has been synthesized and its structure determined by X-ray diffraction analysis, which consists of a quasi-ladder-like double chain running along *a* axis where Fe(II) ions are linked through the carboxylic groups acting as the edges of the ladder and pyrazine rings functioning as the rungs. Variable-temperature magnetic susceptibility study indicates the presence of spin frustration in the double chain compound.

Recent studies on synthesis, structure and magnetic properties of ordered polymetallic chains opened a new perspective in the field of low-dimensional electronic and magnetic systems.[1-4] Pyrazine has been known to function as an excellent bridging ligand. When coordinated to metallic ions, it affords a wide variety of polynuclear compounds. It allows coupling between the metals via orbital overlap with ligand orbits and is therefore a potential transmitter of magnetic exchange interaction. Carboxylic acid ligands are also capable of bridging and providing effective magnetic exchange pathway. When the two ligands are combined, such as pyrazinecarboxylic acid, pyrazinedicarboxylic acid and pyrazineteracarboxylic acid, it is very likely to obtain some structurally novel and magnetically interesting complexes. For 2,3-pyrazinedicarboxylic acid, several complexes were previously structurally characterized and magnetically investigated.[5-11] Qusai-one-dimensional complexes $M(HPZDA)_2(H_2O)_2$ (M=Co, Ni) showed a weak antiferromagnetic intrachain interaction transmitting through hydrogen bonds. Antiferromagnetic interaction also was observed in one-dimensional linear chain $M(PZDA)(H_2O)_2\ 2H_2O$ (M=Cu, Co, Ni).[6,11] Whereas linear chain Cu(PZDA)·HCl where Cl is also coordinated to the Cu^{2+} ion exhibited ferromagnetic intrachain coupling.[10] Here, we report a novel quasi-ladder-like double chain $\{[Fe(PZDA)(H_2O)_2]\cdot 2H_2O\}_n$ bridged through PZDA molecules, which displays a spin frustrated magnetic interaction. Spin frustration which is an essential ingredient to generate a spin glass can be obtained due to next-nearest-exchange or triangulation.[12] Up to now, known experimental molecular-based frustrated systems remain quite limited, especially for coordination polymers.[12,13] Two-dimensional triangular-*kagome* antiferromagnet $Cu_9X_2(cpa)_6$ suggested a high degree of spin frustration.[14] This work provides another example of one-dimensional spin frustration.

The title compound $\{[Fe(PZDA)(H_2O)_2]\cdot 2H_2O\}_n$ was prepared by slowly adding 10 ml $FeCl_3\cdot 4H_2O$ (1 mmol) aqueous solution into a 20 ml H_2PZDA solution (1.5 mmol) neutralized by NaOH (3mmol). The resulting clear brown reddish solution was filtered and allowed to stand at room temperature. The single crystals suitable for X-ray diffraction were obtained in a month and separated by filtration, washed with water and ethanol and dried in air (yield: 34%). Element analysis confirmed the formula in line with the results of X-ray diffraction.[15-17] The trivalent Fe was converted to divalent Fe, probably due to the reduction of the PZDA. The reason is not very clear and further investigation is needed. This situation also occurs for other system.[18]

The X-ray diffraction analysis reveals that the complex consists of a ladder-like chain running along crystallographic *a* axis, where Fe(II) are linked by bridging carboxylic groups. Fe (II) atom is coordinated by one N atom of pyrazine ring and a monodentate carboxylato O atom, two O atoms from two other PZDA's carboxylic groups and two O atoms of water molecules, forming a distorted octahedral environment, as depicted in Figure 1. The plane defined by carboxylic group O(1)-O(2)-C(2)-C(1) is nearly coplanar to the pyrazine ring with the dihedral angle of 3.26(3)°, while another carboxylate plane defined by the O(3)-O(4)-C(4)-C(3) is approximately perpendicular to the pyrazine ring, intersecting at 85.10(8)°. The edges of the ladder are made of Fe-O-C-O units in which carboxylato group bridge adjacent Fe(II) atoms in *anti-anti* mode with the Fe(1a)-O(3)-C(4)-C(3) and Fe(1c)-O(4)-C(4)-C(3) torsion angles of -7.38(8)° and 20.16(4)°, respectively. As for the rungs of the ladder, they are made of pyrazine rings which link one Fe(II) ion and one C atom. Strictly speaking, the connection of Fe atoms should not be regarded as a ladder-like chain. Here, we call it as quasi-ladder-

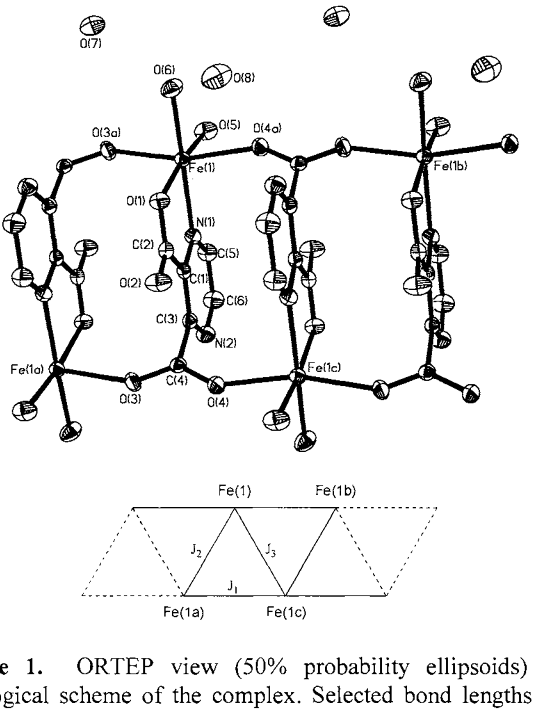

Figure 1. ORTEP view (50% probability ellipsoids) and topological scheme of the complex. Selected bond lengths (Å): Fe(1)-O(5) = 2.048(2), Fe(1)-O(1) = 2.083(2), Fe(1)-O(6) = 2.103(2), $Fe(1)\text{-}O(3)^a$ = 2.152(2), $Fe(1)\text{-}O(4)^b$ = 2.179(2), Fe(1)-N(1) = 2.186(2). a: -x, -y+2, -z+1; b: -x+1, -y+2, -z+1.

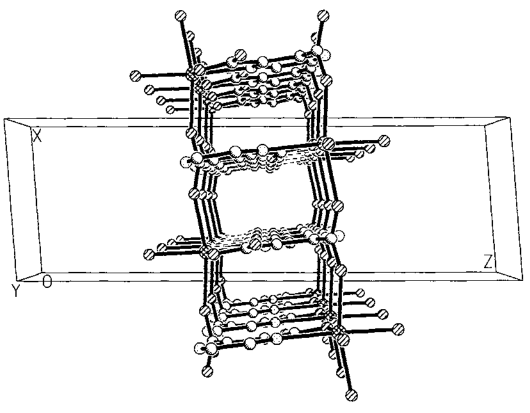

Figure 2. Perspective view down along *b* axis showing channel structure.

like motif. The nearest Fe-Fe separation in the edge of ladders is 6.5023(3) Å and the nearest separations of Fe-Fe between the edges are 6.7448(7) and 6.4816(7) Å, respectively.

Within the lattice, the ladders are parallel to each other, and organized in such a way that each ladder is surrounded by four identical ladders. Such organization produces channels perpendicular to the plane of the ladders (Figure 2). The size has interatomic dimensions of 5.5 Å × 3.3 Å. No water molecules are included within the channels, since the distance between the two pyrazine rings in the π-π interaction is in the range of 3.3-3.4 Å. Instead, they are filled between the ladders and link the ladders into a two-dimensional sheets through hydrogen bonding.

Variable-temperature magnetic susceptibility was measured on the crystal samples in the temperature 2-280 K at 10 kOe magnetic field. The results are presented in Figure 3. The observed value of χ_mT is 3.10 $cm^3\ mol^{-1}$ K at room temperature, slightly higher than the spin-only value of 3.00 $cm^3\ mol^{-1}$ K for high spin Fe(II) with g=2. χ_mT increases gradually as the temperature is lowered, appearing a maximum value of 3.69 $cm^3\ mol^{-1}$ K around 50 K, then sharply going down to 0.3 $cm^3\ mol^{-1}$ K at 2.2 K. The data above 50 K was fitted to the Curies-Weiss law ($\chi_m^{-1}=(T-\theta)/C$) giving C=3.16 $cm^3\ mol^{-1}$ K and $\theta=+10.5$ K. Why the χ_mT increases upon cooling and Weiss constant is positive? Based on the structure, the connection of the nearest Fe(II) ions in the ladder shows a topologically triangular double chain arrangement (Figure 1). Fe(II) ions are located at the corners of near equal-edge-triangle, suggesting the similar order of the magnetic couplings (J_1,J_2,J_3). On the other hand, the octahedral ligand environment of Fe(II) ions favors antiferromagnetic exchange.[19,20] Therefore a parallel alignment of two neighboring spins must be present due to the spin frustration, which results in the increase of χmT. The sharply decrease of χ_mT at lower temperature may result from the interactions between the double chains and/or spin transition of Fe(II). A detailed investigation of magnetic behavior on the unusual quasi-ladder-like chain, together with the isostructural Mn(II) complex will be reported in due course.

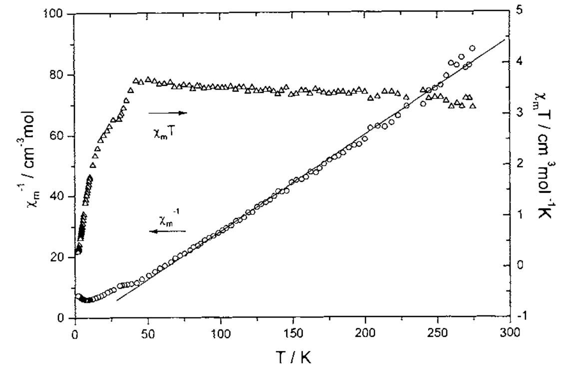

Figure 3. Magnetic susceptibility plotted as χ_m^{-1} versus T (O) and χ_mT versus T (Δ). Solid line is the fit result of Curies-Weiss law for the data in the range of 50-275 K.

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References and Footnotes

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15 Element analysis: Found: C, 24.44; H, 3.69; N, 9.29%. Calcd for $C_6H_{10}FeN_2O_8$: C, 24.49; H, 3.40; N, 9.52%.
16 Crystal data for complex $C_6H_{10}FeN_2O_8$: M=294.01, monoclinic, space group P2/m, a=6.5023(3) Å, b=7.5897(5) Å, c=20.4670(10) Å, β=94.122(1)°, U=1007.45(9) Å^3, Z=4, μ=1.534 cm^{-1}, F(000)=600, R1=0.030 for 1908 reflections ($I>2\sigma(I)$) and wR2=0.076 for all reflections.
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