Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis, Structure and Magnetism of New Bimetallic Assemblies, $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (chxn = 1,2-trans-cyclohexane-diamine; M^{III}=Fe, Co)

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Version of record first published: 24 Sep 2006

To cite this article: Nobuo Fukita, Masaaki Ohba & Hisashi Ōkawa (2000): Synthesis, Structure and Magnetism of New Bimetallic Assemblies, $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (chxn = 1,2-trans-cyclohexane-diamine; M^{III}=Fe, Co), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 217-224

To link to this article: http://dx.doi.org/10.1080/10587250008038268

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 217-224
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Synthesis, Structure and Magnetism of New Bimetallic Assemblies, $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (chxn = 1,2-*trans*-cyclohexane-diamine; M^{III}= Fe, Co)

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A new type of cyanide-bridged bimetallic assemblies, $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (chxn = 1,2-*trans*-cyclohexanediamine; M^{3+} = Fe (**1**), Co (**2**)), have been prepared. The X-ray crystallography for the assemblies has proved a 2-D network comprised of M_6Ni_6 dodecagon units extended by M-CN-Ni linkage. Compound **1** shows a ferromagnetic spin-exchange interaction between the adjacent Fe(III) and Ni(II) ions through cyanide bridge and a long-range magnetic ordering below 13.1 K.

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

INTRODUCTION

Crystal engeneering of metal-extended systems is a current subject of major research focusing on the design of molecular-based magnets.[1-3] Bimetallic assemblies derived from hexacyanometallate ions $[M(CN)_6]^{n-}$ and simple metal ions form a family of magnetic materials exhibiting spontaneous magnetization, and high T_C or T_N is reported for some of the assemblies.[4-6] We have studied bimetallic assemblies derived from $[M(CN)_6]^{n-}$ and $[Ni(diamine)_2]^{2+}$ complexes and reported a 1-D compound of a rope-ladder structure $[Ni(en)_2]_3[Fe(CN)_6]_2.2H_2O$,[7a] 2-D compounds of a square structure $[Ni(L)_2]_2[Fe(CN)_6]X.nH_2O$ (L = pn, 1,1-dmen (1,1-dimethylethylene-diamine); X = ClO_4^-, PF_6^-, BF_4^- *etc.*)[7b] and 3-D compounds of a cubane unit $[Ni(L)_2]_3[Fe(CN)_6]X_2$ (L = en, tn; X = ClO_4^-, PF_6^-).[7c] Here we report a new type of bimetallic assemblies, $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (chxn = 1,2-*trans*-cyclohexanediamine; M^{3+} = Fe (**1**), Co (**2**)), that have a 2-D network comprised of M_6Ni_6 dodecagon units extended by M-CN-Ni linkage.

RESULTS AND DISCUSSION

Preparations and General Characterization

$[Ni(chxn)_3]Cl_2$ and $K_3[M(CN)_6]$ were reacted in the 3 : 2 molar ratio in an aqueous solution to obtain $[Ni(chxn)_2]_3[M(CN)_6] \cdot 2H_2O$ (M^{3+} = Fe (**1**), Co (**2**)). Compound **1** was obtained as brown plates and compound **2** as purple plates.

Compound **1** shows three ν(CN) modes of cyanide group at 2122^{sh}, 2115 and 2105^{sh} cm^{-1}. Similarly, **2** shows three ν(CN) modes at 2139^{sh}, 2131 and 2116 cm^{-1}. The IR spectral feature of the compounds suggests two or three types of cyanide groups existing in their network.

Crystal Structure

An ORTEP drawing of the asymmetric unit for **1** with atom numbering scheme is given in Figure 1. The asymmetric unit consists of two $[Fe(CN)_6]^{3-}$, one *trans*-$[Ni2(chxn)_2]^{2+}$ moieties, one *trans*-$[Ni2(chxn)_2]^{2+}$ molecule and one water molecule. Each metal center adopts a pseudo octahedral geometry. The Fe1, Fe2 and Ni2 are located on special equivalent positions (0, 0, -0.5), (0, 0.5, 0) and (0, 0, 0), respectively. The existence of optical isomers for chxn in the chair form makes the thermal parameters of the chxn carbon atoms large. The Fe-C, C-N and N-Ni bond distances range from 1.921(5) to 1.952(6) Å, from 1.135(6) to 1.152(6) Å and from 2.096(4) to 2.175(4) Å, respectively. $[Fe1(CN)_6]^{3-}$ coordinates to the axial site of four adjacent $[Ni(chxn)_2]^{2+}$ units through its N1, N2, N1* and N2* on a plane (* indicates the symmetry operation (-x, -y, -1-z)). The Ni1-N1 and Ni2-N2 bond distances are 2.175(4) and 2.165(4) Å, respectively. On the other hand, $[Fe2(CN)_6]^{3-}$ coordinates to two $[Ni1(chxn)_2]^{2+}$ units through its N4 and N4' in trans (' indicates the symmetry operation (-x, 1-y, -z)). The Ni1-N4 distance is 2.096(4) Å. The C-N-Ni bridging bonds are significantly bent (C1-N1-Ni1: 130.5(4)°; C4-N4-Ni1: 148.5(4)°; C2-N2-Ni2: 124.1(4)°). The alternate array of $[Ni1(chxn)_2]^{2+}$, $[Fe1(CN)_6]^{3-}$, $[Ni1(chxn)_2]^{2+}$ and $[Fe2(CN)_6]^{3-}$ forms a chain of Ni1-N1*-C1*-Fe1-C1-N1-Ni1-N4-C4-Fe2-C4'-N4'- linkage along *b* axis, and the chains are combined by $[Ni2(chxn)_2]^{2+}$ to form the -C2-N2-Ni2-N2"-C2"- linkage along *c* axis (" indicates the symmetry operation (-x, -y, -z)). The resulting network is of a 2-D sheet comprised of Fe_6Ni_6 dodecagon units (Figure 2, left); each unit consists of four Ni1, two Ni2, four Fe1 and two Fe2 atoms and forms a distorted parallelogram-like cavity. The Fe1···Fe1 separation along *b* axis is 16.994(3) Å and the Fe1···Fe1 separation along *c* axis is 9.139(2) Å. In the lattice the 2-D sheets align along *a* axis with the nearest intersheet Fe···Fe (Ni···Ni) separation

(=*a* axis) of 12.717(3) Å (Figure 2; right). The chxn molecules are situated perpendicularly to the 2-D sheet, forming a fence around each cavity. The lattice water molecules reside in the cavities and form hydrogen-bonds with N5, N6, N9 and N12.

Compound **2** is isomorphous with **1**. The nearest intersheet Co···Co (Ni···Ni) separation is 12.72(1) Å.

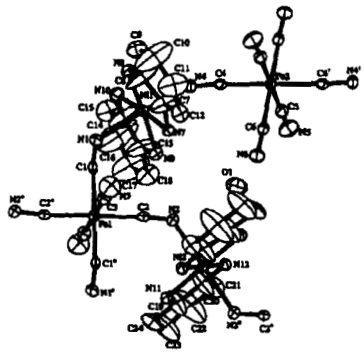

FIGURE 1 An ORTEP drawing of the asymmetric unit of **1** with atom numbering scheme (water molecules are omitted for clarity).

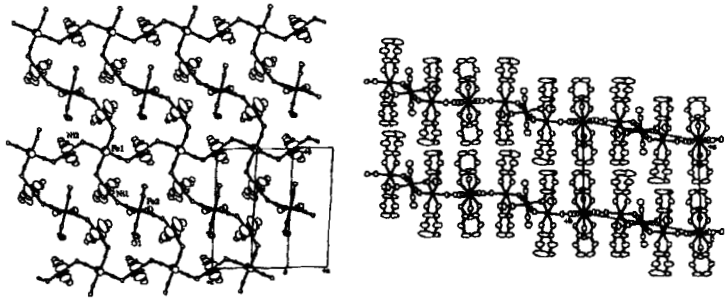

FIGURE 2 Polymeric structure of **1**: (left) top view and (right) side view of the 2-D sheet.

These assemblies have two crystallographically independent $[M(CN)_6]^{3-}$ units in the network. To our best knowledge, this is the

first case with two non-equivalent hexacyanometallate ions in a network structure.

Magnetic Property

The $\chi_M T$ *vs.* T and χ_M *vs.* T plots of **1** are shown in Figure 3. The $\chi_M T$ value at room temperature is 4.24 cm^3Kmol^{-1} (5.83 μ_B) per Fe_2Ni_3, that is slightly larger than the value expected for two low-spin Fe(III) and three paramagnetic Ni(II) ions (3.75 cm^3Kmol^{-1}; 5.48 μ_B). The $\chi_M T$ increases with decreasing temperature up to a maximum value of 652 cm^3Kmol^{-1} (72.2 μ_B) at 12 K and then decreases below this temperature. The Curie-Weiss plots ($\chi_M = C/(T-\theta)$) indicated a positive Weiss constant of $\theta = +19.7$ K. The results clearly indicate a ferromagnetic ordering of spins within the 2-D sheet due to the strict orthogonality of magnetic orbitals between Ni(II) and low-spin Fe(III). The drop in $\chi_M T$ below 12 K can be ascribed to a saturation of χ_M.

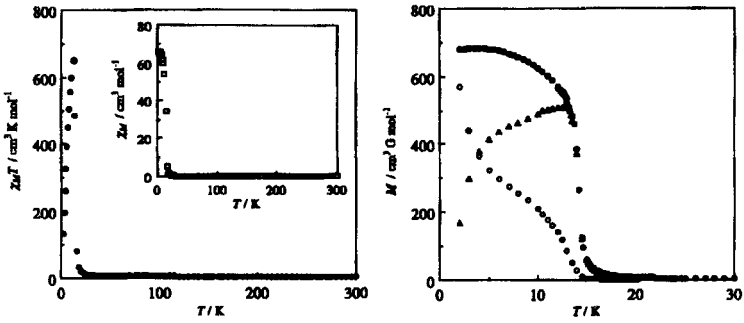

FIGURE 3 Cryomagnetic properties of **1**: (left) temperature-dependences of χ_M (G) and $\chi_M T$ (J); (right) FCM (J), RM(E), ZFCM (H) under an applied field of 5 G.

The field-cooled magnetization (FCM) showed a rapid increase around 15 K up to 680 cm^3Gmol^{-1} at 2 K. The remnant magnetization

(RM) at 2 K was 570 cm^3Gmol^{-1} that decreased with increasing temperature to vanish until 14 K. The zero-field-cooled magnetization (ZFCM) curve showed a break at 13.1 K ($=T_c$).

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 = 8.3 $N\mu_B$ at 50 kG corresponds to 8 $N\mu_B$ resulting from the ferromagnetic coupling of threee Ni(II) (S = 1) and two Fe(III) (S = 1/2) ions. The magnetization in the applied field of 0 – 30 kG is larger than the value based on Brillouin function for S_T = 4 with $g_{ave.}$ = 2.1. The magnetic hysteresis loop measured at 2 K demonstrates that **1** is a soft magnet with a remnant magnetization of 4.4 × 10^4 cm^3Gmol^{-1} and a coercive field of 110 G (Figure 4, right).

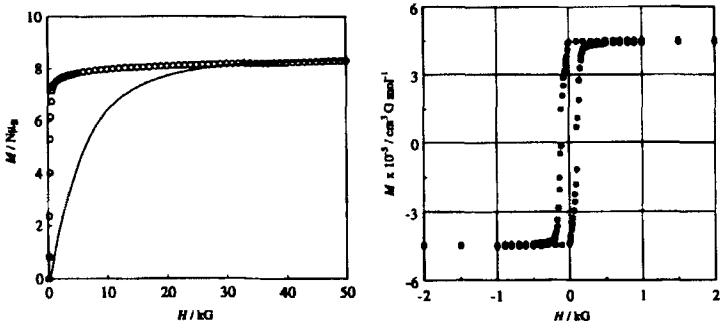

FIGURE 4 Field-dependence of magnetization M (left) and magnetic hysteresis loop (right) for **1** at 2 K. The solid line in the left is drawn based on Brillouin function for S_T = 4 with $g_{ave.}$ = 2.1.

The magnetic property of **2** is shown in Figure 5 as $\chi_M T$ *vs.* T and M *vs.* H plots. The $\chi_M T$ value at room temperature is 3.65 cm^3Kmol^{-1} (5.40 μ_B) per Co_2Ni_3, that is practically independent of temperature down to 14 K. The magnetization curve is well simulated by Brillouin function for three isolated S = 1 spins with g = 2.06. Evidently, little

magnetic interaction occurs within the 2-D sheet because of the diamagnetic nature of Co(III). The decreases in $\chi_M T$ below 14 K can be attributed to a zero-field splitting for the Ni(II) ions.

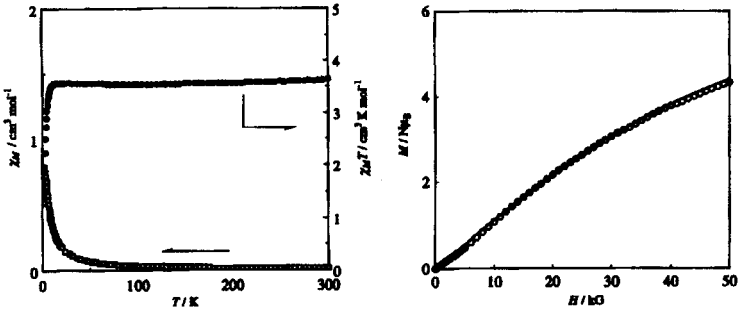

FIGURE 5 Temperature-dependence of χ_M (G) and $\chi_M T$ (J) (left) and field-dependences of magnetization M at 5 K (right) for **2**.

Previously we have reported that the magnetic nature of 2-D sheet compounds depends on the intersheet separation (d); metamagnetism occurs in the case of d < 10 Å due to an antiferromagnetic intersheet interaction whereas ferromagnetism occurs in the case of d > 10 Å. The magnetic property of **1** is in harmony with this empirical rule. Evidently, the chxn ligand plays an essential role to provide a large intersheet separation (12.717(3) Å) and to achieve a ferromagnetic ordering (T_c = 13.1 K) in the bulk.

CONCLUSION

Bimetallic assemblies $[Ni(chxn)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (M^{3+} = Fe(**1**) and Co(**2**)) have a 2-D sheet structure based on M_6Ni_6 dodecagon units formed by the M-CN-Ni linkages. The 2-D sheets stack along a axis, with the Fe···Fe (Ni···Ni) separation of 12.717(3) Å in **1** and the Co···Co

(Ni···Ni) separation of 12.72(1) Å in **2**. In the case of **1**, 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. The intersheet magnetic interaction is weakly ferromagnetic to show a ferromagnetic ordering below 13.1 K ($=T_c$).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area 'Metal-assembled Complexes' (No. 09044093) from the Ministry of Education, Science, Sports and Culture, Japan and a foundation advanced technology institute, Japan.

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