Synthesis, crystal structure and magnetic properties of a two-dimensional mixed-valence assembly [Fe(salen)]$_2$[Fe(CN)$_5$NO]

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Abstract

A cyanide-bridged Fe^{III}–Fe^{II} mixed-valence assembly, [Fe^{III}(salen)]$_2$[Fe^{II}(CN)$_5$NO] [salen = N,N'-ethylene*bis*(salicylideneiminato)dianion], prepared by slow diffusion of an aqueous solution of Na$_2$[Fe(CN)$_5$NO]·2H$_2$O and a MeOH solution of [Fe(salen)NO$_3$] in an H tube, has been characterized by X-ray structure analysis, i.r. spectra and magnetic measurements. The product assumes a two-dimensional network structure consisting of pillow-like octanuclear [—Fe^{II}—CN—Fe^{III}—NC—]$_4$ units with dimensions: Fe^{II}—C = 1.942(7) Å, C—N = 1.139(9) Å, Fe^{III}—N = 2.173(6) Å, Fe^{II}—C—N = 178.0(6)°, Fe^{III}—N—C = 163.4(6)°. The Fe^{II}—N—O bond angle is linear (180.0°). The variable temperature magnetic susceptibility, measured in the 4.8–300 K range, indicates the presence of a weak intralayer antiferromagnetic interaction and gives an Fe^{III}–Fe^{III} exchange integral of −0.033 cm^{-1}.

Introduction

Recently, there has been a growing interest in coordination polymers having a two-(2D) or three-dimensional (3D) structure, because of the unique physicochemical properties arising from the bulk of these systems [1]. In particular, much effort has been expended in designing molecular-based magnets exhibiting spontaneous magnetization. It is known that Prussian blue analogues, derived from hexacyanometalate ions [M(CN)$_6$]$^{n-}$ and simple transition metal ions, exhibit magnetic orders at considerably high temperatures and form a family of magnetic materials [2]. In order to clarify the magneto-structural correlation of cyano-bridged bimetallic systems, a wide variety of hybrid Prussian blue complexes derived from [M(CN)$_6$]$^{n-}$ (M = Fe, Cr, and Mn) and coordinatively unsaturated transition metal complexes have been studied structurally and magnetically [3]. These complexes assume oligonuclear, one-dimensional (1D), 2D and 3D structures and exhibit ferro- or meta-magnetic behavior. *E.g.*, the reaction between [M′(BS)]$^+$ [M′ = Mn, Fe; BS = salen-substituted

ligand; salen = N,N'-ethylene*bis*(salicylideneiminato)dianion] and [M(CN)$_6$]$^{3-}$ has already led to a variety of lattice structures depending on the nature of the Schiff base, the countercation and the reaction solvent *etc.*, *e.g.*, the heptanuclear complex [Cr{(CN) Mn(salen·H$_2$O)}$_6$] [Cr(CN)$_6$]·6H$_2$O [4], the 1D chain complex [NEt$_4$]$_2${Mn(acacen)}[Fe(CN)$_6$] [5], 2D network complexes K{Mn(3-MeO(salen))}$_2$[Fe(CN)$_6$] [6] and [{Fe(salen)}$_3${Fe(CN)$_6$}(MeOH)$_2$]·3H$_2$O [7] have been synthesized and characterized in detail; they exhibit a ferromagnetic or antiferromagnetic interaction between adjacent paramagnetic centers through the cyano bridge. Considering that Prussian blue itself is both a ferromagnet with T_c = 5.6 K and a typical mixed-valence complex, in which the magnetic interactions are mediated by diamagnetic [Fe(CN)$_6$]$^{4-}$ anions, it is useful to investigate the magnetic interaction between paramagnetic transition metal ions connected by another diamagnetic ion such as [Fe(CN)$_5$NO]$^{2-}$. Recently, we have succeeded in preparing a mixed-valence Fe^{III}–Fe^{II} cyano-bridged coordination polymer, [Fe(salen)]$_2$[Fe(CN)$_5$NO], using [Fe(CN)$_5$NO]$^{2-}$ as a template. Here we report the synthesis, structure and magnetic properties of the new 2D assembly with neutral layers.

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Experimental

Physical measurements

Elemental analysis for C, H and N were performed at a Perkin-Elmer 240C microanalysis instrument (USA). Fe analysis was made on a Jarrell-Ash 1100 + 2000 inductively coupled plasma quantometer. I.r. spectra were recorded on a Nicolet FT-IR 170SX spectrometer with KBr pellets in the 4000–400 cm^{-1} range. Magnetic susceptibilities on crystalline samples were measured with a Quantum Design MPMS-5 SQUID susceptometer under an applied magnetic field of 10 kOe in the 4.8–299 K range. Diamagnetic corrections were made using Pascal's constants. Effective magnetic moments were calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}} \times T)^{1/2}$, where χ_{M} is the magnetic susceptibility per formula unit.

General procedures and materials

All chemicals and solvents used for the synthesis were reagent grade. The quadridentate Schiff base ligand, H_2salen, was prepared by mixing salicylaldehyde and ethylenediamine in a 2:1 molar ratio in MeOH according to the literature [8, 9]. [Fe(salen)NO$_3$] was prepared by mixing Fe(NO$_3$)$_3 \cdot$9H$_2$O, H$_2$salen and LiOH·H$_2$O in a 1:1:1.5 molar ratio in MeOH according to the method reported previously [10].

[Fe(salen)]$_2$[Fe(CN)$_5$NO]

Well-shaped black crystals of the title compound were grown at room temperature by slow diffusion of a dark brown MeOH solution (15 cm^3) of [Fe(salen)NO$_3$] (0.15 mmol) and an aqueous solution (15 cm^3) of Na$_2$[Fe(CN)$_5$NO]·2H$_2$O (0.15 mmol) in an H tube. The resulting crystals were collected, washed with H$_2$O and MeOH respectively, and dried in air. (Found: C, 52.0; H, 3.15; N, 16.0; Fe, 19.3; C$_{37}$H$_{28}$Fe$_3$N$_{10}$O$_5$ calcd.: C, 51.7; H, 3.3; N, 16.3; Fe, 19.5%.) I.r. (cm^{-1}): ν(C=N)(imine): 1631(vs), 1596(s); ν(C≡N)(cyanide): 2160(s); ν(NO)(nitrosyl): 1926(vs).

X-ray crystallography

C$_{37}$H$_{28}$Fe$_3$N$_{10}$O$_5$, $M_{\text{r}} = 860.24$, tetragonal, space group P4/ncc, $a = b = 14.356(2)$ Å; $c = 17.673(3)$ Å, $V = 3642.3(9)$ Å^3, $Z = 4$, $D_{\text{c}} = 1.569$ mg m^{-3}, $\mu = 1.238$ mm^{-1}, $T = 295(2)$ K.

A crystal of the title complex with dimensions $0.48 \times 0.36 \times 0.36$ mm was fixed to the end of a glass fiber, which was mounted on an Siemens P4 diffractometer in order to perform X-ray diffraction using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined from 28 reflections in the $3.37° \le \theta \le 15.28°$ range. The intensity data were collected using the ω scan mode in the $2.01° \le \theta \le 24.99°$ range. Of a total of 3973 reflections measured, 1608 were considered unique ($R_{\text{int}} = 0.0303$). The structure was solved by direct methods and expanded using the Fourier technique. All non-hydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogen atoms were located using a riding model. The contributions of these hydrogen atoms were included in the structure factor calculations. A full matrix least-squares refinement was based on F^2. The unweighted and weighted agreement factors of the forms $R_1 = \sum ||F_{\text{o}}|-|F_{\text{c}}||/\sum|F_{\text{o}}|$ and $wR_2 = [\sum[w(F_{\text{o}}^2 - F_{\text{c}}^2)^2]/\sum[w(F_{\text{o}}^2)^2]]^{1/2}$ were used. The final R_1 (wR_2) value is 0.0747 (0.1573) for 130 parameters and 1185 observed reflections ($I \ge 2\sigma(I)$) with the weighting scheme, $w = 1/[\sigma^2(F_{\text{o}}^2) + (0.0249P)^2 + 29.3218P]$, where $P = (F_{\text{o}}^2 + 2F_{\text{c}}^2)/3$. All computations were carried out on a PC-586 computer using the SHELXTL program. CCDC reference number: CCDC 175781.

Results and discussion

Spectroscopic studies

Relevant i.r. spectral data for the title complex are given in the Experimental section. In the 2000–2200 cm^{-1} range, the complex shows a strong peak at 2160 cm^{-1}, attributed to intermetallic bridging, ν(C≡N), as observed for other cyano-bridged complexes containing nitroprusside. The result suggests that nearly all the cyanide groups in [Fe(CN)$_5$NO]$^{2-}$ are involved in coordination. A very strong band at 1926 cm^{-1} is reasonably assigned to the NO stretching vibration, thus implying that the Fe—N—O bond is linear [11], as has been established by crystallography.

Crystal structure

An ORTEP diagram of the title complex with the atom numbering scheme is shown in Figure 1. The projections along the c-axis and a-axis are given in Figures 2 and 3, respectively. The selected bond distances and angles are listed in Table 1. The molecular structure consists of one [Fe^{II}(CN)$_5$NO]$^{2-}$ anion and two [Fe^{III}(salen)]$^+$ cations. The anion and cation are linked by Fe^{II}—CN—Fe^{III} assemblies to form a 2D neutral network structure consisting of pillow-like octanuclear [—Fe^{II}—CN—Fe^{III}—NC—]$_4$ units (Figure 2). Each [Fe(CN)$_5$NO]$^{2-}$ anion uses four equivalent equatorial —C≡N groups to connect with four [Fe(salen)]$^+$ cations, whereas each [Fe(salen)]$^+$ cation is linked to two [Fe(CN)$_5$NO]$^{2-}$ ions in trans positions. As usual, the [Fe(CN)$_5$NO]$^{2-}$ fragment exhibits a distorted octahedral structure, in which the Fe^{II} atom is coordinated by four carbon atoms of the CN$^-$ ligands occupying equatorial positions, whereas a carbon atom of the CN$^-$ ligand and a nitrogen atom of the nitrosyl group occupy axial positions. According to MO theory, M—NO$^+$ will be linear which is proved by the Fe^{II}—N—O bond angle of
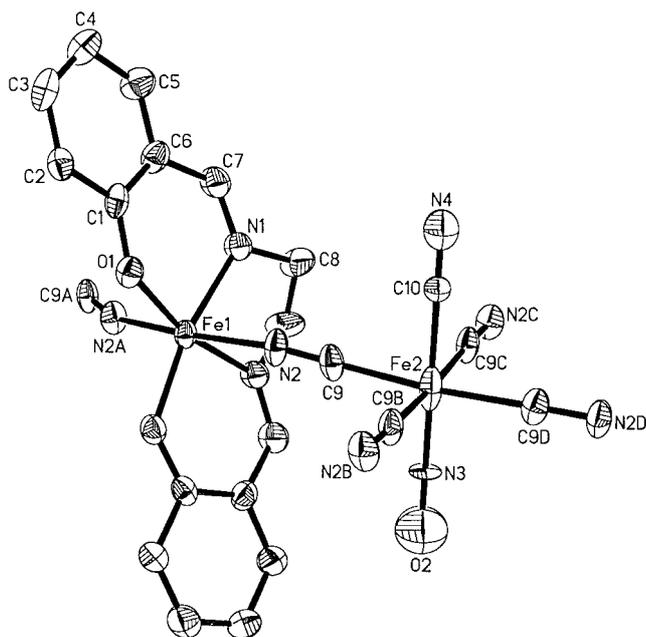
Fig. 1. An ORTEP drawing of the title complex; atom-numbering scheme shown.
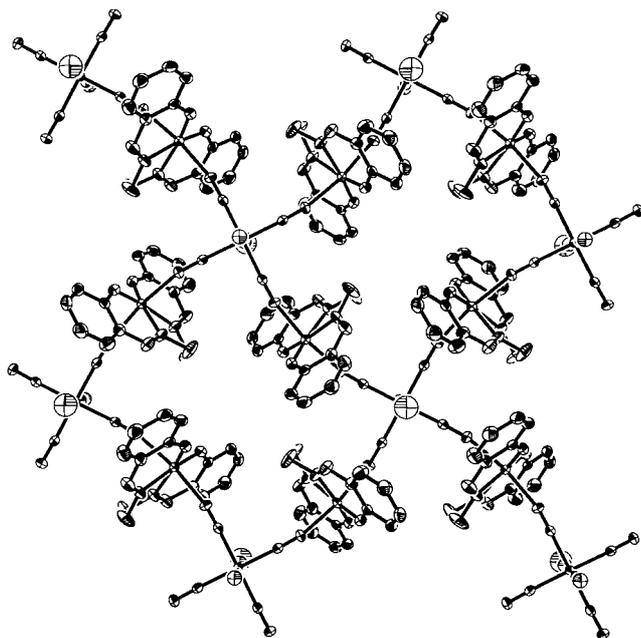

Fig. 2. Projection along the c-axis for the title complex, showing a 2D network structure, in which a net unit is composed of a pillow-like octamer [—Fe^{II}—CN—Fe^{III}—NC—]$_4$.

180.00°. The bond angles of Fe^{II}—C—N are 178.0(6)° for bridging CN$^-$ and 180.00° for terminal CN$^-$, both of which are nearly linear. The Fe^{II}—CN and C—N bond distances for bridging CN$^-$ are 1.942(7) and 1.139(9) Å, respectively; whereas those for the terminal CN$^-$ are 1.902(15) and 1.090(18) Å. The Fe^{II}—NO and N—O bond distances are 1.638(11) and 1.192(19) Å, respectively. All of these bond distances are comparable with those observed in other nitroprussides [12]. The greater electronegativity of the nitrosyl group with respect to
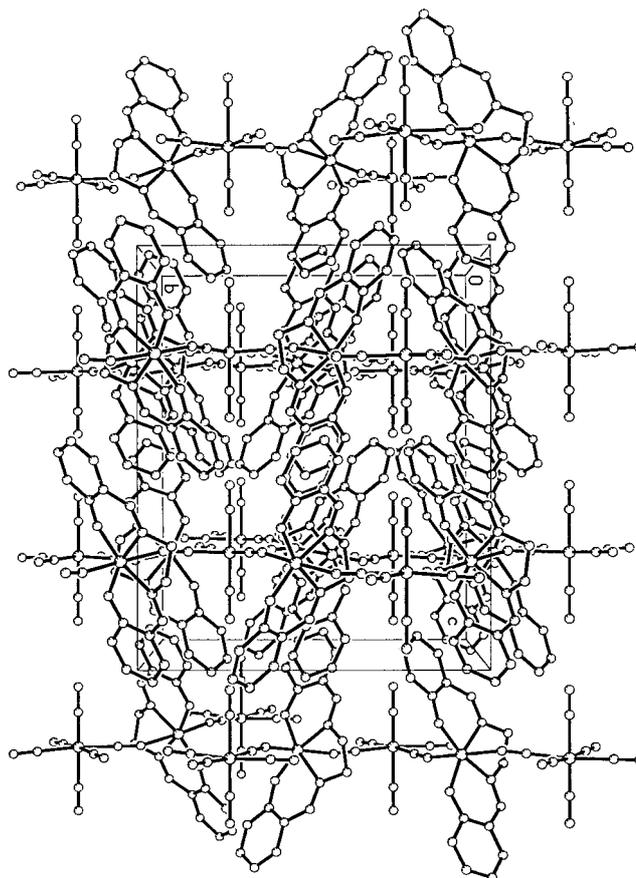

Fig. 3. Projection along the a-axis for the title complex, showing stacking of the layer structure.

Table 1. Selected bond lengths (Å) and angles (°) for the title complex estimated standard deviations in parentheses

Bond lengths

Fe(1)—O(1)	1.898(5)	Fe(1)—N(1)	2.109(6)
Fe(1)—N(2)	2.173(6)	Fe(2)—N(3)	1.638(11)
Fe(2)—C(10)	1.902(15)	Fe(2)—C(9)	1.942(7)
O(1)—C(1)	1.311(9)	O(2)—N(3)	1.192(19)
N(2)—C(9)	1.139(9)	N(4)—C(10)	1.090(18)

Bond angles

O(1)—Fe(1)—O(1)^a	106.6(3)	O(1)—Fe(1)—N(1)^a	164.8(2)
O(1)—Fe(1)—N(1)	88.6(2)	N(1)^a—Fe(1)—N(1)	76.3(3)
O(1)—Fe(1)—N(2)^a	90.8(2)	N(1)—Fe(1)—N(2)^a	85.4(2)
O(1)—Fe(1)—N(2)	94.3(2)	N(1)—Fe(1)—N(2)	87.8(2)
N(2)^a—Fe(1)—N(2)	171.4(3)	N(3)—Fe(2)—C(10)	180.000(2)
C(9)—Fe(2)—C(9)^b	174.8(5)	N(3)—Fe(2)—C(9)	92.6(3)
C(10)—Fe(2)—C(9)	87.4(3)	C(9)^c—Fe(2)—C(9)	89.88(2)
C(1)—O(1)—Fe(1)	130.8(4)	C(7)—N(1)—Fe(1)	124.4(5)
C(8)—N(1)—Fe(1)	115.4(5)	C(9)—N(2)—Fe(1)	163.4(6)
O(2)—N(3)—Fe(2)	180.000(1)	N(2)—C(9)—Fe(2)	178.0(6)
N(4)—C(10)—Fe(2)	180.000(2)		

Symmetry transformations used to generate equivalent atoms: ^{a} $y + 1/2$, $x − 1/2$, $−z + 1/2$; ^{b}$−x + 1/2$, $−y + 1/2$, z; ^{c}$−y + 1/2$, x, z; ^{d} y, $−x + 1/2$, z.

the cyanide groups causes deformation away from the nitrosyl end of the octahedral geometry. The C(9)—Fe^{II}—NO angles (92.6°) are greater than 90°, whereas the C(9)—Fe^{II}—C(10) angles (87.4°) are less than 90°, in agreement with the electronegativity calcu-

lations of Huheey ($NO^+ > CN^- > H_2O$) [13]. The Fe^{III} atom of the [Fe(salen)]$^+$ unit lies on the twofold axis, which crosses the middle of the $-CH_2-CH_2-$ bond. Two nitrogen atoms of the bridging CN ligands coordinate to the Fe^{III} center, thus constructing a slightly distorted octahedral coordination geometry about the Fe^{III} in which the two axial positions are occupied by two nitrogen atoms from CN^- groups with $Fe^{III}-N$ distances of 2.173(6) Å, and the equatorial sites are occupied by N_2O_2 donor atoms of the quadridentate Schiff-base ligand salen with $Fe^{III}-N$ and $Fe^{III}-O$ distances of 2.109(6) and 1.898(5) Å, respectively. The Fe^{III} ion is bound by two equally strong π-bonding CN^- groups, which is different from those observed in the 2D [M(salen-substituted)]$^+$/[Fe(CN)$_6$]$^{3-}$ adducts [6, 7, 14]. The $Fe^{III}-N-C$ (cyanide) angle of 163.4(6)° is the average of those angles observed in above adducts. As far as the salen ligand is concerned, its bonding parameters are similar to those found in related complexes reported previously.

As shown in Figures 2 and 3, the CN^- ligands bridge Fe^{II} and Fe^{III} centers to give a wave-like chain. The $Fe^{II}-Fe^{III}$ and $Fe^{III}-Fe^{III}$ separations within the chain are 5.194 and 10.377 Å, respectively. The shortest distance between two chains is 7.998 Å. The nearest intralayer and interlayer $Fe^{III}-Fe^{III}$ separations through space are 7.338 and 9.095 Å, respectively.

Magnetic properties

Plots of the magnetic susceptibility, χ_M, and the effective magnetic moment, μ_{eff}, *versus* temperature (T) are shown in Figure 4. The μ_{eff} per $Fe_2^{III}Fe^{II}$ unit at room temperature, 8.3 μ_B, is consistent with the spin-only value of 8.37 μ_B expected for the magnetically dilute system including two high spin Fe^{III} ions (S = 5/2) and one low spin Fe^{II} ion (S = 0), where the spin-only value was calculated by assuming g_{Fe} = 2.00. On lowering the temperature, the μ_{eff} value almost remains constant until 110 K, then decreases gradually in the 110–48 K range, and finally decreases sharply with further decreasing

Fig. 4. The temperature-dependence of magnetic susceptibility χ_M (■) and the effective magnetic moment μ_{eff} (○) for the title complex. The solid line represents the fit discussed in the text.

temperature to 6.96 μ_B at 4.8 K. The $1/\chi_M$ *versus* T plot obeys the Curie–Weiss law $\chi_M = C/(T - \theta)$ with a negative Weiss constant $\theta = -2.0$ K. These results indicate the existence of a weak antiferromagnetic interaction. As [Fe(CN)$_5$NO]$^{2-}$ is diamagnetic, the exchange interaction between Fe^{II} and Fe^{III} through the cyanide bridging ligand is negligible. On the basis of the crystal structure, two exchange pathways are available; one of which is the intralayer interaction between iron(III) ions through the diamagnetic [Fe(CN)$_5$NO]$^{2-}$ units and the other is the interlayer interaction through space. Considering that the shortest Fe^{III}–Fe^{III} separation between the layers (9.095 Å) is longer than that within each layer (7.338 Å), the intralayer interaction is dominant and the interlayer interaction is negligible. Thus, the data were modeled in a similar way to that reported previously [15]. The susceptibility can be approximated by Equations (1)–(4).

$$\chi_t = 2Ng^2\beta^2 A/3kT B \qquad (1)$$

where

$$A = 330\exp(30J_t/kT) + 180\exp(20J_t/kT) + 84$$
$$\times \exp(12J_t/kT) + 30\exp(6J_t/kT) + 6\exp(2J_t/kT)$$
$$B = 11\exp(30J_t/kT) + 9\exp(20J_t/kT) + 7$$
$$\times \exp(12J_t/kT) + 5\exp(6J_t/kT) + 3\exp(2J_t/kT) + 1$$

$$\chi_t = Ng^2\beta^2 S_t(S_t + 1)/3kT \qquad (2)$$

$$\chi_{chain} = Ng^2\beta^2(1 + u)S_t(S_t + 1)/3kT(1 - u) \qquad (3)$$

where

$$u = \coth[J_c S_t(S_t + 1)/kT] - kT/J_c S_t(S_t + 1)$$

$$\chi_M = \chi_{chain}/[1 - \chi_{chain}(2zJ'/Ng^2\beta^2)] \qquad (4)$$

where $z = 2$, J_t, J_c and J' stand for the exchange integrals between two S_{Fe} (S = 5/2) spins within the $Fe^{III}Fe^{II}$ trimer, between the S_t effective spins of trimers and between the chains, respectively, and were treated as equivalent. The symbols N, g, β and k have their usual meanings. By allowing the g and J values to vary, we obtained the best fit to the experimental data with parameters $J_t = J_c = J' = -0.033$ cm^{-1}, $g = 2.03$ and the disagreement factor $R = 1.5 \times 10^{-4}$ [$R = \Sigma(\chi_{obs} - \chi_{calc})^2/\chi_{obs}^2$]. As shown in Figure 4, the fit may be considered to be fairly good. The results ($J_t = J_c = J' < 0$) show the presence of a weak antiferromagnetic interaction between the nearest Fe^{III} ions within each sheet through the $-NC-Fe^{II}-CN-$ bridges. It is observed that two paramagnetic centers usually give rise to antiferromagnetic interaction when bridged by the [Fe(CN)$_5$NO]$^{2-}$ group [12a–d], but ferromagnetic interaction occured when bridged by the [Fe(CN)$_6$]$^{4-}$ group [16]. It is interesting to note that the intervening diamagnetic iron(II) ions can lead to two different ways
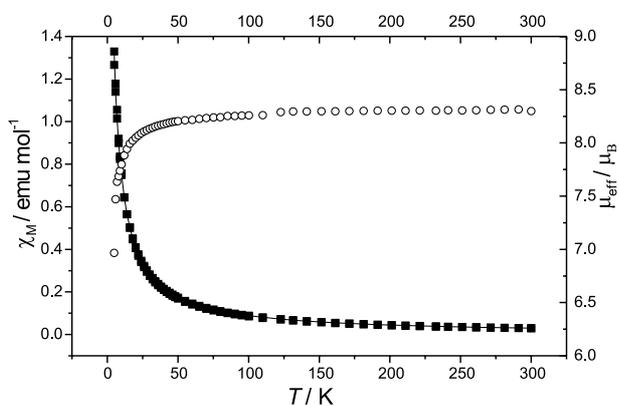
of coupling depending on the specific iron (II) complex ions, $[Fe(CN)_5NO]^{2-}$ or $[Fe(CN)_6]^{4-}$. Regarding the $[Fe(CN)_6]^{4-}$ ion, a σ-superexchange pathway has been proposed [16a], which can account for the ferromagnetic coupling between paramagnetic centers. However, to our knowledge, the antiferromagnetic mechanism for $[Fe(CN)_5NO]^{2-}$ is still unclear. The NO^+ group of $[Fe(CN)_5NO]^{2-}$ may be relevant to the antiferromagnetic coupling, a further study must be done in this context.

Acknowledgement

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