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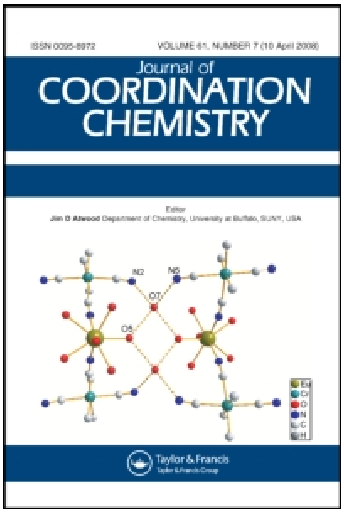

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Cyanide-bridged Fe^{III}-Mn^{III} bimetallic chain derived from $[Fe(bipy)(CN)_4]^-$: synthesis, structure and magnetic characteristics

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Cyanide-bridged Fe^{III}–Mn^{III} bimetallic chain derived from $[Fe(bipy)(CN)_4]^-$: synthesis, structure and magnetic characteristics

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A chain-like compound of $[Mn(salpn)][Fe(bipy)(CN)_4]$ (**1**) (salpn = *N*,*N'*-propylenebis(salicylideneiminato)dianion; bipy = 2,2'-bipyridine), assembled from building blocks of $[Fe(bipy)(CN)_4]^-$ and $[Mn(salpn)]^+$, has been characterized by elemental analyses, ICP, IR, thermoanalysis, single crystal X-ray structure analysis and magnetic measurements. In **1**, each $[Fe(bipy)(CN)_4]^-$ anion coordinates with two $[Mn^{III}(salpn)]^+$ cations via two *trans*-CN^- groups, and each $[Mn^{III}(salpn)]^+$ cation is axially coordinated by two $[Fe(bipy)(CN)_4]^-$ ions, resulting in a straight 1-D chain. The chains stack *via* aromatic π–π-type interactions. Magnetic studies reveal the presence of weak antiferromagnetic interactions between adjacent Fe^{III} and Mn^{III} ions through cyanide-bridges.

Keywords: Cyanide-bridged; Crystal structure; Magnetic properties; Iron; Manganese

1. Introduction

Cyanide-bridged complexes have remarkable magnetic, magneto-optical, and electrochemical properties [1–6]. Many cyanide-based molecular materials have been prepared by using quite stable hexacyanometallate complexes $[M(CN)_6]^{(6-m)-}$ as ligands. Highly insoluble 3-D Prussian blue analogues are prepared by reaction of such precursor with fully solvated metal ions $[M'(H_2O)_6]^{p+}$, and their properties closely depend on the nature of the metal ions and counterions [7–10]. Lower dimensional compounds with very different topologies and structures can be obtained if the outer metal ions are partially blocked with polydentate ligands $[M'(L)]^{m+}$ [11, 12]. Recently, as a new strategy, the employment of capped molecular entities $[ML_p(CN)_q]^{n-}$ (L = polydentate ligand) instead of $[M(CN)_6]^{n-}$ as building blocks has been studied by several research groups [13–17]. This strategy has afforded a rich family of compounds whose diversity of structures and properties can be controlled to some extent by choice of metal ions

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and blocking ligands. A few bimetallic assemblies in this new family with interesting magnetic properties such as SMM and SCM have been reported [18–21]. With enhanced Jahn-Teller effects and magnetic anisotropy, Mn^{III}-Schiff bases are good precursors in constructing cyanide-bridged magnetic materials [22–26]. As part of our continuous efforts to develop new cyano-bridged heterobimetallic magnetic complexes, we now use tailored cyanometalate precursors to construct low-dimensional, cyano-bridged systems. In this article, we present a new cyanide-bridged chain complex $[Mn(salpn)][Fe(bipy)(CN)_4]$ (**1**) derived from $[Fe(bipy)(CN)_4]^-$ and $[Mn(salpn)]^+$ (bipy = 2,2′-bipyridine; salpn = *N*,*N*′-propylenebis(salicylideneiminato)dianion); the magnetic and thermal properties of **1** were investigated.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 C microanalysis instrument (USA). Mn and Fe analyses were made on a Jarrell–Ash 1100 + 2000 inductively coupled plasma quantometer. IR spectra were recorded on a Nicolet FT-170SX spectrometer with KBr pellets in the 4000–400 cm^{-1} region. The thermoanalysis was measured by a NETZSCH STA449C differential scanning calorimeter. Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer and corrected for diamagnetism estimated as -368×10^{-6} emu mol^{-1} from Pascal's constants. Effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$, where χ_M is the paramagnetic susceptibility after correction for diamagnetism per formula unit.

2.2. *Preparations*

All chemicals and solvents were reagent grade and used without purification. The precursors $PPh_4[Fe^{III}(bipy)(CN)_4]\cdot H_2O$ [27] and $[Mn^{III}(salpn)]ClO_4\cdot 2H_2O$ [28, 29] were synthesized according to methods reported previously.

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care.

$[Mn(salpn)][Fe(bipy)(CN)_4]$ (1). A solution of $[Mn^{III}(salpn)]ClO_4\cdot 2H_2O$ (0.1 mmol) in methanol (10 mL) was added to a solution of $PPh_4[Fe(bipy)(CN)_4]\cdot H_2O$ (0.1 mmol) in acetonitrile (10 mL). The resulting solution was filtered and the filtrate slowly evaporated in the dark at room temperature. Black crystals of **1** were obtained after two days, washed with MeOH and H_2O, and dried in air. Anal. Calcd for $C_{31}H_{24}FeMnN_8O_2$ (%): C, 57.16; H, 3.71; N, 17.20; Fe, 8.57; Mn, 8.43. Found: C, 57.32; H, 3.78; N, 17.44; Fe, 8.45; Mn, 8.31. IR: $\nu_{C\equiv N}$(cyanide): 2139, 2118 cm^{-1}.

2.3. *X-ray crystallography*

Diffraction data were collected at 291(2) K on a Bruker SMART APEX CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with φ and ω scan mode. Empirical absorption corrections were made with SADABS. The structure was solved by direct methods and refined by full matrix least-squares techniques based on F^2. All nonhydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogens were located by using a riding model. All computations were carried out using the SHELXTL-PC program package.

Crystal data for **1**: $C_{31}H_{24}FeMnN_8O_2$, $M = 651.37$, monoclinic, space group P2(1)/c (No. 14), $a = 9.292(9)$, $b = 21.07(2)$, $c = 15.04(2)$ Å, $\beta = 97.74(2)^\circ$, $U = 2918(5)$ Å^3, $Z = 4$, $D_c = 1.483\,\mathrm{g\,cm^{-3}}$, $F(000) = 1332$, $\mu = 0.973\,\mathrm{mm^{-1}}$ and $S = 1.06$. 22217 reflections measured, 5710 unique ($R_{\mathrm{int}} = 0.067$). The final $R_1 = 0.0501$ and $wR_2 = 0.0848$ for 3854 observed reflections [$I > 2\sigma(I)$] and 389 parameters.

3. Results and discussion

3.1. *Crystal structure*

The structure of **1** is shown in figures 1 and 2. Selected bond distances and angles are listed in table 1. The structure of **1** consists of one $[Fe(bipy)(CN)_4]^-$ anion and one $[Mn^{III}(salpn)]^+$ cation (figure 1a). Each $[Fe(bipy)(CN)_4]^-$ anion coordinates with two $[Mn^{III}(salpn)]^+$ cations via two *trans*-CN^- groups, while two *cis*-CN^- groups act as end ligands, and each $[Mn^{III}(salpn)]^+$ cation is axially coordinated by two $[Fe(bipy)(CN)_4]^-$ ions. $[Fe(bipy)(CN)_4]^-$ and $[Mn(salpn)]^+$ alternately linked by the cyanide-bridges produce a straight neutral Fe–Mn bimetallic chain (figure 1b). The Mn^{III} is a distorted octahedral, in which the equatorial sites are occupied by N_2O_2 donors of the quadridentate Schiff-base with Mn–N/O bond distances of 1.885–1.992 Å, while the axial positions are occupied by two nitrogens from bridging CN^- groups with Mn–N_{ax} distances of 2.254 and 2.309 Å. The axial elongation is from the well-known Jahn-Teller effect on an octahedral high-spin Mn^{III}. The Mn–N$\equiv$C bond angles deviate significantly from linearity with angles Mn(1)–N(5)–C(28) = 161.4(2) and Mn(1B)–N(6)–C(29) = 171.1(2)°. $[Fe(bipy)(CN)_4]^-$ exhibits a distorted octahedral structure consisting of two nitrogens from a planar bipy and four carbons from CN^-. The Fe–C$\equiv$N angles for both terminal [176.5(3) and 178.2(3)°] and bridging [175.0(3) and 176.7(3)°] CN^- deviate somewhat from linearity. The bond distances of Fe–C [1.918(4) and 1.922(4) Å] and C–N [1.175(4) and 1.177(4) Å] for the bridging CN^- are slightly longer than those for the terminal CN^- [1.915(3) and 1.901(4) Å for Fe–C and 1.150(4) and 1.167(4) Å for C–N distances]. Values of Fe–N(bipy) bond distances [1.983(3) and 1.982(3) Å] and the angle subtended by the chelating bipy [80.9(1)° at N(3)–Fe(1)–N(4)] are practically the same as those observed in $PPh_4[Fe(bipy)(CN)_4]$ and $[\{Fe^{III}(bipy)(CN)_4\}_2M^{II}(H_2O)_4]\cdot 4H_2O$ (M = Mn or Zn) [27]. Bonding parameters of the salen are close to those found in related complexes [25, 26].

The intrachain Fe···Mn distances through CN^- bridges are 5.331 and 5.319 Å, somewhat in agreement with that of the Fe–Mn system with mpzcq and pzcq [30, 31]. The nearest interchain Fe···Mn, Mn···Mn and Fe···Fe distances are 7.927, 8.023 and 7.768 Å. Packing of bimetallic chains is often dominated by aromatic π–π stacking interactions in the case of the presence of large aromatic ligands [26]. The chains in **1** run along the *c* direction and form layers parallel to the *ab* plane. In the layer each chain interacts with two adjacent chains via face-to-face π–π stacking between the benzene rings of the salpn of $[Mn(salpn)]^+$ units (figure 2a). The plane-to-plane distance is

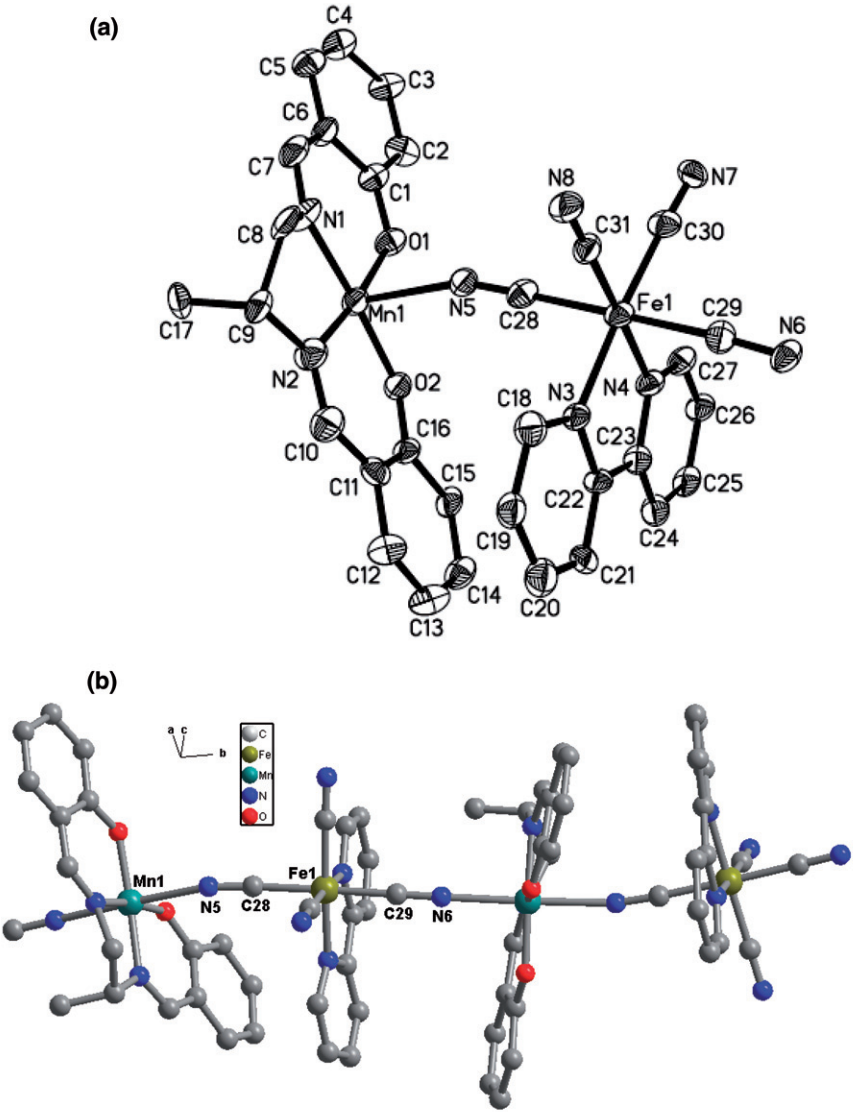

Figure 1. Molecular views of **1** showing (a) the atom-labeling scheme and (b) bimetallic chain structure.

3.87 Å and the dihedral angle is 5.7°. Adjacent chains are also held together by weak H-bonds between terminal cyanides of $[Fe(bipy)(CN)_4]^-$ units in one chain and C–H donors of bipy in neighboring chains. The 3D structure is formed by the layers stacking along *c*-axis direction mainly via van der Waals interactions (figure 2b).

3.2. *Thermal analysis*

Thermoanalysis was performed in nitrogen with a heating rate of 10°C min^{-1}. The TG-DSC curve of **1** is provided in Supplemental Material. The complex is stable until *ca* 186°C. After that, the complex decomposes with a series of continuous weight loss processes. The weight loss of 43.23% from 186°C to 405°C is consistent with loss of

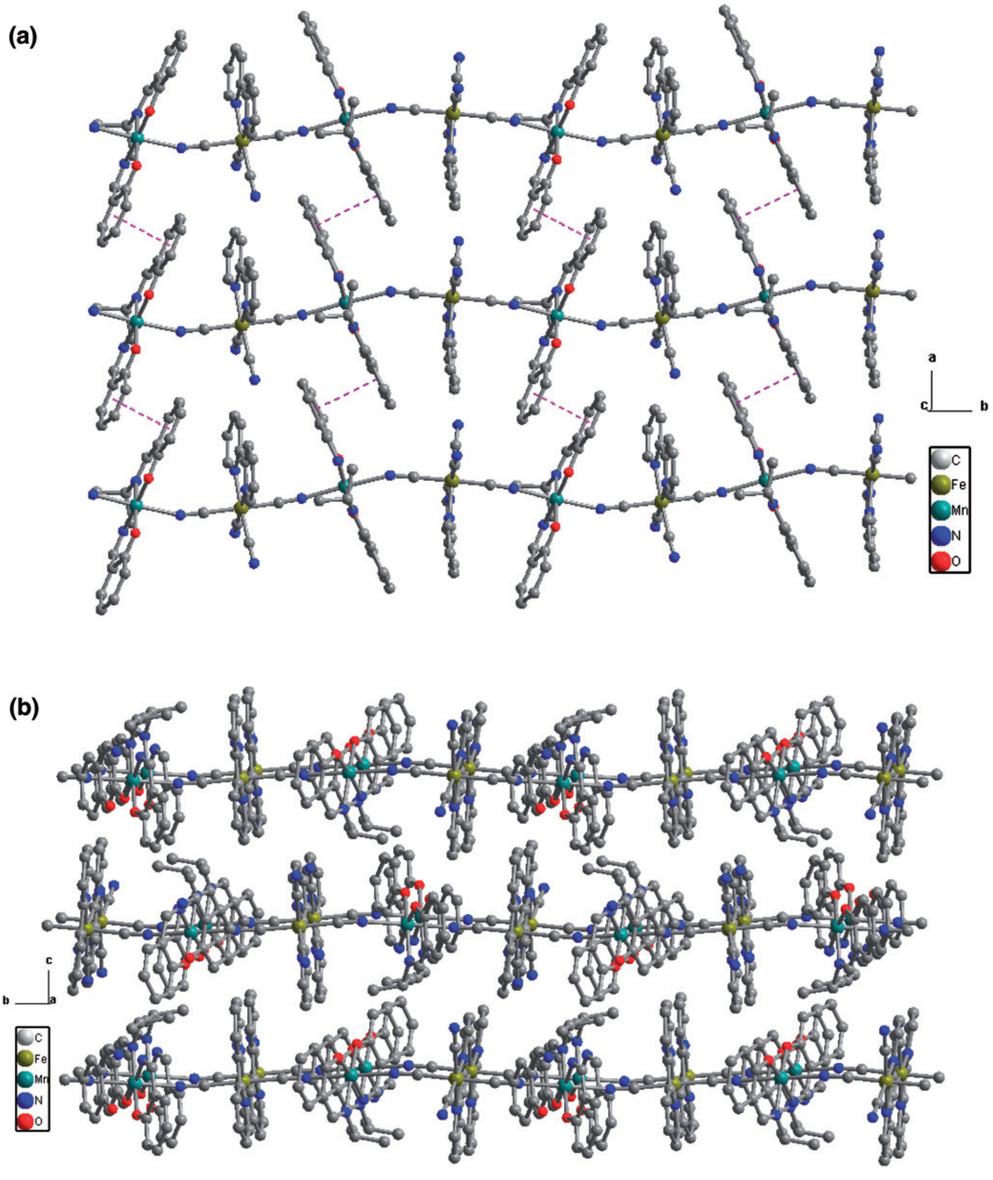

Figure 2. (a) Projection of **1** along the *c*-axis, showing the layer structure. (b) Packing diagram viewed from the *a*-axis.

salen (Calcd 43.04%). The weight loss of 24.03% from 405°C to 804°C might be due to the loss of bipy (Calcd 23.98%). With further heating, the decomposition continues with accompanying further weight loss.

3.3. *Magnetic properties*

Magnetic susceptibilities of **1** were measured with an applied field of 2 kOe from 1.8 to 300 K. Plots of $\chi_M T$ *versus* T and $1/\chi_M$ *versus* T are given in figure 3. At room

Table 1. Selected bond distances (Å) and bond angles (°) for **1**.

Fe1–N3	1.982(3)	Mn1–N1	1.992(3)
Fe1–N4	1.983(3)	Mn1–N2	1.998(3)
Fe1–C28	1.918(4)	Mn1–N5	2.309(3)
Fe1–C29	1.922(4)	Mn1–N6a	2.254(3)
Fe1–C30	1.915(3)	N5–C28	1.177(4)
Fe1–C31	1.901(4)	N6–C29	1.175(4)
Mn1–O1	1.885(3)	N7–C30	1.150(4)
Mn1–O2	1.862(3)	N8–C31	1.167(4)
N4–Fe1–N3	80.92(10)	O1–Mn1–O2	96.98(9)
N4–Fe1–C28	91.69(11)	O1–Mn1–N1	90.65(10)
N4–Fe1–C29	89.07(11)	O1–Mn1–N2	170.63(10)
N4–Fe1–C30	95.31(12)	O1–Mn1–N6a	90.86(10)
N4–Fe1–C31	176.44(12)	O2–Mn1–N1	172.25(11)
N3–Fe1–C28	90.56(11)	O2–Mn1–N2	92.10(11)
N3–Fe1–C29	88.59(11)	O2–Mn1–N5	87.38(10)
N3–Fe1–C30	175.76(12)	O2–Mn1–N6a	90.71(10)
N3–Fe1–C31	95.85(11)	N1–Mn1–N2	80.23(12)
C28–Fe1–C29	178.76(13)	N1–Mn1–N5	91.24(11)
C28–Fe1–C30	91.48(14)	N1–Mn1–N6a	90.50(11)
C28–Fe1–C31	89.83(13)	N2–Mn1–N5	87.54(11)
C29–Fe1–C31	89.36(13)	N2–Mn1–N6a	91.35(11)
C30–Fe1–C31	87.87(13)	N5–Mn1–N6a	177.75(10)
Mn1–N5–C28	161.4(2)	Fe1–C29–N6	175.0(3)
Mn1b–N6–C29	171.1(2)	Fe1–C30–N7	176.5(3)
Fe1–C28–N5	176.7(3)	Fe1–C31–N8	178.2(3)

Symmetry transformations used to generate equivalent atoms: a = 1 − x, −1/2 + y, 3/2 − z; b = 1 − x, 1/2 + y, 3/2 − z.

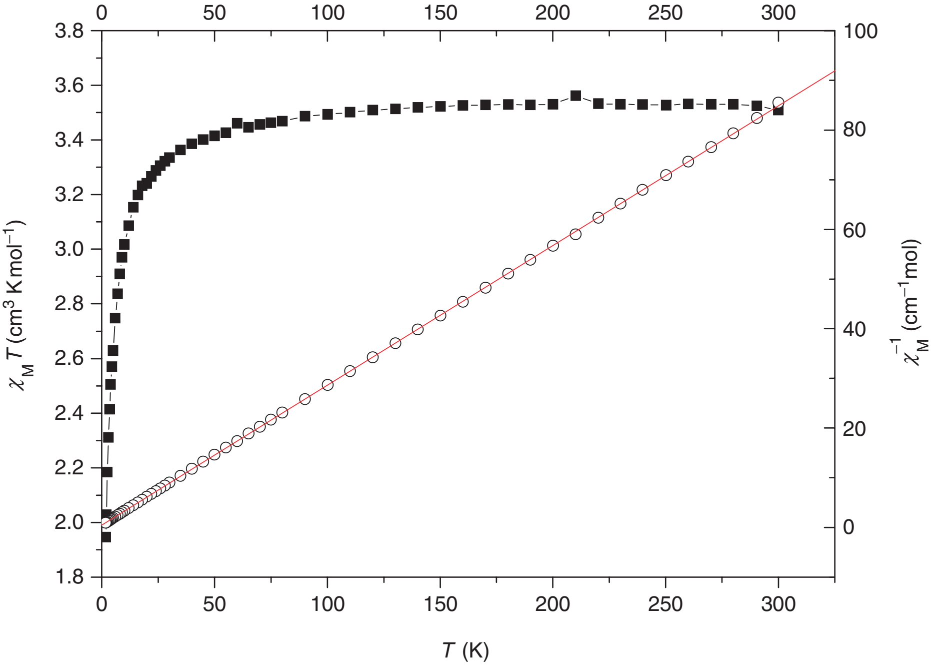

Figure 3. Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) for **1** measured at 2 kOe. The solid line represents the fit obtained by the Curie–Weiss law.

temperature, the $\chi_M T$ per MnFe unit is 3.51 emu K mol^{-1} (5.30μ_B), consistent with the spin-only value of 3.38 emu K mol^{-1} (5.2μ_B) expected for an uncoupled spin system (one $S_{Fe} = 1/2$, one $S_{Mn} = 2$) with $g = 2.0$. On lowering the temperature, the $\chi_M T$ value is most constant until 60 K, then gradually decreases to 3.20 emu K mol^{-1} (5.06μ_B) at 16 K and finally sharply decreases to 1.95 emu K mol^{-1} (3.95μ_B) at 1.8 K. The plot of $1/\chi_M$ *versus* T obeys the Curie–Weiss law with a negative Weiss constant $\theta = -1.8$ K. These results indicate the presence of a weak antiferromagnetic interaction in **1**, attributed to antiferromagnetic coupling between Fe^{III} and Mn^{III} through cyanide bridges. The antiferromagnetic interaction between the Mn^{III} ($S = 2$) and Fe^{III} ($S = 1/2$) can be rationalized in terms of the overlap of the magnetic orbitals of these ions [12]. In addition, the possibility cannot be excluded that there exists a very weak interchain antiferromagnetic interaction in **1** [26].

4. Conclusion

A new chain-like cyano-bridged bimetallic assembly, [Mn(salpn)][Fe(bipy)(CN)$_4$], has been synthesized and characterized structurally and magnetically. In this complex, each [Fe(bipy)(CN)$_4$]$^-$ unit connects two [Mn(salen)]$^+$ units with two *trans*-cyanide groups, while each [Mn(salen)]$^+$ unit is linked to two [Fe(bipy)(CN)$_4$]$^-$ ions in *trans*-positions, resulting in a straight 1-D chain. The chains stack via aromatic π–π-type interactions. Magnetic studies show a weak antiferromagnetic interaction between the adjacent Fe^{III} and Mn^{III} ions through cyanide-bridges. The present example further demonstrates [Fe(bipy)(CN)$_4$]$^-$ as an effective building block in constructing cyano-bridged, low-dimensional systems; new bimetallic systems with other transition metals are in progress.

Supplementary material

CCDC 711526 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

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