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A Novel One-Dimensional Cyano-Bridged Ni_3Fe_2 Ferromagnet Constructed from Bimetallic Molecular Squares

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Reaction of the complex $[\mathrm{Ni}(rac\text{-CTH})]^{2+}$ (*rac*-CTH = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) with $[\mathrm{Fe(CN)_6}]^{3-}$ leads to a novel cyano-bridged Ni_3Fe_2 complex, $\{[\mathrm{Ni}(rac\text{-CTH})]_3[\mathrm{Fe(CN)_6}]_2\}_4$. The structure consists of an alternating arrangement of $\{\mathrm{Fe(CN)_6Ni}(rac\text{-CTH})\}_2$ squares and *trans*-planar $[\mathrm{Ni}(rac\text{-CTH})]^{2+}$ units bridged by cyanide groups to give a neutral 1D chain running along the *a* axis. Magnetic measurements reveal the occurrence of ferromagnetic coupling between $\mathrm{Fe^{III}}$ and $\mathrm{Ni^{II}}$ ions and 3D magnetic ordering at 3 K due to interchain interactions. Canting of the moments is inferred from the low value of the magnetization of the saturation below T_c.

In recent years, much research interest has been focused on the application of homo- and heteroleptic cyanometalates as building blocks for cyanide-bridged bimetallic assemblies with intriguing structures and interesting magnetic, magneto-optical, and zeolitic properties.[1] Among these systems, those prepared from $[\mathrm{M(CN)_6}]^{3-}$ ($\mathrm{Cr^{III}}$, $\mathrm{Mn^{III}}$, $\mathrm{Fe^{III}}$, and $\mathrm{Co^{III}}$) and coordinatively unsaturated complexes $\mathrm{M'L}_x$ ($\mathrm{M'} = \mathrm{Ni^{II}}$, $\mathrm{Mn^{II}}$, $\mathrm{Cu^{II}}$; L_x = polyamine, tetraazamacrocyclic ligand, Schiff base, etc.) generally are $\mathrm{M'_3M_2}$ based polymeric compounds,[2−13] which have been assembled on the basis of the charge ratio 2:3 of the cation and anion. The dimensionality and topology of these $\mathrm{M'_3M_2}$ assemblies strongly depend on the nature of $\mathrm{M'L}_x$ (number and disposition of empty or available coordination positions on M′, coordination geometry, volume of the ligands, etc.) and the connectivity of the hexacyanometalate building block (number and arrangement of $\mathrm{M'L}_x$ units around M). Thus, for cyanide-bridged $\mathrm{M'_3M_2}$ complexes containing $[\mathrm{M'(L)_2}]^{2+}$ (L = diamine) or $[\mathrm{M'(L)}]^{n+}$ (n = 2, 4; L = tetraazamacrocyclic ligand) units with two

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available *trans* coordination positions, a relatively limited number of M'_3M_2 structural types have been observed: pentanuclear,[2] 1D (rope-ladder chain,[3] zig-zag alternating cationic[2] and anionic[4] chains), and 2D (honeycomb,[2,5] brick-wall[6] and rectangular[7] grid). Coordinatively unsaturated ML_x complexes with at least two *cis* available coordination positions, however, have been infrequently used as building blocks in the design of cyano-bridged bimetallic assemblies, despite the fact that new and interesting architectures can be obtained (pentanuclear and decanuclear containing square $M_2M'_2$ units,[8] pentanuclear,[9] 1D double zigzag cationic chain,[10] intricate 2D[11] and 3D[12] networks, etc.). In view of this, we have envisaged the use of hexacyanometalate to connect high thermodynamically stable $[M'L]^{2+}$ units (L = tetraazamacrocycle) that can adopt both *trans*-planar and *cis*-folded configurations. We think that, in a first step, the folded configuration might lead to cyanide-bridged cyclic structures containing terminal cyanide groups, which, in a second step, might connect other folded or planar $[M'L]^{2+}$ units increasing the dimensionality and leading to novel systems. Along this end, we are using $[M'(rac\text{-CTH})]^{2+}$ (*rac*-CTH = *rac*-5,7,7,-12,14,14-hexamethyl-1,4,8,11-tetraazacyclo tetradecane) building blocks for the synthesis of new cyano-bridged bimetallic assemblies. Herein we report the synthesis, crystal structure, and magnetic properties of $\{[Ni(rac\text{-CTH})]_3[Fe(CN)_6]_2\}_\infty$, **1**, a novel one-dimensional cyano-bridged compound which exhibits an unusual structure and ferromagnetic ordering.

The reaction of an orange water solution (20 mL) of $[Ni(rac\text{-CTH})](ClO_4)_2$ [13] (0.2 mmol) and an aqueous solution (15 mL) of $K_3[Fe(CN)_6]$ (0.2 mmol) leads to a brown solution which when kept at room temperature for several days affords brown crystals of **1** (IR νCN/cm^{-1}: 2155, 2108) suitable for X-ray analysis[14] (yield ca. 30%).

The structure consists of an alternating arrangement of $\{Fe(CN)_6Ni(rac\text{-CTH})\}_2$ squares and *trans*-planar $[Ni(rac\text{-CTH})]^{2+}$ units bridged by cyanide groups to give a neutral 1D chain running along the *a* axis (see Figure 1). Within the squares units, Ni^{II} and Fe^{III} ions are alternatively bridged by cyanide groups, with $Fe^{III}-Ni^{II}$ distances of 5.13(1) and 4.99(5) Å and $Ni^{II}\cdots Ni^{II}$ and $Fe^{III}\cdots Fe^{III}$ distances of 7.03(4) and 7.27(1) Å, respectively. In the bridging region of the square units, Fe−C−N bond angles are 172.4(16)° and 169.7(15)° whereas C−N−Ni angles are 172.9(14)° and 157.0(16)°.

The existence of a center of symmetry at the barycenter of the square forces Fe_2Ni_2 metal atoms to be coplanar with Fe−Ni−Fe and Ni−Fe−Ni angles of 92.0(6)° and 88.0(6)°, respectively. Iron(III) ions exhibit a slightly distorted octahedral coordination geometry with Fe−C and C−Fe−C bond distances and angles similar to those observed for other complexes containing $[Fe(CN)_6]^{3-}$ bridging units. Nickel(II) ions exhibit a NiN_6 distorted octahedral coordination environment, made of four nitrogen atoms from *rac*-CTH ligand and two nitrogen cyanide atoms, with *cis* and *trans* angles in the ranges 80.6(5)−106.8(5)° and 166.1(5)−173.0(5)°, respectively, and $Ni-N_{macro}$ bond distances (2.12(1)−2.17(2) Å) longer than the $N_{cyanide}$ ones (2.09(1) and 2.10 (1) Å). The macrocyclic ligand adopts a folded conformation, and then, the cyanide nitrogen atoms are situated in *cis* positions. The size of the square is of the same order as that observed for $[Fe_2Cu_2(\mu\text{-CN})(bpy)_6](PF_6)_6\cdot CH_3CN\cdot 2CHCl_3$.[15] Square units are further connected to *trans*-$[Ni(rac\text{-CTH})]^{2+}$ ions through one of the cyanide groups of each $[Fe(CN)_6]^{3-}$ unit to form the chain, with the cyanide bridging groups of the tridentate $[Fe(CN)_6]^{3-}$ anion exhibiting a *mer* disposition. A similar extension of the structure by addition of extra ML building blocks to square Fe_2M_2 units has been recently shown to occur in the pentamer and decamer compounds $\{[Ni(bpy)_2(H_2O)][Ni(bpy)_2]_2[Fe(CN)_6]_2\}$[8a] and $\{[Zn(phen)_2][Fe(CN)_6]\}_2\{[Zn(phen)_2][Zn(phen)_2(H_2O)][Fe(CN)_6]\}_2$.[8b] The Fe−C−N and Ni−N−C angles in the bridging region are 166.5(18)° and 158.5(16)°, respectively, with an Fe···Ni distance of 4.99(18) Å. Ni^{II} ions of *trans*-$[Ni(rac\text{-CTH})]^{2+}$ units, which are placed on an inversion center, exhibit a tetragonally compressed distorted geometry with the in plane $Ni-N_{macro}$ bond distances of about 2.1 Å and $Ni_{cyanide}-Ni$ distances of 2.08(2) Å. The *cis* bond angles are in the range 84.8(7)−95.2(10)°, whereas *trans* angles have crystallographically imposed values of 180°.

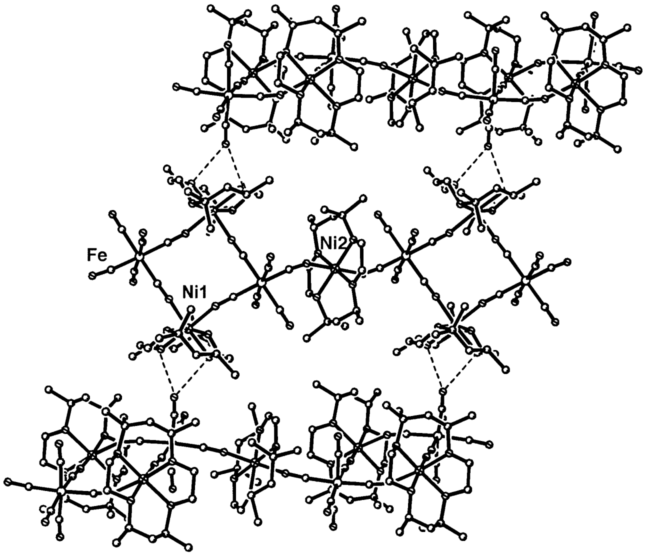

Figure 1. A view of the chains arrangement and hydrogen bonds interactions (- - -) in the *ab* plane of **1**.

Chains running along the *a* axis are not isolated but connected by hydrogen bonds involving one of the terminal

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[14] Crystallographic analysis for **1** ($C_{60}H_{111}N_{24}O_{1.5}Ni_3Fe_2$): monoclinic, space group $P2_1/n$, $a = 16.224(2)$ Å, $b = 16.1250(15)$ Å, $c = 16.815(3)$ Å, $\beta = 112.194(18)$°, $U = 4081.8(10)$ Å^3, $Z = 2$, $D_c = 1.205$ g cm^{-3}, μ(Mo Kα) = 1.076 mm^{-1}, $F(000) = 1574$, $T = 153(2)$ K, Stoe image plate diffraction system, Mo Kα radiation ($\lambda = 0.71069$ Å), $2\theta_{max} = 52.1$°, 31721 reflections measured, 7969 of which were unique ($R_{int} = 0.1775$). The structure was solved by direct methods and refined on F^2 by the SHELX-97[20] program. An empirical absorption correction was applied, and the SQUEEZE routine in PLATON[21] was used, 31 electrons for a volume of 613 Å^3. This was equated to 3 water molecules per unit cell. Only the iron and N atoms were refined anisotropically. The whole molecule undergoes considerable thermal motion especially the moiety involving atom Ni2. The final refinement gave $R = 0.0806$ and $R_w = 0.1670$, 1149 observed reflections ($I > 2\sigma(I)$), and 244 variables.

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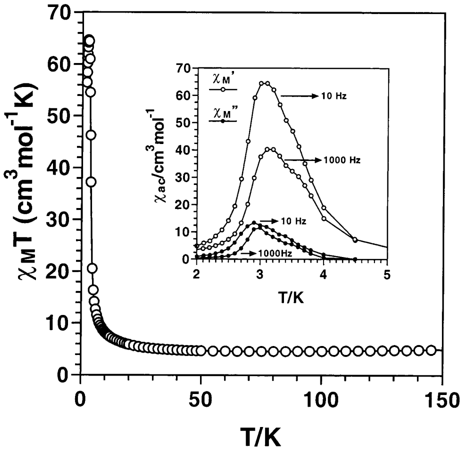

Figure 2. Temperature dependence of χ_MT for **1**. The solid line does not represent a fitting and is just for eye-guide. In phase (χ_M') and out-of-phase (χ_M'') *ac* magnetic susceptibilities (inset).

cyanide groups of a chain and one of the NH groups of a folded [Ni(*rac*-CTH)]$^{2+}$ unit of the neighboring chain, with N8···N2^i and N8···N4^i (i = 1.5 − *x*, −0.5 + *y*, 0.5 − *z*) distances of 3.07(3) and 3.117(1) Å. As a consequence of these hydrogen bond interactions in the *ab* plane, neighboring chains are turned by 63° with respect to each other and shifted by half of a square unit, the shortest interchain metal−metal distance being 6.74 Å (Figure 1). It has been only quite recently that a relatively similar structure has been reported for a cyano-bridged Mn^{II}Mo^{V} bimetallic compound, which was prepared in a less controlled manner from [Mo(CN)$_8$]$^{3-}$ and a DMF solution containing MnCl$_2$·4H$_2$O and 2,2′-bipyridine.[16]

The temperature dependence of the $\chi_M T$ product per Ni$_3$Fe$_2$ unit in the range 2−300 K, under an applied field of 0.025 T is shown in Figure 2. The $\chi_M T$ at room temperature of 5.3 cm^3 mol^{-1} K is higher than that expected for isolated Fe^{III} and Ni^{II} ions of 3.75 cm^3 mol^{-1} K with $g_{Fe} = g_{Ni} = 2$, which is due to the orbital contribution of the low-spin Fe^{III} ions. As the temperature is lowered, $\chi_M T$ decreases smoothly until 60 K, and below this temperature, it increases. This slight decrease of $\chi_M T$, in the high temperature range, can be attributed to the well-known spin−orbit coupling of the $^2T_{2g}$ ground term.[4] Below 60 K, the $\chi_M T$ increases smoothly and then sharply with decreasing temperature, reaching a maximum value of about 65 cm^3 mol^{-1} K (22.6 μ_B) at about 3 K. This behavior is indicative of a ferromagnetic interaction between Fe^{III} and Ni^{II} (strict orthogonality between $t_{2g}{}^6e_g{}^2$ Ni^{II} and $t_{2g}{}^5e_g{}^0$ low-spin Fe^{III} magnetic orbitals) and suggestive of the existence of magnetic ordering. Below 3 K, the magnetization is strongly dependent on the magnetic field, so $\chi_M T$ decreases rapidly with temperature due to saturation effects rather than to zero-field splitting effects on Ni(II) ions. In-phase and out-of-phase ac dynamic susceptibility measurements (inset, Figure 2) confirm the ferromagnetic ordering at 3 K and reveal no significant frequency dependence of the position of the maximum, thus excluding the occurrence of slow magnetic relaxation.

It should be noted that, in one of the directions perpendicular to the chain axis, the shortest interchain separation (6.74(4) Å) involves the Fe^{III} ions of a chain and one of the Ni^{II} ions of the Fe$_2$Ni$_2$ square unit of the adjacent chain. This disposition is similar to that found in other chains that exhibit a three-dimensional ferromagnetic ordering.[17]

In this case, the interchain interactions (dipolar and hydrogen bonds) promote the observed 3D order. The ordering temperature is lower than those found in other neutral Ni$_3$Fe$_2$ systems,[6,7,12] mainly as a consequence of the lower dimensionality of **1**. The field dependence of the magnetization (0−5 T) measured at 1.9 K reaches an M_s value of 5 Nβ at 5 T, which is smaller than the saturation value (M_0 ca. 8−9 Nβ) expected for a ferromagnetic Ni$_3$Fe$_2$ system ($M_0 = 3g_{Ni} + g_{Fe}$). This low value may be indicative of a canted ferromagnet which would be related to the fact that the planes of the Fe$_2$Ni$_2$ square units, belonging to two adjacent chains, make an angle of about 63° ($M_s = M_0$ cos 59°), assuming that the magnetic moment in each chain is perpendicular to the square plane. Similar magnetic phenomena have also been observed in one-dimensional Ni^{II}, Fe^{II}, and Mn^{II} systems in which the planes orthogonal to the magnetic moment on two neighboring chains make angles between 66° and 90°.[18] At 2 K, this ferromagnet exhibits a small magnetic hysteresis with a coercive field lower than 25 Oe, typical of a soft magnet.

It is interesting to note that this type of anisotropic ferromagnetic chain is the subject of special attention because these chains exhibit slow relaxation and hysteresis effects.[19] To observe these magnetic features, the chains must be highly anisotropic and well isolated from each other. Compound **1**, however, exhibits 3D ferromagnetic ordering at 3 K, due to interchain interactions, which precludes the occurrence of slow magnetic relaxation effects. Studies on similar systems, prepared from building blocks that incorporate highly anisotropic metal ions, such as [Mn(CN)$_6$]$^{3-}$ and [Co(*rac*-CTH)]$^{2+}$, are in progress.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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