

Preparation, characterization and crystal structure of [Ni(bpy)₃][Fe(CN)₅(NO)]·3H₂O and one-dimensional cyano-bridged [Ni(en)₂Fe(CN)₅(NO)]H₂O

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Abstract

Two new double complexes [Ni(bpy)₃][Fe(CN)₅(NO)]·3H₂O (1) and [Ni(en)₂Fe(CN)₅(NO)]H₂O (2) have been isolated from the reactions of the mixture of NiCl₂·6H₂O and Na₂[Fe(CN)₅(NO)] in water, with bipyridine (bpy) and ethylenediamine (en) in ethanol, respectively, and have been characterized by X-ray analysis, IR, EPR, Mössbauer spectroscopy and magnetic measurements. Crystallographic data for 1 and 2 are as follows: 1: triclinic, *P*1, *a* = 10.752(4), *b* = 13.321(3), *c* = 13.791(5) Å, *α* = 79.834(25), *β* = 81.39(3), *γ* = 72.93(3)°, *Z* = 2; 2: triclinic, *P*1, *a* = 8.622(16), *b* = 8.832(3), *c* = 12.417(3) Å, *α* = 94.81(3), *β* = 92.322(19), *γ* = 112.820(23)°, *Z* = 2. The bond angles of Fe–N–O are nearly linear for 1 (178.3(4)°) and 2 (179.4(3)°). The structure of 1 consists of a double complex of a cation [Ni(bpy)₃]²⁺ and an anion [Fe(CN)₅(NO)]²⁻. The structure of 2 consists of a one-dimensional polymeric chain –Ni(en)₂–NC–Fe(CN)₅(NO)–CN–Ni(en)₂– in which the Ni(II) and Fe(II) centers are linked by two CN groups. Cryomagnetic investigations (4–300 K) reveal a paramagnetic behavior for 1 and the presence of a one-dimensional Heisenberg weak antiferromagnetic chain with *J* = –0.47 cm⁻¹ for 2. EPR spectra observed at ambient temperature for the Ni(II) ions in both complexes are also reported.

Keywords: Crystal structures; Dinuclear complexes; Iron complexes; Nickel complexes; Cyano complexes; Magnetic properties

1. Introduction

The coordination chemistry of transition metal cyanides, especially of ferro- and ferricyanide complexes, has become of remarkable interest in recent years due to their unusual electronic state [1,2] and magnetic behaviors [3–7]. It has been shown that hexacyanometalate ions [M(CN)₆]³⁻ (*M* = Mn, Fe, Cr, etc.) act as good building blocks to provide bimetallic assemblies exhibiting spontaneous magnetization [5–7]. Recently we have reported a series of ferromagnetic M₃[Fe(CN)₆]₂ (*M* = Ni, Co, Cu) with *T*_c = 10–25 K depending upon the combination of metal (*M*) ions [8].

Very recently, Okawa and co-workers [9–11] reported several complexes with ferromagnetism of [Ni(en)₂]₃–[Fe(CN)₆]₂ [10], [Ni(pn)₂]₂[Fe(CN)₆]ClO₄ [11] and K₂[Mn(BS)]₂[Fe(CN)₆]₂ [12] (BS = substituted Schiff-base salens) in which the cyano groups of Fe(CN)₆³⁻ in

the meridional mode coordinate to adjacent Ni ions of [Ni(en)₂]²⁺, [Ni(pn)₂]²⁺ or [Mn(BS)(H₂O)]⁺ to form a 2-D or multidimensional polymeric structure. Furthermore, Tang and co-workers [12] reported an antiferromagnetic 2-D cyano-bridged polymeric [Cu₂(oxpn)Fe(CN)₅(NO)]_{*n*} complex, in which a nitrogen atom of a cyano group of [Fe(CN)₅(NO)]₂⁻ coordinated to one of the adjacent Cu(II) ions of Cu₂(oxpn) (oxpn = *N,N'*-bis(3-amino-propyl)oxamide).

As the intention of these studies was to clarify more deeply the structural correlation with magnetic property of double complexes with the [Fe(CN)₅(NO)]²⁻ anion, we have prepared two new bimetallic complexes, the discrete double complex [Ni(bpy)₃][Fe(CN)₅(NO)]·3H₂O (1) (bpy = bipyridine) and a one-dimensional polymeric complex [Ni(en)₂Fe(CN)₅(NO)]H₂O (2) (en = ethylenediamine) in which two cyano groups serve as a bridge to the Ni(II) atom through nitrogen. Here the results of crystal structure, IR, EPR, Mössbauer, and cryomagnetic studies of these species are described.

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2. Experimental

2.1. Materials

$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]_2 \cdot 2\text{H}_2\text{O}$, bipyridine (bpy), ethylenediamine (en), and other materials were of analytical grade (Aldrich) and used as supplied.

2.1.1. $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5(\text{NO})]3\text{H}_2\text{O}$ (1) and $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]\text{H}_2\text{O}$ (2)

To a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol in 20 ml water) and 2,2'-bipyridine (2 mmol in 20 ml methanol) or ethylenediamine (2 mmol in 20 ml methanol) was slowly added a solution of $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) in 10 cm^3 water. The solution turned violet to pink for 1 and violet to dark brown for 2. Upon standing for several days, the resulting pink crystals of 1 (80% yield) and brown crystals of 2 (85% yield) were filtered off, air dried and recrystallized from methanol/water (1:1) to form single crystals, suitable for X-ray diffraction analysis. *Anal.* Found: C, 49.27; H, 3.81; N, 20.12. Calc. for $\text{C}_{35}\text{H}_{30}\text{N}_{12}\text{O}_2\text{FeNi}$ (1): C, 49.33; H, 4.23; N, 19.74%. Found: C, 25.45; H, 4.09; N, 33.05. Calc. for $\text{C}_5\text{H}_{18}\text{N}_{10}\text{O}_2\text{FeNi}$ (2): C, 25.23; H, 4.20; N, 32.70%.

2.2. Physical measurements

IR spectra were recorded on a Bio-Rad FTS-40FTIR spectrophotometer as KBr pellets in the $4000\text{--}400 \text{ cm}^{-1}$ region. X-band EPR spectra at 300 K for the complexes in powder were recorded on a Bruker ECS-106 spectrometer. Mössbauer spectra at 80 K were recorded on a conventional Austin S-600 Mössbauer spectrometer. ^{57}Co (Pd) was used as the source and all isomer shifts are represented with respect to α -iron foil. Temperature dependence of the magnetic susceptibilities of the polycrystalline samples was measured between 4 and 300 K at a field 1 T using a Quantum Design model MPMS computer-controlled SQUID magnetometer. Corrections for the diamagnetism of complexes 1 and 2 were estimated from Pascal's constants.

2.3. X-ray crystal structure analysis

Crystallographic data for complexes 1 and 2 were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation at 25°C . The unit-cell parameters were determined from 25 reflections in the range $42 \leq 2\theta \leq 62^\circ$ for 1 and $32 \leq 2\theta \leq 48^\circ$ for 2. The details of data collection, crystallographic data, and reduction are summarized in Table 1.

The structures were solved by the standard heavy-atom method and refined by full-matrix least-squares. Reliability factors were defined as $R_f = \sum ||F_o| - |F_c|| / \sum |F_o|$ and the function minimized was $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$, where in the final least-squares calculation the unit weight was used. The hydrogen atoms were refined with isotropic thermal parameters. Final Fourier difference syn-

Table 1

Crystallographic data $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5(\text{NO})]3\text{H}_2\text{O}$ (1) and $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]\text{H}_2\text{O}$ (2)

	1	2
Formula	$\text{C}_{35}\text{H}_{30}\text{N}_{12}\text{O}_4\text{FeNi}$	$\text{C}_5\text{H}_{18}\text{N}_{10}\text{O}_2\text{FeNi}$
<i>M</i>	797.25	410.00
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	10.752(4)	8.6221(16)
<i>b</i> (Å)	13.321(3)	8.832(3)
<i>c</i> (Å)	13.791(5)	12.417(3)
α (°)	79.834(25)	94.81(3)
β (°)	81.39(3)	92.322(19)
γ (°)	72.93(3)	112.820(23)
<i>V</i> (Å ³)	1848.5(10)	865.7(4)
<i>Z</i>	2	2
<i>D_c</i> (g cm ⁻³)	1.432	1.573
<i>F</i> (000)	814	417
μ (Mo <i>K</i> α) (cm ⁻¹)	40.095	82.123
Crystal size (mm)	0.25 × 0.35 × 0.35	0.25 × 0.35 × 0.40
No. of data used	7511	3422
<i>R_f</i>	0.051	0.056
<i>R_w</i>	0.055	0.066

Table 2

Selected final atomic positional parameters and B_{eq} values (Å²) for 1

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
Fe	0.37586(6)	0.28791(5)	0.16886(5)	2.91(3)
Ni	0.13996(6)	0.79595(5)	0.28706(5)	2.73(3)
N(6)	0.3182(4)	0.4181(3)	0.1475(3)	4.30(19)
O(1)	0.2779(5)	0.5072(3)	0.1307(4)	8.61(3)
C(1)	0.3844(5)	0.2750(4)	0.3107(4)	3.95(2)
C(2)	0.5565(4)	0.2925(4)	0.1439(4)	3.89(22)
C(3)	0.4427(4)	0.1349(4)	0.1902(3)	3.23(19)
C(4)	0.3808(4)	0.2672(4)	0.0327(3)	3.40(21)
C(5)	0.2042(4)	0.2637(4)	0.2151(3)	3.89(22)
N(7)	0.0519(3)	0.7399(3)	0.19093(24)	2.98(15)
N(8)	0.1930(3)	0.8778(3)	0.15121(24)	2.97(15)
N(9)	0.3084(3)	0.6681(3)	0.2872(3)	3.23(16)
N(10)	0.0948(3)	0.6966(3)	0.41233(24)	3.04(16)
N(11)	-0.0201(3)	0.9275(3)	0.31249(24)	2.97(14)
N(12)	0.2174(3)	0.8783(3)	0.36849(24)	2.89(14)

^a B_{eq} is the mean of the principal axes of the thermal ellipsoid.

theses were featureless. All refinement calculations were performed using the NRCVAX computer program [13]. Selected positional parameters of the non-hydrogen atoms of 1 and 2 are given in Tables 2 and 3, respectively.

3. Results and discussion

3.1. IR spectra

The most important aspects concerning the IR spectra of 1 and 2 deal with the vibrational stretching frequencies of NO and CN. Nitric oxide has an extra electron, occupying a π^* antibonding orbital, which is relatively easily lost. In the case

Table 3
Selected final atomic positional parameters and B_{eq} values (\AA^2) for 2

Atom	x	y	z	B_{eq}^a
Fe	0.4607(10)	0.10630(10)	0.29693(6)	1.31(3)
Ni(1)	1	0.5	0.5	1.35(5)
Ni(2)	0	0	0	1.54(5)
N(1)	0.7544(6)	0.3210(6)	0.4615(4)	2.03(19)
N(2)	0.1578(6)	-0.0300(6)	0.1259(4)	2.01(20)
N(6)	0.4966(6)	-0.0638(6)	0.3020(4)	1.89(19)
N(7)	0.9198(6)	0.6695(6)	0.4324(4)	2.23(20)
N(8)	1.0555(6)	0.4551(6)	0.3404(4)	1.94(20)
N(9)	0.0628(6)	0.2433(6)	0.0685(4)	2.09(20)
N(10)	-0.2173(6)	-0.1086(6)	0.0817(4)	2.29(22)
C(1)	0.6426(6)	0.2404(6)	0.4030(4)	1.61(20)
C(2)	0.2702(7)	0.0128(7)	0.1889(4)	1.71(21)
C(3)	0.6123(7)	0.1888(7)	0.1841(5)	2.08(23)
C(4)	0.4179(7)	0.3067(7)	0.2869(5)	2.13(24)
C(5)	0.3098(7)	0.0650(7)	0.4112(4)	1.88(22)
O(1)	0.5214(6)	-0.1825(6)	0.3046(5)	4.4(3)

^a B_{eq} is the mean of the principal axes of the thermal ellipsoid.

of terminally bound NO, simple MO theory predicts that whilst $M\text{-NO}^+$ will be linear, $M\text{-NO}^-$ may be a bent bond. The potential thus exists to establish the formal oxidation state of the metal center in nitric oxide by examining the IR spectra [14]. The nitroprusside anion of $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ (SNP) has an Fe–N–O angle of nearly 180° and IR active NO stretching frequency of 1940 cm^{-1} indicating an NO^+ complex of iron(II) with extensive π -bonding. In general, IR absorption bands in the region $2200\text{--}1900\text{ cm}^{-1}$ are due to the phonon involving CN^- and NO^+ stretching vibrations [1, 2, 14, 15]. In the present system, the IR spectrum of **1** shows a single absorption at 2143 cm^{-1} which can be assigned to CN stretching, whereas two strong absorptions at 2141 and 2162 cm^{-1} have been observed for complex **2**, which probably arise from the bridging CN and terminal CN stretching vibrations, respectively. Strong single peaks at 1911 for **1** and 1933 cm^{-1} for **2** are assigned to NO stretching, thus implying that the Fe–N–O bonds are nearly linear.

Table 4
Selected bond distances (\AA) and angles ($^\circ$) for 1

Fe–N(6)	1.650(4)	Fe–C(1)	1.947(5)
Fe–C(2)	1.937(5)	Fe–C(3)	1.937(5)
Fe–C(4)	1.936(4)	Fe–C(5)	1.936(4)
Ni–N(7)	2.086(3)	Ni–N(8)	2.085(3)
Ni–N(9)	2.090(3)	Ni–N(10)	2.072(3)
Ni–N(11)	2.103(3)	Ni–N(12)	2.100(3)
N(6)–O(1)	1.131(6)		
Fe–N(6)–O(1)	178.3(4)	Fe–C(1)–N(1)	177.6(5)
Fe–C(2)–N(2)	176.7(4)	Fe–C(3)–N(3)	179.0(4)
Fe–C(4)–N(4)	178.0(4)	Fe–C(5)–N(5)	176.8(4)
C(1)–Fe–C(4)	167.44(20)	C(2)–Fe–C(5)	172.60(19)
N(6)–Fe–C(3)	178.42(19)	N(6)–Fe–C(2)	93.26(20)
N(6)–Fe–C(1)	97.26(20)	N(6)–Fe–C(4)	94.83(20)
N(7)–Ni–N(9)	94.35(13)	N(7)–Ni–N(10)	95.77(13)
N(7)–Ni–N(12)	169.91(13)	N(7)–Ni–N(11)	95.48(13)
N(8)–Ni–N(10)	172.20(13)	N(9)–Ni–N(11)	169.30(13)

3.2. Structure of complex 1

An ORTEP drawing of complex **1** with the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 4.

As depicted in Fig. 1, complex **1** consists of a discrete $[\text{Ni}(\text{bpy})_3]^{2+}$ cation and $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ anion which form a double complex. The geometry of $[\text{Ni}(\text{bpy})_3]^{2+}$ has approximate point-group symmetry D_3 . The average Ni–N bond distance of 2.09 \AA is in agreement with the previous reported value of 2.09 \AA for $[\text{Ni}(\text{bpy})_3]\text{Cl}_2$ [16].

The geometry of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is in good agreement with those of the previous studies [4, 17, 18]. The mean Fe–C, Fe–N, C–N and N–O bond distances in $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ are 1.939 , 1.650 , 1.390 and 1.131 \AA , respectively. These values are in accordance with the reported values for other nitroprusside metal salts [2–4, 17–19]. The bond angle of Fe–N–O ($178.3(4)^\circ$) is nearly linear.

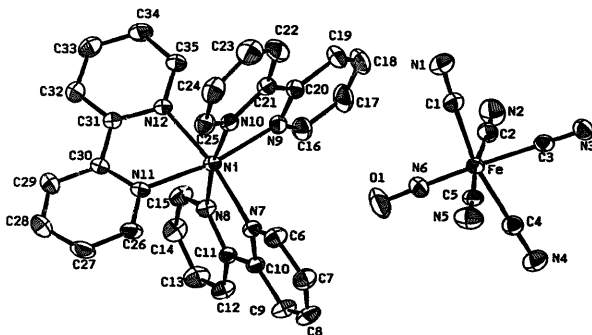


Fig. 1. ORTEP stereoview of $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5(\text{NO})]$ (without H_2O ; 30% probability thermal ellipsoids).

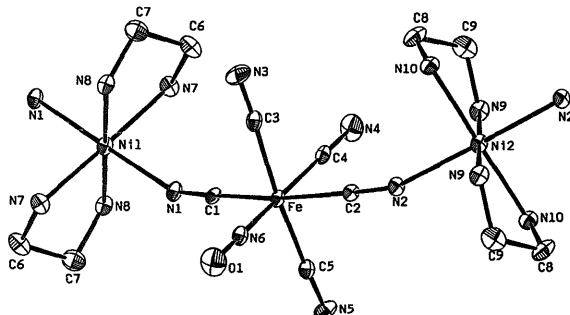


Fig. 2. ORTEP stereoview of $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{CO})]$ (without H_2O ; 30% probability thermal ellipsoids).

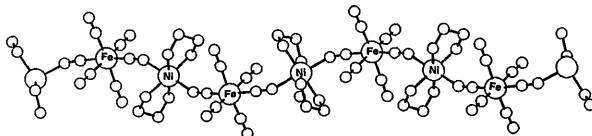


Fig. 3. View of the CN-bridged polymeric $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]$ without H_2O .

3.3. Structure of complex 2

An ORTEP drawing of complex 2 with the atom numbering scheme is shown in Fig. 2. A view of the polymeric chain structure is given in Fig. 3. Relevant bond distances and angles are given in Table 5. The structure of 2 shows that the asymmetric unit consists of one $\text{trans-}[\text{Ni}(\text{en})_2]^{2+}$ cation and one $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ anion. Two cyano nitrogens (N(1) and N(2)) in *trans* mode coordinate to the adjacent Ni ions, through N(1) to Ni(1) of $\text{trans-}[\text{Ni}(\text{en})_2]^{2+}$ and through N(2) to Ni(2) of another $\text{trans-}[\text{Ni}(\text{en})_2]^{2+}$, to form a quasi wave form of the alternate array of the linear

chain $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]_n$, as shown in Fig. 3. As shown in Fig. 2 and Table 5, the average bond angle 176.8° of $\text{Fe-C}(1)\text{-N}(1)$ and $\text{Fe}(2)\text{-C}(2)\text{-N}(2)$ is near linearity, but the bond angle of $\text{Ni}(1)\text{-N}(1)\text{-C}(1)$ or $\text{Ni}(2)\text{-N}(2)\text{-C}(2)$ is non-linear with an angle of $153.5(3)^\circ$. The geometry of the ligand field of the Ni ions is a six-coordination with tetragonal distorted-octahedral symmetry, the Ni–N bond lengths ranging from 2.093(5) to 2.099(4) Å. The mean bond lengths of Fe–C, Fe–N, C–N and N–O in the $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ moiety are in accordance with the corresponding observed values in complex 1. The bond angle of Fe-N-O ($179.4(5)^\circ$) is also nearly linear.

Table 5

Selected bond distances (Å) and angles ($^\circ$) for 2

Fe–N(6)	1.653(5)	Fe–C(1)	1.930(5)
Fe–C(2)	1.940(5)	Fe–C(3)	1.945(6)
Fe–C(4)	1.956(6)	Fe–C(5)	1.926(6)
Ni(1)–N(1)	2.099(4)	Ni(1)–N(7)	2.095(5)
Ni(1)–N(8)	2.099(4)	N(1)–C(1)	1.135(5)
Ni(2)–N(9)	2.095(5)	Ni(2)–N(10)	2.093(5)
N(6)–O(1)	1.151(7)		
Fe–N(6)–O(1)	179.4(5)	Fe–C(1)–N(1)	176.8(5)
Fe–C(2)–N(2)	174.6(5)	Ni(1)–N(1)–C(1)	153.5(5)
C(1)–Fe–C(2)	168.26(23)	N(1)–Ni(1)–N(10)	179.9(5)
C(3)–Fe–C(5)	169.31(24)	N(6)–Fe–C(1)	95.40(24)
N(6)–Fe–C(2)	95.33(23)	N(6)–Fe–C(4)	178.55(23)
N(6)–Fe–C(5)	95.68(24)	N(6)–Fe–C(3)	94.81(24)
N(1)–Ni(1)–N(7)	87.79(19)	N(1)–Ni(1)–N(8)	88.84(18)
N(7)–Ni(1)–N(8)	97.01(19)	N(8)–Ni(1)–N(7)	82.99(19)
N(9)–Ni(2)–N(10)	96.84(19)	N(10)–Ni(2)–N(9)	96.84(19)

3.4. EPR and Mössbauer spectra

The X-band (9.81 GHz) EPR spectra of the polycrystalline powder recorded at 300 K for 1 and 2 show a typical transition of high-spin Ni(II) with the spin state of $S = 1$. The observed absorptions with transitions arise from $\Delta M_S = \pm 1$ and $\Delta M_S = \pm 2$ are located at 3406, 1801 G for 1 and 3406, 1860 G for 2, respectively. $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is diamagnetic, thus no EPR signal can be observed. In general, it is observed that Ni(II) often gives rise to quite broad EPR lines, even in presumably octahedral environments. Since Ni(II) has an even number of electrons, Kramer's theorem does not apply [20]. Nevertheless, in some cases of Ni(II)-doped low symmetry diamagnetic lattices, two resonances are observable at X-band [20–22]. One corresponds to the $\Delta M_S = \pm 2$ transition, while the other results from either the $M_S = 0 \rightarrow M_S = +1$ or $M_S = -1 \rightarrow 0$ transition (depending on the sign

of the zero field splitting D). In the present work, the spin-Hamiltonian parameters of **1** and **2** were determined from the experimental data and fitted to the equation [21,22]

$$\mathcal{H} = g\beta H S + D s_z^2 \quad (1)$$

with $g = 2.34$, $D = -0.18 \text{ cm}^{-1}$ for **1** and $g = 2.11$, $D = -0.31 \text{ cm}^{-1}$ for **2**.

Mössbauer spectra at 80 K for complexes **1** and **2** show a quadrupole doublet with the parameters of isomer shift (IS), -0.39 for **1**, -0.18 mm s^{-1} for **2** and quadrupole splitting (QS), 1.87 for **1**, 1.80 mm s^{-1} for **2**, respectively. The negative IS value at 80 K of **1** is higher than that of **2** indicating that total s -electron density at the iron nucleus in complex **2** is lower than that of **1**. This can be interpreted by the additional shielding effect of the $3d$ -electron at the iron atom of **2** by donating a $3d$ -electron from the nickel ion to the iron ion through the bridging CN ligand [23].

3.5. Magnetic susceptibility studies

The cryomagnetic behavior of the complexes $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5(\text{NO})]3\text{H}_2\text{O}$ and $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]\text{H}_2\text{O}$ is shown in Figs. 4 and 5, respectively, in the forms of plots of χ_M versus T and $\chi_M T$ versus T . As shown in Fig. 4, the plot of $\chi_M T$ versus T for **1** appears to be invariant as a function of temperature indicative of a classical paramagnet following Curie–Weiss law behavior, fitted to $\chi_M = C/(T - \theta)$, with $C = 0.98 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\theta = 0.0$ suggesting no intermolecular magnetic exchange interaction in the present system.

In the plot $\chi_M T$ versus T shown in Fig. 5 for **2**, the $\chi_M T$ values keep invariant in the region 300 ($\chi_M T = 1.22 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\mu = 3.10 \mu_B$) to 20 K . As the temperature is lowered from 20 K , the $\chi_M T$ value gradually decreases to $1.04 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($\mu = 2.85 \mu_B$) at 5 K , suggesting a very weak anti-

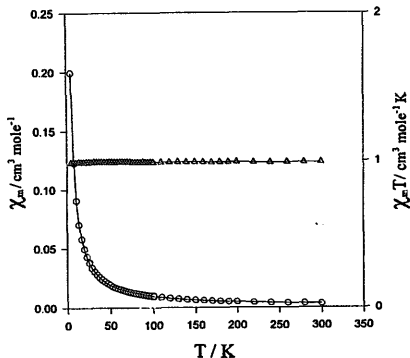


Fig. 4. Thermal variation of the molar magnetic susceptibility for $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5(\text{NO})]3\text{H}_2\text{O}$.

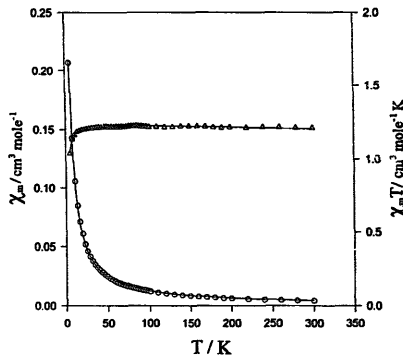


Fig. 5. Thermal variation of the molar magnetic susceptibility for $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]\text{H}_2\text{O}$. The solid lines represent a fit based on Eq. (1).

ferromagnetic interaction. It is known that $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is diamagnetic, therefore the exchange interaction between $\text{Ni}(\text{II})$ – $\text{Fe}(\text{II})$ through the cyanide bridging ligand is negligible. However, the coupling between two adjacent $\text{Ni}(\text{II})$ ions could be through the $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ group. We have attempted to reproduce theoretically the experimental susceptibility in this one-dimensional regime by using the modified expression (2) calculated by Kahn [24,25] for a classical-spin Heisenberg chain, scaled to a real spin $S = 1$ which is valid for an antiferromagnetic coupling

$$\chi_M = N g^2 \beta^2 / k(T - \theta) [A/B] + C/(T - \theta) + N_a \quad (2)$$

$$A = 2.0 + 0.0194x + 0.777x^2, \\ B = 3.0 + 4.346x + 3.232x^2 + 5.834x^3$$

where $x = J/kT$. The symbols N , β , g and k have their usual meanings, C is the Curie constant for an impurity assumed in this model to be a simple $S = 1$ Curie paramagnet (non-coupled paramagnetic species), θ is the Weiss constant of the impurity, and N_a is the temperature-independent component of susceptibility. A very close agreement with experiment is obtained with $J = -0.47 \text{ cm}^{-1}$, $g = 2.10$, $\theta = -0.44 \text{ K}$, $C = 0.93 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $N_a = 100 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and the disagreement factor $R = (\sum (\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2)^{1/2} = 4 \times 10^{-5}$. It is worthy of note that the fitted g value of 2.10 is in good agreement with 2.11 calculated from the result of the EPR measurement of **2**.

One can notice that the magnitude of the exchange interaction J of -0.47 cm^{-1} in $[\text{Ni}(\text{en})_2\text{Fe}(\text{CN})_5(\text{NO})]\text{H}_2\text{O}$ is much lower than -31.9 cm^{-1} which was reported previously in the strong antiferromagnetic one-dimensional $[\text{Ni}(\text{en})_2(\text{NO}_2)]^+$ chain [24]. In the complex $[\text{Ni}(\text{en})_2(\text{NO}_2)]^+$ ion, two $\text{Ni}(\text{II})$ ions are linked by an NO_2 group along the chain with an intrachain Ni – Ni distance of 5.15 \AA , whereas the nearest intrachain Ni – Ni distance in the $[\text{Ni}(\text{en})_2$

$[\text{Fe}(\text{CN})_5(\text{NO})]$ chain is relatively large, namely 7.9143(23) Å, thus making a very weak coupling.

As a final comment, we emphasize that this study gives new evidence that the formation of a discrete or cyano-bridged polymeric double complex of $[\text{Ni}(\text{L})_n]^{2+}$ with $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is dependent on the nature of the ligands L of the cation.

4. Supplementary material

Tables containing atom positions, anisotropic displacement parameters, hydrogen atom locations, and bond lengths and angles are available from the authors on request.

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References

- [1] N.W. Alcock, A. Samotus and J. Szklarzewicz, *J. Chem. Soc., Dalton Trans.*, (1993) 885.
- [2] S. Das, S. Ganguli and M. Bhattacharya, *J. Phys. Chem. Solids*, **46** (1985) 143.
- [3] Y.Y. Yang and J.I. Zink, *J. Am. Chem. Soc.*, **107** (1985) 4799.
- [4] M.R. Pressprich, M.A. White, Y. Vekhter and P. Coppens, *J. Am. Chem. Soc.*, **116** (1994) 5233.
- [5] V. Gadet, M. Bujoli-Doeuff, L. Force, M. Verdaguer, K. El Malkhi, A. Deryn and J.P. Besse, in D. Gatteschi et al. (eds.), *Molecular Magnetic Material*, NATO ASI Series 198, Kluwer, Dordrecht, 1990, p. 281.
- [6] V. Gadet, T. Mallah, I. Castro and M. Verdaguer, *J. Am. Chem. Soc.*, **114** (1992) 9213.
- [7] W.R. Entley and G.S. Girolomi, *Inorg. Chem.*, **33** (1994) 5165.
- [8] (a) H.H. Wei and Y.H. Chang, *Mater. Res. Soc. Symp. Proc.*, **247** (1992) 463; (b) H.L. Shyu, S.N. Lin and H.H. Wei, *J. Chin. Chem. Soc. (Taipei)*, **42** (1995) 791.
- [9] M. Ohba, N. Maruono, H. Okawa, T. Enoki and J.M. Latour, *J. Am. Chem. Soc.*, **116** (1994) 11566.
- [10] M. Ohba, H. Okawa, T. Ito and A. Ohto, *J. Chem. Soc., Chem. Commun.*, (1995) 1545.
- [11] H. Miyasaki, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *J. Am. Chem. Soc.*, **118** (1996) 981.
- [12] Z.N. Chen, J.L. Wang, J. Qiu, F.M. Miao and W.X. Tang, *Inorg. Chem.*, **34** (1995) 2255.
- [13] E.J. Gabe, Y. Le Page, J.P. Charland, F.L. Lee and P.S. White, *J. Appl. Crystallogr.*, **22** (1989) 384.
- [14] P.N. Hawker and M.V. Twigg, in S.G. Wilkinson, R. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 4, Pergamon, Oxford, 1989, p. 1187.
- [15] R.K. Khanna, C.W. Brown and L.H. Jones, *Inorg. Chem.*, **8** (1969) 2195.
- [16] K. Yanagi, Y. Ohashi, Y. Sasada, Y. Kaizu and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54** (1981) 118.
- [17] A.G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, New York, 1976.
- [18] C.R. Johnson, C.M. Jones, S.A. Asher and J.E. Abola, *Inorg. Chem.*, **30** (1991) 2120.
- [19] A. Navaza, G. Chevrier and P.M. Alzari and P.J. Aymonino, *Acta Crystallogr., Sect. C*, **45** (1989) 839.
- [20] J.A. Weil, J.R. Baton and J.E. Wertz, *Electron Paramagnetic Resonance*, Wiley, New York, 1994, p. 226.
- [21] G.L. McPherson, R.C. Koch and G.D. Stucky, *J. Chem. Phys.*, **60** (1974) 1424.
- [22] J.A. Ochi, W. Sano, S. Isotani and C.E. Hennies, *J. Chem. Phys.*, **62** (1975) 2115.
- [23] N.N. Greenwood and T.C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971, p. 183.
- [24] A. Meyer, A. Gleizes, J.J. Girerd, M. Verdaguer and O. Kahn, *Inorg. Chem.*, **21** (1982) 1729.
- [25] O. Kahn, *Molecular Magnetism*, VCH, New York, 1993, p. 257.