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Synthesis and magnetism of multi-dimensional cyanide-bridged bimetallic assemblies

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Contents

Abstract

The structures and magnetism of complex-based metal assemblies derived from $[M(CN)_6]^{n-}$ ($M = Cr^{3+}$, Mn^{3+}, Fe^{3+}, Co^{3+}, Fe^{2+}; $n = 3, 4$) and coordinatively unsaturated $[M_A(L)_x]^{m+}$ ($M_A = Mn^{2+}$, Ni^{2+}, Cu^{2+}, Mn^{3+}, Fe^{3+}; L = polyamine ligand, salen^{2-} derivatives) are reviewed. The reaction of the constituents in different ratios, in the absence or presence of an appropriate cation or anion and by the change of ligand L provides multi-dimensional bimetallic assemblies of various networks extended through M–CN–M_A–NC– linkages. The magnetic properties of the assemblies are discussed with respect to their network structures and M_A/M combinations. These assemblies provide

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Abbreviations: acacen^{2-}, *N,N′*-ethylenedi(acetylacetonilideneaminato); bpm, bis(1-pyrazolyl)methane; cyclam 1,4,8,11-tetraazacyclodecane; dien diethylenetriamine; 1,1-dmen, 1,1-dimethylethylenediamine; en, ethylenediamine; N-men, *N*-methylethylenediamine; pn, *rac*-1,2-propanediamine; PPh_4^+, tetraphenylphosphonium; salen^{2-}, *N,N′*-ethylenedi(salicylideneaminato); tren, tris(2-aminoethyl)amine; tn, 1,3-propanediamine.

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significant insights into magnetostructural correlation and design of magnetic materials.

Keywords: Metal assemblies; Molecular-based magnets; Multi-dimensional network; Cyanide bridge; Prussian blue

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1. Introduction

The design and synthetic strategies of multi-dimensional complex-based metal assemblies are current interests in developing new molecular-based magnetic materials [1–103]. A promising approach for the purpose is based on a bimetallic network that can be constructed by a 'donative metal complex' having donor groups capable of acting as bridges, such as $[M(CN)_6]^{n-}$ [39–103] and $[M(ox)_3]^{3-}$ [30–38], and a simple metal ion or 'coordinatively unsaturated complex'. Typical examples of such bimetallic compounds are Prussian blue and its analogs. The magnetic nature of Prussian blue $Fe_4[Fe(CN)_6]_3 \cdot nH_2O$ ($T_c = 5.6$ K) was first reported in 1928 [39]. It is now known that Prussian blue analogs such as $CM_A[M(CN)_6] \cdot nH_2O$ ($C = K^+$, Cs^+ etc.) and $(M_A)_X[M(CN)_6]_y \cdot nH_2O$ form a family of complex-based magnets and a very high magnetic ordering temperature is reported for some of them [39–68]. It is generally considered that the Prussian blue family has a face-centered cubic structure based on octahedral symmetric $[M(CN)_6]^{n-}$. However, structural information for the Prussian blue family is very limited, although local structures were studied by means of X-ray photoelectron spectroscopy [44,68–75]. The compounds of this family, except for those of type $CM_A[M(CN)_6] \cdot nH_2O$, can have a disorder in the network because the area surrounding M_A is formed with cyano nitrogens and water molecules.

Magnetostructural studies for Prussian blue analogs must be important for providing a fundamental basis to develop high-T_c complex-based magnets. A modification of Prussian blue compounds with the aim to reduce the complexity in network structure can be achieved by substituting coordinatively unsaturated metal complexes for the simple metal ion in the Prussian blue family. Thus, this short review deals with bimetallic assemblies derived from: (1) $[M_A(L)_x]^{2+} + [M(CN)_6]^{n-}$ ($M_A = Ni^{II}$, Mn^{II}, Cu^{II}; L = diamine or polyamine) [76–86,94–103]; and (2) $[M_A(L)]^+ + [M(CN)_6]^{n-}$ ($M_A = Mn^{III}$, Fe^{III}; L = quadridentate Schiff base) [87–93]. The main focus is placed on rational synthesis of bimetallic compounds of various networks and magnetostructural correlation in magnetic ordering.

2. One-dimensional assemblies

One-dimensional bimetallic assemblies, $[Ni(en)_2]_3[M(CN)_6]_2 \cdot 2H_2O$ (M^{III} = Fe (**1**), Mn (**2**), Cr (**3**), Co (**4**)), were first reported by the present authors in 1994 [76,81]. The reaction of $[Ni(en)_2Cl_2]$ and $K_3[M(CN)_6]$ in the 3:2 stoichiometry in aqueous solution resulted in the immediate precipitation of compounds **1**–**4** which, however, were found to be polycrystalline based on magnetic studies. Good crystalline samples could be prepared by the reaction of $[Ni(en)_3]Cl_2$ and $K_3[M(CN)_6]$ in the 3:2 molar ratio in aqueous solution [76]. In this synthesis, the slow dissociation of $[Ni(en)_3]^{2+}$ into $[Ni(en)_2]^{2+}$ in aqueous solution leads to the growth of large single crystals in a self-assembling process [81]. This synthetic method is applicable to cyanide-bridged bimetallic assemblies of other networks, as described later.

X-ray crystallography for compounds **1** and **4** has revealed that they are isomorphous. The asymmetric unit consists of one $[M(CN)_6]^{3-}$ anion, one *cis*-$[Ni(en)_2]^{2+}$ cation, one-half of *trans*-$[Ni(en)_2]^{2+}$ cation, and one water molecule, with the inversion center at the Ni of *trans*-$[Ni(en)_2]^{2+}$. Three cyano nitrogens in the meridional mode coordinate to the adjacent Ni ions. A polymeric zigzag chain is formed by the alternate array of $[M(CN)_6]^{3-}$ and *cis*-$[Ni(en)_2]^{2+}$, and two zigzag chains are combined by *trans*-$[Ni(en)_2]^{2+}$ providing a one-dimensional rope-ladder chain running along the *c* axis (Fig. 1). In the lattice, the chains align along the diagonal line of the *ab* plane (*n*-glide) to form a pseudo-two-dimensional (2D) sheet. The nearest intersheet M···M, Ni···Ni and Ni···M separations are 9.709, 7.713 and 6.494 Å, respectively, for compound **1** and 9.698, 7.699 and 6.498 Å, respectively, for compound **4**.

Compounds **1**–**3** show a ferromagnetic intramolecular interaction between M^{III} (t_{2g}^n; $n = 1$ for Fe^{III}, 2 for Mn^{III}, 3 for Cr^{III}) and Ni^{II} (e_g^2), as expected from the strict orthogonality of t_{2g} (M^{III}) and e_g (Ni^{II}) orbitals. A trend toward increasing ferromagnetic interaction is observed in the order: Weiss constant $\theta_w = 6.3$ (for Ni_3Fe_2, compound **1**) < 13.8 (Ni_3Mn_2, compound **2**) < 18.4 K (Ni_3Cr_2, compound **3**). The exchange interaction parameter J (16.8 cm^{-1}) has been estimated for a heptanuclear complex, $[Ni(tetren)]_6[Cr(CN)_6](ClO_4)_9$, which has been reported by Mallah et al. [94] No magnetic ordering occurs in compounds **1**–**3** because of an antiferromagnetic intermolecular interaction between the pseudo-2D sheets. The polycrystalline form of compound **1**, prepared by rapid precipitation by the reaction of $[Ni(en)_2Cl_2]$ and $[Fe(CN)_6]^{3-}$, is metamagnetic [76]. It is likely that the metamagnetic behavior arises from a disorder in the network providing quasi-2D

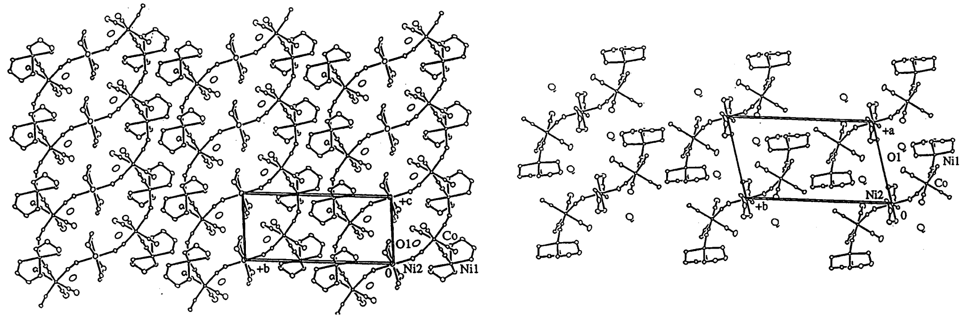


Fig. 1. Projection of the polymeric structure of $[Ni(en)_2]_3[Co(CN)_6]_2 \cdot 2H_2O$ (**4**) onto the *bc* (left) and *ab* (right) planes [81].

and -3D domains. This result warns that magnetic studies of assembly compounds should be based on crystalline samples of an ordered network. Different magnetic properties between crystalline and polycrystalline samples are also shown for $[Ni(bpm)_2]_3[Fe(CN)_6]_2 \cdot 7H_2O$ by Murray et al. [97]

Another class of 1D assembly, $PPh_4[Ni(pn)_2][M(CN)_6] \cdot H_2O$ ($M^{III} = Fe$ (**5**), Cr (**6**), Co (**7**)) has been prepared from the reaction of $[Ni(pn)_3]Cl_2$, $K_3[M(CN)_6]$ and PPh_4Cl in the 1:1:1 molar ratio in an aqueous solution [78,82]. They have a 1D zigzag chain structure constructed by the alternate array of $[M(CN)_6]^{3-}$ and planar $[Ni(pn)_2]^{2+}$ along the *c* axis (Fig. 2). The nearest intrachain Ni···M separations of compounds **5**, **6** and **7** are 5.116(1), 5.215(1) and 5.079(1) Å, respectively. The PPh_4^+ cation resides between the 1D chains so as to expand the interchain separation. The nearest M···M, Ni···Ni and Ni···M interchain separations are 8.437(3), 8.437(3) and 8.134(2) Å, respectively, for compound **5**, 8.454(2), 8.454(2) and 7.149(2) Å, respectively, for compound **6** and 8.437(1), 8.437(1) and 7.128(1) Å, respectively, for compound **7**.

Compounds **5** and **6** show a ferromagnetic intrachain interaction with $\theta_w = 2.0$ and 9.8 K, respectively, due to the strict orthogonality of the magnetic orbitals of the two metal ions. A tendency of magnetic ordering over the lattice is observed for compound **6** but this is overcome by an antiferromagnetic interchain interaction. Compound **7** is essentially paramagnetic within the 1D chain, showing a weak antiferromagnetic interchain interaction. The $[M(CN)_6]^{3-}$ in the assemblies has the local symmetry C_{2v} with the d-orbital order of $d_{xy} > d_{xz}, d_{yz}$ (x and y axes are taken along the M–CN–Ni bridges) and the ferromagnetic interaction in the M^{III}–CN–Ni^{II} unit increases with unpaired electrons on the d_π orbital (i.e. $Fe^{III} < Cr^{III}$).

The use of [Mn(acacen)Cl] as the cationic constituent forms a 1D linear chain compound, $[NEt_4]_2[Mn(acacen)][Fe(CN)_6]$, that suggests a ferromagnetic nature based on ferromagnetic coupling ($\theta_w = 12.3$ K) between Mn^{III} and Fe^{III} ions [90]. A $Fe^{III}Fe^{III}$ assembly, $[Fe(cyclam)][Fe(CN)_6] \cdot 6H_2O$, was prepared when

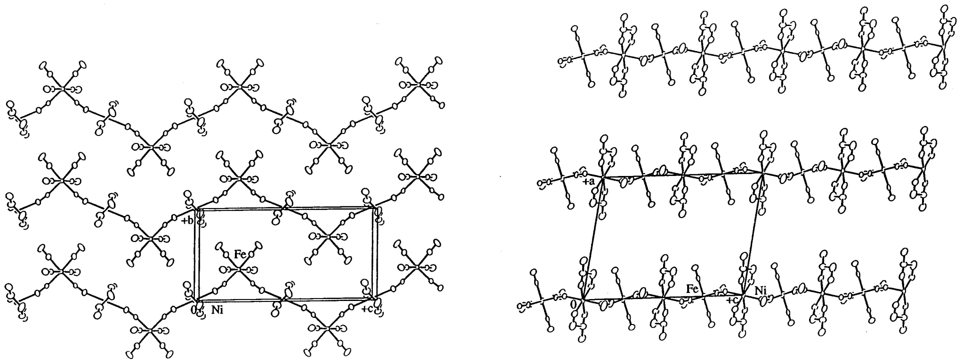


Fig. 2. Projection of the polymeric structure of $PPh_4[Ni(pn)_2][Fe(CN)_6]_2 \cdot H_2O$ (**5**) onto the *bc* (left) and *ac* (right) planes (PPh_4^+ and H_2O omitted) [78,82].

[Ni(cyclam)]$(ClO_4)_2$ was reacted with excess $K_3[Fe(CN)_6]$ [98]. This has a 1D chain structure and shows a ferromagnetic intrachain interaction between the nearest low-spin Fe^{III} ions but no magnetic ordering in the bulk. When $[Cu(dien)]^{2+}$ was used as a constituent, $[\{Cu(dien)\}_2\{Cr(CN)_6\}][\{Cu(dien)\}\{Cr(CN)_6\}]\cdot 4H_2O$ was obtained. The cationic part forms a 1D chain, and the anionic part exists between these 1D chains. No magnetic ordering occurs in this compound [99].

3. Two-dimensional assemblies

Bimetallic assemblies, $[Ni(N\text{-}men)_2]_3[M(CN)_6]_2\cdot nH_2O$ (M^{III} = Fe (**8**), Co(**9**)), have been prepared by the reaction of $[Ni(N\text{-}men)_3]Cl_2$ and $K_3[M(CN)_6]$ in the 3:2 molar ratio in water [84]. X-Ray crystallographic study revealed that their network is two-dimensional based on a honeycomb sheet structure (Fig. 3), although detailed structures could not be completely determined because of their efflorescent nature. In spite of the different space groups ($P\bar{3}$ for compound **8** and $C2/c$ for compound **9**), their network structures are essentially the same. Three cyano nitrogens of $[M(CN)_6]^{3-}$ in the facial mode coordinate to the adjacent *trans*-$[Ni(N\text{-}men)_2]^{2+}$ forming a hexagonal unit having M^{III} at each corner and Ni^{II} at the center of each edge. The nearest M···M, Ni···Ni and Ni···M intersheet separations are 8.916(3),

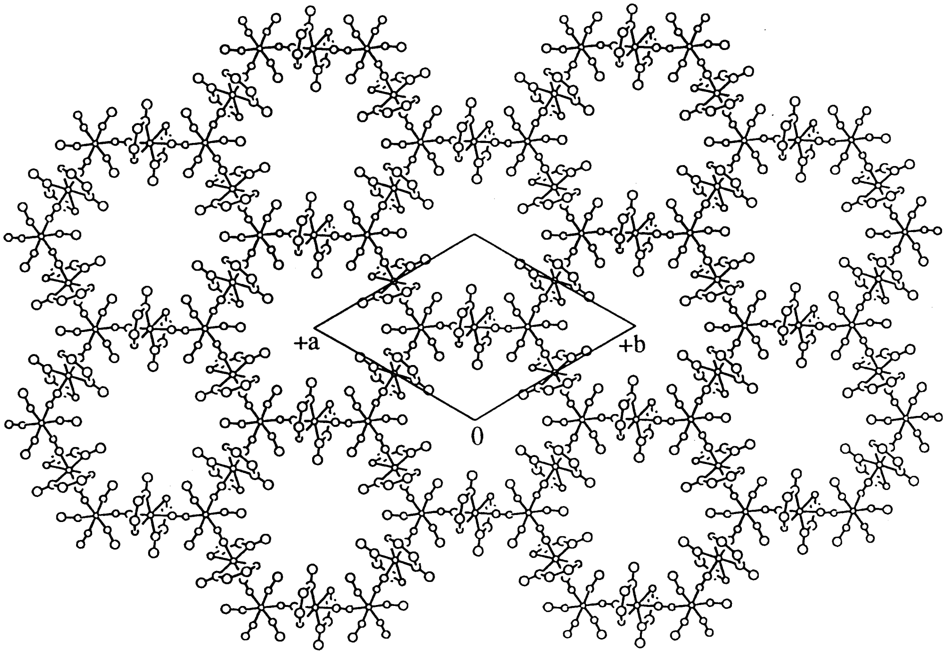


Fig. 3. Projection of the polymeric structure of $[Ni(N\text{-}men)_2]_3[Fe(CN)_6]_2\cdot 15H_2O$ (**8**) onto the *ab* plane (H_2O omitted) [84].

8.916(3) and 7.843(3) Å, respectively, for compound **8** and 8.280(1), 8.280(1) and 7.060(3) Å, respectively, for compound **9**. Thus, the introduction of one methyl substituent into ethylenediamine nitrogen gives rise to a drastic change in the network structure of $[Ni(L)_2]_3[M(CN)_6]_2 \cdot nH_2O$, from the 1D zigzag chain with L = en [76,81] to the 2D honeycomb sheet with L = N-men. At least 15 water molecules per unit exist in the porous sheet structure of the crystalline sample. Elemental, thermogravimetric and differential scanning calorimetry analyses indicate a partially dehydrated formula, $[Ni(N\text{-}men)_2]_3[M(CN)_6]_2 \cdot 12H_2O$, after allowing to stand in open air.

Compound **8** shows ferromagnetic ordering below 10.8 K (Fig. 4). The M versus H plots show a rapid increase typical of ordered magnetism at 4 K. A flexion point is observed at ca. 5 kG in magnetization curve, which can be attributed to the disorder in network caused by a partial dehydration. The anhydrous sample $[Ni(N\text{-}men)_2]_3[Fe(CN)_6]_2$ (**8′**) was obtained by heating compound **8** at 100°C in vacuo. It shows a ferromagnetic interaction but no spontaneous magnetization (Fig. 4). This fact suggests that the honeycomb sheet structure is disordered by the dehydration. Both compound **9** and its anhydrous sample $[Ni(N\text{-}men)_2]_3[Co(CN)_6]_2$ (**9′**) are paramagnetic and show a weak antiferromagnetic intersheet interaction. A related two-dimensional compound $[Ni(cyclam)]_3[Cr(CN)_6]_2 \cdot 20H_2O$ (**10**) is reported by Verdaguer et al. It has a honeycomb sheet structure similar to that of compound **9**, with the nearest intersheet separations, Cr···Cr = 9.06, Ni···Ni = 9.06 and Ni···Cr = 8.06 Å. Magnetic studies were made for a powdered sample, $[Ni(cyclam)]_3[Cr(CN)_6]_2 \cdot 5H_2O$ (**10′**), which shows a short-range ferromagnetic interaction between the nearest Cr^{III} and Ni^{II} ions but no phase transition [101].

A series of bimetallic assemblies of the general formula $[Ni(L)_2]_2[Fe(CN)_6]X \cdot nH_2O$ (L = en, pn, 1,1-dmen; X = counter anion) have been obtained by the reaction of $[Ni(L)_3]X_2$ and $K_3[Fe(CN)_6]$ in the 2:1 molar ratio

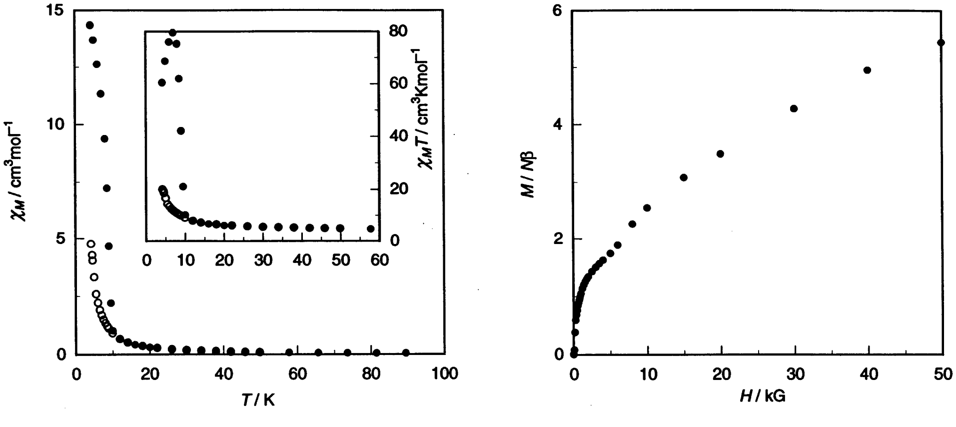


Fig. 4. Plots of χ_M versus T for $[Ni(N\text{-}men)_2]_3[Fe(CN)_6]_2 \cdot 12H_2O$ (**8**, ●) and $[Ni(N\text{-}men)_2]_3[Fe(CN)_6]_2$ (**8′**, ○) (left, insert: $\chi_M T$ versus T plots for compunds **8** and **8′**) and field dependence of the magnetization M at 4.3 K for compound **8** (right) [84].

[77–80]. Bimetallic assemblies of L = en and pn are obtained with limited counter anions: X = ClO_4^- (**11**), BF_4^- (**12**) and PF_6^- (**13**) for L = en and X = ClO_4^- (**14**), BF_4^- (**15**) and PF_6^- (**16**) for L = pn. On the other hand, 1,1-dmen provides bimetallic assemblies with various counter ions: X = ClO_4^- (**17**), BF_4^- (**18**), PF_6^- (**19**), $CF_3SO_3^-$ (**20**), BzO^- (**21**), I^- (**22**), N_3^- (**23**), NCS^- (**24**), NO_3^- (**25**). X-Ray crystallographic studies for some compounds of L = pn or 1,1-dmen have revealed a 2D square-sheet structure extended by Fe–CN–Ni–NC– linkages (Fig. 5). Four cyano nitrogens in a plane of $[Fe(CN)_6]^{3-}$ coordinate to adjacent *trans*-$[Ni(L)_2]^{2+}$ units to form an octanuclear square unit with Fe^{III} ion at each corner and Ni^{II} ion at the center of each edge. The counter anion resides in the square cavity. The methyl substitute(s) on the ethylene backbone of the diamine ligand (pn or 1,1-dmen) forms a 'fence' around the square cavity. The cavity formed with 1,1-dmen is deep, relative to that formed with pn, so as to accommodate various counter anions. The 2D sheet structures of the pn and 1,1-dmen compounds are essentially similar to each other, but the intersheet separation is generally larger in the 1,1-dmen compounds because of the bulkiness of the diamine ligand.

Compounds **14**–**25** show a ferromagnetic intrasheet interaction and a long-range magnetic ordering over the lattice [80]. The magnetic nature is ferromagnetic or metamagnetic depending upon intersheet magnetic interaction. Metamagnetism appears when the intersheet separation is small (<10 Å) to cause an antiferromagnetic interaction between the 2D sheets. Ferromagnetism appears when the intersheet separation is large (>10 Å) so that the intersheet magnetic interaction is negligible. The diamine ligand, the counter anion and the number of hydrogen water determine the intersheet separation. The ferromagnetic nature is observed for compounds **20**–**25**, which have bulky 1,1-dmen, three or more hydration water molecules or a relatively large anion (Fig. 6). Dehydration of the ferromagnetic compounds results in shortening in the intersheet separation and, hence, metamagnetism (Scheme 1). The significance of the intersheet separation in determining ferromagnetism or metamagnetism, is further supported by analogous bimetallic

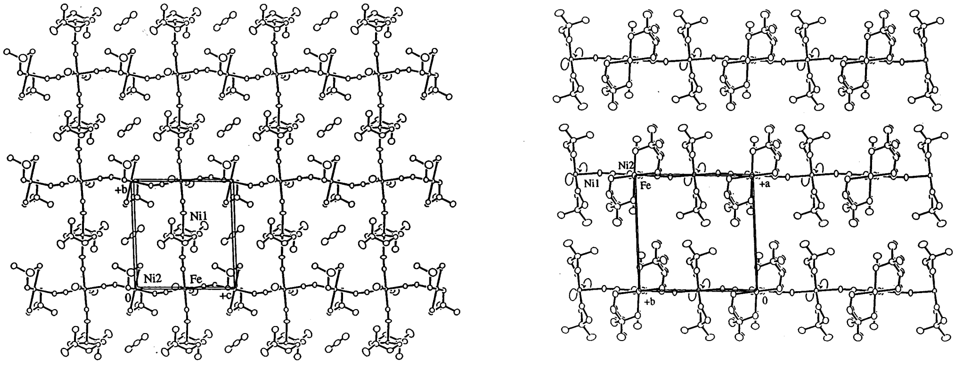


Fig. 5. Projection of the polymeric structure of $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6]N_3{\cdot}4H_2O$ (**23**) onto the *bc* (left) and *ac* (right) planes (H_2O omitted) [80].

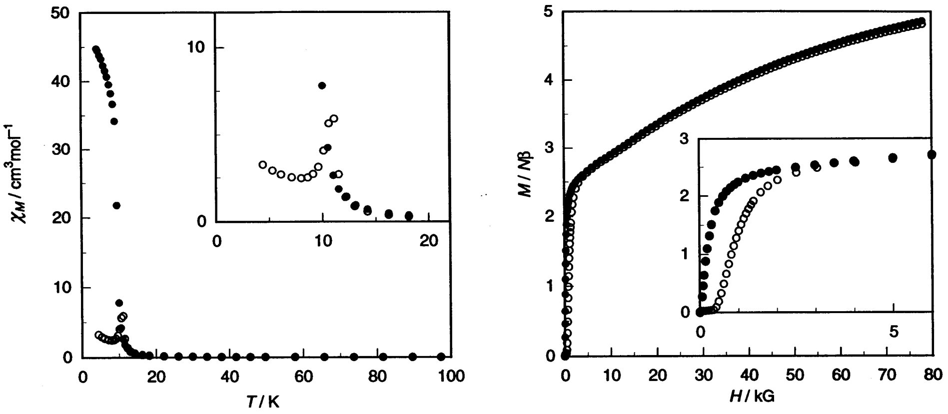
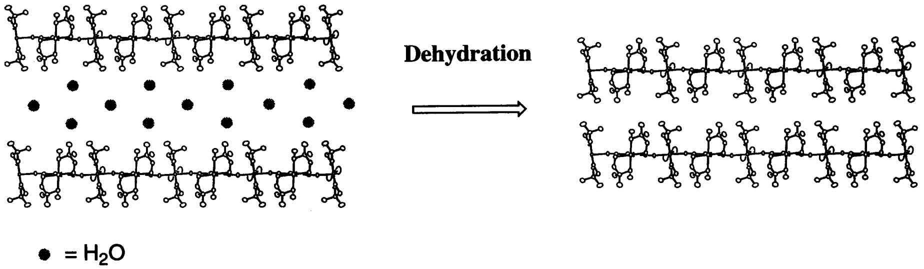


Fig. 6. Temperature dependences of χ_M (left) and field dependences of the magnetization M (right) for $[Ni(1,1\text{-}dmen)_2]_2[Fe(CN)_6]CF_3SO_3 \cdot 2H_2O$ (**20**, ●) and $[Ni(1,1\text{-}dmen)_2]_2[Fe(CN)_6]CF_3SO_3$ (**20′**, ○) [80].



Scheme 1.

assemblies with a bulky counter anion, $[Ni(1,1\text{-}dmen)_2]_2[Fe(CN)_6]X \cdot nH_2O$ (X = p-TolSO$_3^-$ and $n = 2$ (**26**); X = p-PhBSO$_3^-$ and $n = 4$ (**27**)). p-Tolylsulfonate anion (p-TolSO$_3^-$) and p-phenylbenzenesulfonate anion (p-PhBSO$_3^-$) (ca. 7.3 and 10.7 Å in height, respectively) provides a large intersheet separation (11.46 and 12.795 Å for compounds **26** and **27**, respectively) [85]. The dehydrated samples of compounds **26** and **27** may retrain an intersheet separation larger than 10 Å and show ferromagnetic nature. The correlation between the intersheet separation and magnetism for the 2D sheet compounds is summarized in Table 1.

In the case of compounds **11**–**13** with ethylenediamine ligand, a short-range ferromagnetic interaction occurs between the adjacent Fe^{III} and Ni^{II} ions but no magnetic ordering in the bulk. Recently, analogous bimetallic assemblies, $[Ni(L)_2]_2[Fe(CN)_6]NO_3 \cdot nH_2O$ (L = en (**28**) and tn (**29**)), were reported by Liao et al. [102]. Compound **29** has a similar two-dimensional network with a short intersheet separation of ca. 8.9 Å. Both compounds show magnetic behavior similar to that of compounds **11**–**13**.

Table 1
Correlation between the magnetic nature and the intersheet structure of two-dimensional assemblies, $[Ni(L)_2]_2[Fe(CN)_6]X \cdot nH_2O$

Compound	**14**	**20**	**21**	**26**	**27**
Anion X	ClO_4^-	$CF_3SO_3^-$	BzO^-	*p*-$TolSO_3^-$	*p*-$PhBSO_3^-$
Estimated size (height) of anion (Å)	ca. 2.2	ca. 3.5	ca. 5.8	ca. 7.3	ca. 10.7
Space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$	$C2/m$	$P2_1/n$
Intersheet separation (Å)	8.613	9.91	10.158	11.146	12.795
Magnetic nature					
Crystal	Metamagnetic	Ferromagnetic	Ferromagnetic	Ferromagnetic	Ferromagnetic
Dehydrated sample	Metamagnetic	Metamagnetic	Metamagnetic	Ferromagnetic	Ferromagnetic

Bimetallic assemblies of the general formula, $A[Mn(L)]_2[M(CN)_6] \cdot nH_2O$ (A = univalent cation; M^{III} = Fe, Mn, Cr, Co; L^{2-} = quadridentate Schiff bases) were reported by Miyasaka and coworkers [87–89,91–93]. The assemblies have a 2D structure consisting of an octanuclear repeating unit $(Mn–NC–M–CN)_4$ having M^{III} ions at the corners and Mn^{III} ions on the edges of a deformed square. Some compounds of this network structure were derived by desolvation of oligonuclear precursor in solvated form [92]. When $[K(18\text{-cr})]^+$ was used as the cation A^+ in the reaction in 2-propanol, $[K(18\text{-cr})(2\text{-PrOH})_2][\{Mn(acacen)\}_2\{M(CN)_6\}]$ was derived [93]. The anionic $[\{Mn(acacen)\}_2\{M(CN)_6\}]^-$ part forms a two-dimensional network based on the $(Mn–NC–M_B–CN)_4$ repeating unit. The cationic $[K(18\text{-cr})(2\text{-PrOH})_2]^+$ part, having a hexagonal-bipyramidal geometry about the metal with two 2-PrOH molecules at the apexes, forms another layer, and the cationic and anionic layers are alternately arrayed to provide a hybrid layered structure. The magnetic properties of $A[Mn(L)]_2[M(CN)_6] \cdot nH_2O$ are ferromagnetic, ferrimagnetic or metamagnetic, depending upon the Mn^{III}/M^{III} combination and bulk structure.

4. Three-dimensional assemblies

3D bimetallic assemblies of the general formula $[Ni(L)_2]_3[Fe^{II}(CN)_6]X_2$ ((L, X) = (en, PF_6^-) (**30**), (tn, PF_6^-) (**31**), (tn, ClO_4^-) (**32**)) were obtained from the reaction of $[Ni(L)_3]X_2$ and $K_4[Fe(CN)_6]$ in the 3:1 molar ratio [83]. X-Ray crystallography reveals a 3D network structure extended by the Fe–CN–Ni–NC– linkages, based on a Fe_8Ni_{12} cubic unit with Fe^{II} ions at the corners and Ni^{II} ions at the middle of the edges (Fig. 7). Two counter anions reside in the cubic cavity and align along one diagonal axis.

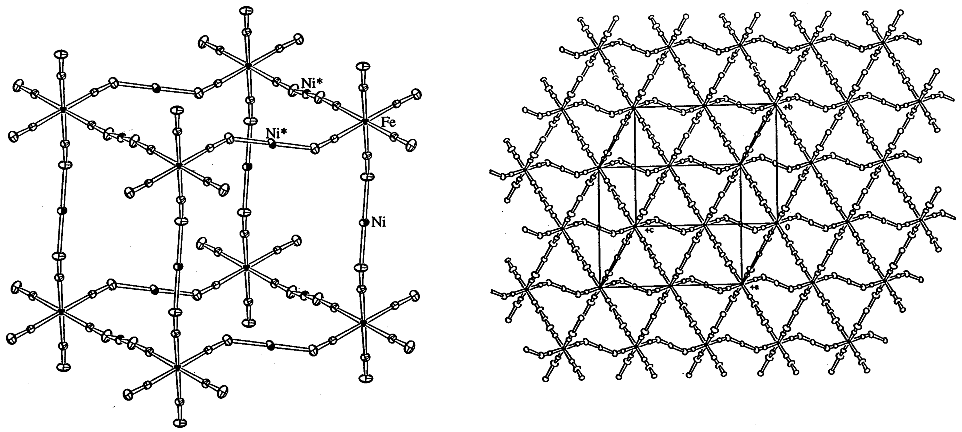


Fig. 7. Projection of the polymeric structure of $[Ni(en)_2]_3[Fe(CN)_6](PF_6)_2$ (**30**) (right) and a Fe_8Ni_{12} cubic unit (PF_6^- and en omitted) [83].

Cryomagnetic studies reveal a ferromagnetic spin-exchange between the nearest Ni^{II} ions through the diamagnetic Fe^{II} ion. The ferromagnetic interaction decreases in the order compound **30** > **32** ≥ **31**. This is in accord with the increasing order of the Fe–C and Ni–N bond distances. No magnetic ordering occurs over the lattice down to 2 K due to the diamagnetic nature of $[Fe^{II}(CN)_6]^{4-}$.

Recently, Gatteschi et al. reported a 3D bimetallic assembly, $[Ni(tren)]_3[Fe(CN)_6]_2 \cdot 6H_2O$, that has a complicated 3D network and shows a ferrimagnetic ordering around 8 K [103]. The ferrimagnetic nature of the compound is explained by a structural strain that causes a weak antiferromagnetic interaction between Fe^{III} and Ni^{II} ions on intersections of one-dimensional chains, and a three-dimensional magnetic lattice arises from the antiferromagnetically coupled one-dimensional ferromagnetic chains.

The bimetallic assembly $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ (**33**) was obtained as light-green crystals by the reaction of $MnCl_2 \cdot 4H_2O$, en and $K_3[Cr(CN)_6]$, in 3:3:2 stoichiometry under anaerobic conditions [86]. X-Ray crystallography reveals that all the cyanide groups of $[Cr(CN)_6]^{3-}$ are involved in the coordination to adjacent Mn^{II} ions. The asymmetric unit consists of one $[Cr(CN)_6]^{3-}$ anion, three halves of $[Mn(en)]^{2+}$ cations and two water molecules. The geometry about Mn is pseudo-octahedral with a chelating en ligand and four cyanide nitrogen atoms from adjacent $[Cr(CN)_6]^{3-}$ units. A 3D network structure is formed by the alternate array of $[Cr(CN)_6]^{3-}$ and $[Mn(en)]^{2+}$ ions (Fig. 8), based on a defective cubane having three Cr atoms and four Mn atom at the corners, and eight Cr–CN–Mn edges.

This shows a ferrimagnetic ordering at 69 K based on a short-range antiferromagnetic interaction between Mn^{2+} and Cr^{3+} ions (Fig. 9). To the best of our knowledge, this magnetic phase-transition temperature is the highest among the structurally characterized molecular-based magnets. The magnetic hysteresis loop at 2 K is typical of soft magnets showing a weak coercive field $H_c = 28$ G.

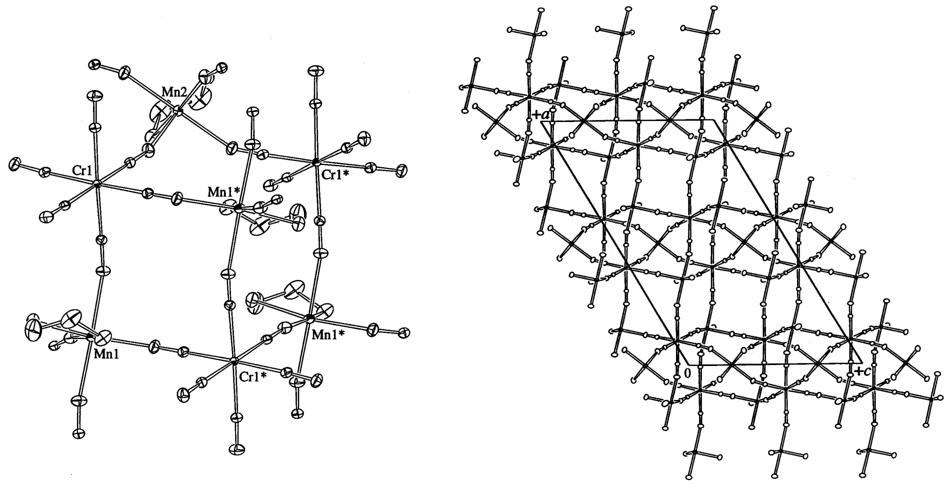


Fig. 8. Projection of the polymeric structure of $[Mn(en)]_3[Cr(CN)_6]_2{\cdot}4H_2O$ (**33**) onto the *ac* plane (right: H_2O and en omitted) and a Cr_3Mn_4 defective cubane unit [86].

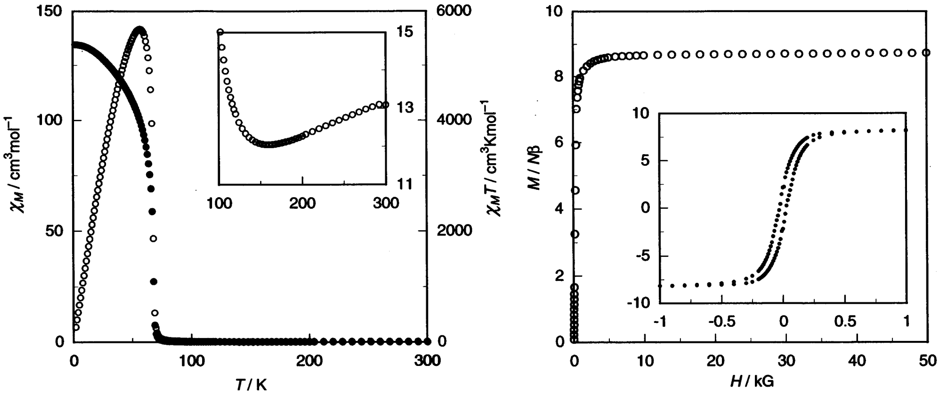
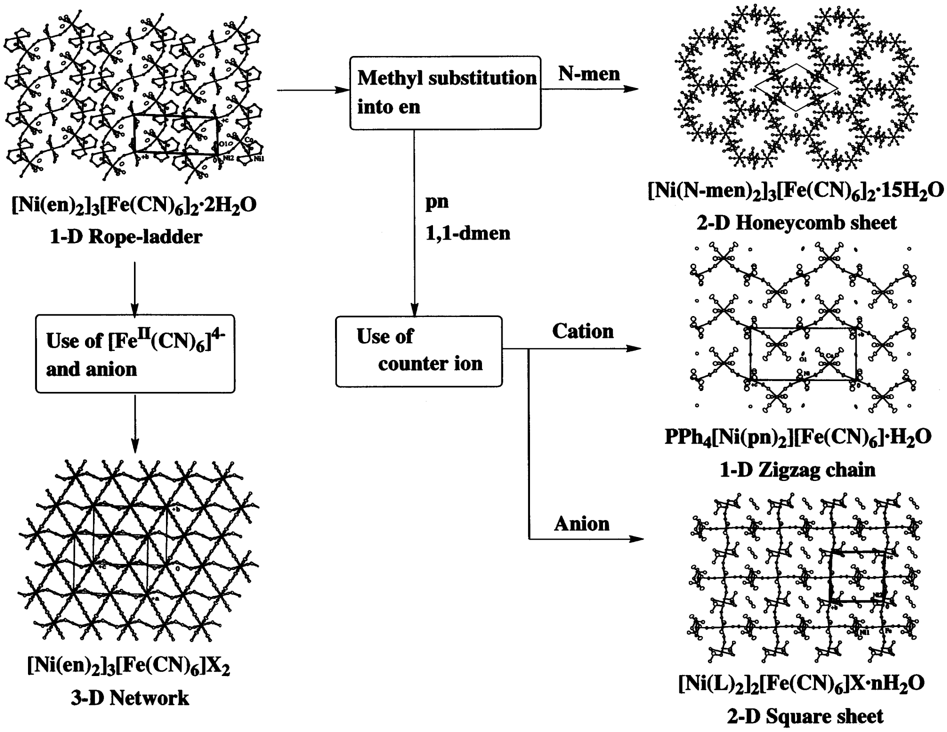


Fig. 9. Plots of χ_M versus T (●) and $\chi_M T$ versus T (○) for $[Mn(en)]_3[Cr(CN)_6]_2{\cdot}4H_2O$ (**33**) (left) and field dependence of the magnetization M at 2 K for compound **33** (right, insert: magnetic hysteresis loop at 2 K) [86].

It is pointed out that compound **33** is compared with one type of Prussian Blue family, $M_3^{II}[M^{III}(CN)_6]_2{\cdot}nH_2O$. This type of Prussian Blue analog can have a similar 3D network structure with $\{M_A(H_2O)_2\}^{2+}$ in place of the $[Mn(en)]^{2+}$ entity in compound **33**.

5. Conclusion

Bimetallic assemblies of various networks can be derived from $[M(CN)_6]^{n-}$ and coordinatively unsaturated $[M_A(L)_x]^{m+}$. In particular, rational synthesis of the



Scheme 2.

bimetallic assemblies derived from $[Ni(L)_2]^{2+}$ (L = diamine ligand) and $[M(CN)_6]^{n-}$ is established (Scheme 2). Neutral complexes $[Ni(en)_2]_3[M(CN)_6]_2\cdot 2H_2O$ (M^{III} = Cr, Mn, Fe, Co) are formed generally in the absence of appropriate counter cation or anion [76,81]. They have a 1D rope-ladder network comprised of *cis*-$\{Ni(en)_2(N)_2\}$ and *trans*-$\{Ni(en)_2(N)_2\}$ units (N, cyano nitrogen from adjacent $[M(CN)_6]^{3-}$). When $[Ni(N\text{-}men)_2]^{2+}$ is chosen in place of $[Ni(en)_2]^{2+}$ (introduction of methyl substituent into one of ethylenediamine nitrogen), the resulting $[Ni(N\text{-}men)_2]_3[M(CN)_6]_2\cdot nH_2O$ (M^{III} = Fe, Co) have a 2D honeycomb sheet structure; a 1D rope-ladder structure cannot be formed in this case because $\{Ni(N\text{-}men)_2(N)_2\}$ prefers the *trans* configuration due to the steric requirement of N-men ligand [84]. After the introduction of one or two methyl substituents into the en backbone (pn or 1,1-dmen), the resulting $\{Ni(L)_2(N)_2\}$ unit in a network definitely assumes the *trans* configuration. Thus, the use of a cation PPh_4^+ leads to the formation of $PPh_4[Ni(pn)_2][M(CN)_6]\cdot H_2O$ (M^{III} = Cr, Fe, Co) with a 1D zigzag chain structure [78,82]. The addition of an appropriate anion X^- leads to the formation of $[Ni(L)_2]_2[Fe(CN)_6]X\cdot nH_2O$ (L = pn, 1,1-dmen) that have a 2D square sheet structure; the anion exists within each square cavity [77–80]. The use of $[Fe^{II}(CN)_6]^{4-}$ as the constituent in the presence of an appropriate anion X^- provides

$[Ni(L)_2]_3[Fe^{II}(CN)_6]X_2$ (L = en, tn; $X = PF_6^-$, ClO_4^-) that have a 3D cubic network; two molecules of the anion exist in each cubic cavity [83].

1D bimetallic compounds (zigzag chain, rope-ladder) show no magnetic ordering, whereas 2D and 3D bimetallic compounds (honeycomb, square sheet, defective cubane, etc.) generally show magnetic ordering over the bulk if the constituting metal ions are both paramagnetic. The magnetic nature (ferromagnetism or metamagnetism) for 2D sheet compounds varies with the intersheet separation (*d*): ferromagnetism for $d > 10$ Å, whereas metamagnetism for $d < 10$ Å [80]. $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ has a 3D network based on a defective cubane and shows a magnetic ordering at $T_c = 69$ K [86]. This is the highest among the structurally characterized complex-based magnets.

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