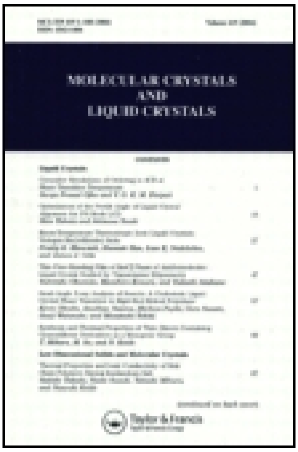

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Effect of Intersheet Interaction Upon Magnetic Ordering in Two-dimensional Bimetallic Assemblies, $[Ni(dmen)_2]_2[Fe(CN)_6]X{\cdot}nH_2O$

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Cyanide-bridged bimetallic assemblies, $[Ni(dmen)_2]_2[Fe(CN)_6]X{\cdot}nH_2O$ (dmen = 1,1-dimethylethylenediamine; X^- = *p*-phenylbenzenesulfonate ($PhBSO_3^-$), n = 5, (**1**); *p*-tolylsulfonate ($TolSO_3^-$), n = 6, (**2**)), have been prepared. The X-ray crystallography for the assemblies has revealed a 2-D network structure based on Fe_4Ni_4 square units extended by Fe-CN-Ni linkage. They show a long-range ferromagnetic ordering around 10 K based on a ferromagnetic interaction between the adjacent Fe(III) and Ni(II) ions through cyanide bridge. And dehydrated compounds of **1** and **2** also show a long-range ferromagnetic ordering.

Keywords: molecular-based ferromagnet; intersheet interaction, two-dimensional network; bimetallic assembly

INTRODUCTION

The design of molecular magnets based on metal-extended systems is a current subject of many studies. We have studied bimetallic assemblies consisting of $[Ni(diamine)_2]^{2+}$ and $[M(CN)_6]^{n-}$, focusing on the correlation between network structure and magnetic property.[1-3] Of particular interest are $[Ni(dmen)_2]_2[Fe(CN)_6]X \cdot nH_2O$ ($X = ClO_4^-$, PF_6^-, *etc.*) which have a 2-D sheet structure show a ferromagnetic ordering or metamagnetic nature depending on the intersheet separation. The metamagnetism is associated with an intersheet antiferromagnetic interaction that is prominent in a small intersheet separation (< 10 Å). The intersheet antiferromagnetic interaction is negligible in a large intersheet separation (> 10 Å) to show a 3-D ferromagnetic ordering. We have also found that the dehydration of crystalline ferromagnets often leads to shortening in the intersheet separation and thence conversion into metamagnets. The crucial intersheet separation determining ferromagnetism or metamagnetism is assumed to be 10 Å. In order to confirm this further, two analogous compounds $[Ni(dmen)_2]_2[Fe(CN)_6]X \cdot nH_2O$ ((X, n) = ($PhBSO_3^-$, 5) (**1**), ($TolSO_3^-$, 6) (**2**)) have been prepared and their structures and magnetic properties are studied

RESULTS AND DISCUSSION

Preparations and General Characterization

$[Ni(dmen)_3]Cl_2$ and $K_3[Fe(CN)_6]$ were reacted in the 2 : 1 molar ratio in an aqueous solution. On addition of a small excess of NaX into reaction mixture $[Ni(dmen)_2]_2[Fe(CN)_6]X \cdot nH_2O$ ((X, n) = ($PhBSO_3^-$, 5; **1**), $TolSO_3^-$, 6 (**2**)) were obtained as brown plates. Anhydrous samples **1'** and **2'** were prepared by heating **1** and **2** at 120 °C for a few hours with weight monitoring. All the hydrated and anhydrous compounds show two ν(CN) modes of cyanide group at 2110 and 2140 cm^{-1}.

Crystal Structure

Crystal parameters: $[Ni(dmen)_2]_2[Fe(CN)_6]PhBSO_3 \cdot 5H_2O$ (**1**), Formula = $C_{34}H_{67}N_{14}FeNi_2O_8S$, f.w. = 1005.30, crystal system = monoclinic, space group = $P2_1/n$, a = 15.202(2), b = 14.265(2), c = 22.792(4) Å, β = 105.311(9) °, V = 4767.08(1) Å^3, Z = 4, Dc = 1.401 gcm^{-3}, μ(MoKα) = 11.85 cm^{-1}, R = 0.055, Rw = 0.084 at 153 K; $[Ni(dmen)_2]_2[Fe(CN)_6]TolSO_3 \cdot 6H_2O$ (**2**), Formula = $C_{29}H_{67}N_{14}FeNi_2O_9S$, f.w. = 961.24, crystal system = monoclinic, space group = $C2/m$, a = 23.299(8), b = 14.172(9), c = 15.137(8), β = 96.14(5) °, V = 4969(4) Å^3, Z = 4, Dc = 1.285 gcm^{-3}, μ(MoKα) = 11.35 cm^{-1} at 295 K

An ORTEP drawing of the asymmetric unit for **1** with atom numbering scheme is given in Figure 1. The asymmetric unit consists of one $[Fe(CN)_6]^{3-}$ anion, two units of "one-half of *trans*-$[Ni(dmen)_2]^{2+}$", one *trans*-$[Ni(dmen)_2]^{2+}$ molecule, one $PhBSO_3^-$ and six water molecules. Each metal center adopts a pseudo octahedral geometry. The Ni2 and Ni3 are located on special equivalent positions (0, 0, 0) and (0, 0.5, 0), respectively. The Fe-C, C-N and N-Ni bond distances range from 1.943(4) to 1.975(4) Å, from 1.146(6) to 1.156(5) Å and from 2.082(3) to 2.158(3) Å, respectively. $[Fe(CN)_6]^{3-}$ coordinates to the axial site of four adjacent $[Ni(dmen)_2]^{2+}$ units through its N1, N2, N5 and N6 on a plane. Ni1-N1, Ni1*-N5 (*; symmetry operation 1/2-x, 1/2+y, -1/2-z), Ni2-N2 and Ni3-N6 bond distances are 2.131(3), 2.127(3), 2.158(3) and 2.193(3) Å, respectively. In the lattice, a 2-D sheet structure is formed which extends on the $(1, 0, \bar{1})$ plane. This structure is essentially similar to a square grid structure previously reported[1-3], except that the Fe-C6-N6-Ni3 linkage is slightly elongated (Fe-C6 = 1.975(4), Ni3-N6 = 2.193(3) Å). In the lattice the 2-D sheets align along the (1, 0, 1) direction with the nearest Fe···Fe, Fe···Ni and Ni···Ni separations of 11.912(2), 11.190(2) and 11.291(2)Å, respectively. The $PhBSO_3^-$ molecules locate in the square cavity with an inclination of *ca.* 60° to the 2-D sheet. The lattice water molecules reside between 2-D sheets.

Compound **2** forms a 2-D square grid similar to **1**. Because of an efflorescent nature of the single crystal, the structure of **2** was not solved completely. However, the intersheet separation was estimated at 11.146 Å by the X-ray structural result and crystal parameters.

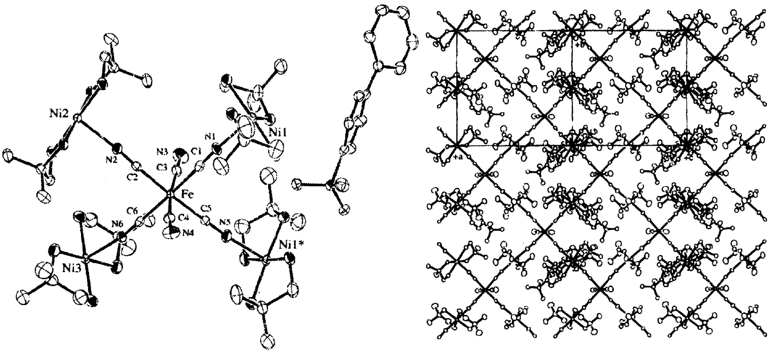

FIGURE 1 (left) An ORTEP drawing of the asymmetric unit of **1** (water molecules are omitted for clarity); (right) Polymeric structure of **1**.

Magnetic Property

The χ_M *vs.* T plots of **1** and **1'** are shown in Figure 3. The $\chi_M T$ value at room temperature is 3.44 cm^{3}Kmol^{-1} (5.25 μ_B) per FeNi$_2$, that is larger than the value expected for one low-spin Fe(III) and two paramagnetic Ni(II) ions (2.38 cm^{3}Kmol^{-1}; 4.36 μ_B). The $\chi_M T$ increases with decreasing temperature up to a maximum value of 684 cm^{3}Kmol^{-1} (74.0 μ_B) at 7.5 K. The χ_M value shows no decrease until 2.0 K. The Curie-Weiss plots ($\chi_M = C/(T-\theta)$) indicated a positive Weiss constant of $\theta = +8.3$ K. The results clearly indicate a ferromagnetic ordering based on the strict orthogonality of magnetic orbitals between Ni(II) and low-spin Fe(III). The phase transition temperature of **1** was determined to be 8.8 K by magnetization measurements under 5 G.

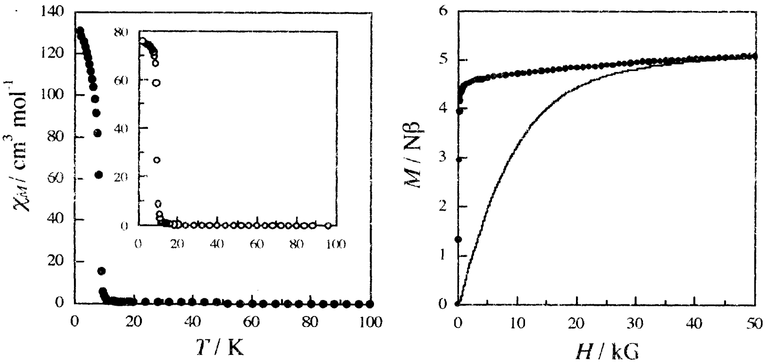

FIGURE 2 (left) χ_M *vs*. T plots of **1** (●) and **1'** (○; insert); (right) M *vs* H plot for **1** at 2 K. The solid line is drawn based on Brillouin function for $S_T = 5/2$ with $g_{ave.} = 2.1$.

The field-dependence of magnetization (0 – 50 kG at 2 K) shows a sharp increase at a weak applied field, and the saturation magnetization $M_S = 5.1\ N\mu_B$ at 50 kG corresponds to 5 $N\mu_B$ resulting from the ferromagnetic coupling of two Ni(II) (S = 1) and one Fe(III) (S = 1/2) ions. The magnetic hysteresis loop at 2 K demonstrates that **1** is a soft magnet with a remnant magnetization of 2.1×10^4 cm^{3}Gmol^{-1} and a coercive field of 150 G.

Anhydrous sample **1'** also shows ferromagnetic ordering below 9.7 K. Although the maximum χ_M value of **1'** is lower than that of **1**, the magnetic nature of **1** and **1'** are essentially the same. Furthermore, crystal **2** and anhydrous sample **2'** also show similar ferromagnetic nature with T_C of 9.5 and 10.7 K, respectively.

According to our previous reports, magnetic nature of 2-D bimetallic assemblies is governed by the intersheet separation. As mentioned in Introduction, the magnetic nature of the bimetallic assemblies of 2-D sheet structure is governed by the intersheet separation. Our X-ray structural studies have indicated that intersheet separations of **1** and **2** are 11.190 and 11.146 Å, respectively. Such large intersheet separations evidently result from the bulkiness of the counter anion used ($PhBSO_3^-$ and $TolSO_3^-$) since the dehydrated samples of **1** and **2** also show a ferromagnetic ordering.

CONCLUSION

Bimetallic assemblies $[Ni(dmen)_2]_2[Fe(CN)_6]X \cdot nH_2O$ ((X, n) = ($PhBSO_3^-$, 5; **1**), $TolSO_3^-$, 6 (**2**)) have a 2-D sheet structure extended by the M-CN-Ni linkages. The 2-D sheets have a large intersheet separation of 11.190 Å in **1** and 11.146 Å in **2**. A ferromagnetic interaction operates between the adjacent Ni(II) (S = 1) and Fe(III) (S = 1/2) ions due to the strict orthogonality of magnetic orbitals and ferromagnetic ordering occurs in **1** and **2**. Furthermore, dehydrated sample **1'** and **2'** also show ferromagnetic nature.

Acknowledgements

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