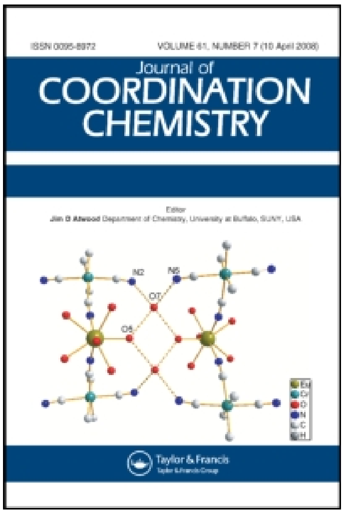

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# Synthesis, Crystal Structure and Magnetic Properties of a Two-Dimensional Heterometallic Assembly |[Mn(salen)]|$_2$|[Ni(CN)$_4$|·1/2H$_2$O

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# SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A TWO-DIMENSIONAL HETEROMETALLIC ASSEMBLY $[Mn(SALEN)]_2[Ni(CN)_4]\cdot 1/2H_2O$

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A heterometallic assembly, $[Mn(salen)]_2[Ni(CN)_4]\cdot 1/2H_2O$ (where salen = N, N′-ethylenebis(salicylideneiminato)-dianion), has been prepared from the reaction of $[Mn(salen)H_2O]ClO_4\cdot H_2O$ with $K_2[Ni(CN)_4]\cdot H_2O$ in methanol/water. The compound crystallizes in the tetragonal space group P 4/ncc with the cell dimensions of $a = 14.604(2)$ Å, $c = 16.949(3)$ Å, and Z = 4. The compound assumes a two-dimensional distorted square network structure, formed from Ni—CN—Mn(salen)—NC—Ni linkages with dimensions of Ni—C = 1.867(7) Å, Mn—N = 2.312(6) Å, Mn—N—C = 163.8(6)° Ni—C—N = 178.4(6)°. The two metal atoms Ni(II) and Mn(III) have square and slightly distorted octahedral arrangements, respectively. Magnetic susceptibility measurements indicate the presence of an intramolecular antiferromagnetic interaction and gives a Mn—Mn exchange integral of $-3.2\,\mathrm{cm}^{-1}$.

*Keywords*: Nickel complex; Manganese complex; Cyano bridge; Crystal structure; Magnetic properties

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## INTRODUCTION

The molecular design of extended structures starting from molecular precursors is an area of intense interest [1, 2]. The use of ionic building blocks, for example, in which one unit contains a potential bridging ligand and another contains a potential coordination site, can result in such molecular species. Extended bimetallic arrays assembled from hexacyanometallate and metal ions bonded to polydentate ligands, have recently received particular attention [3–5]. These assemblies assume 1-D, 2-D and 3-D structures and exhibit ferro- or meta-magnetic behavior. For instance, the reaction between $[Mn(BS)]^+$ [BS = salen-substituted ligand; salen = N, N′-ethylene-bis(salicylideneiminato)-dianion] and $[Fe(CN)_6]^{3-}$ led to a variety of extended structures depending on the nature of the Schiff base, the countercation and the reaction solvent, *e.g.*, a 1-D chain complex $[NEt_4]_2\{Mn(acacen)\}[Fe(CN)_6]$ [6], 2-D network complexes $K\{Mn(3\text{-}MeOsalen)\}_2[Fe(CN)_6]$ [7] and $[\{Mn(saltmen)\}_4\{Fe(CN)_6\}]ClO_4 \cdot H_2O$ [7] have been synthesized and characterized in detail; these complexes invariably exhibit a ferromagnetic interaction between the adjacent manganese(III) and iron (III) ions through the cyano bridge. It has been found that the number of *d*-electrons in the central metal ions and the structure of the complex ions plays a very important role in the magnetic properties. To clarify the relationship between the number of *d*-electrons of central metal, the molecular structure and magnetic property of double complexes with the $[Mn(salen)]^+$ cation, we have synthesized the title complex $[Mn(salen)]_2[Ni(CN)_4] \cdot 1/2H_2O$ from $[Mn(salen)\,H_2O]^+$ and $[Ni(CN)_4]^{2-}$, and studied its structure and magnetic properties.

## EXPERIMENTAL

### Measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C microanalysis instrument. Manganese and nickel analyses were made on a Jarrell-Ash 1100 + 2000 inductively coupled plasma quantometer. Infrared spectra were measured on KBr disks with a Nicolet FT-170SX spectrometer. Magnetic susceptibilities were measured with a MPMS-5 SQUID susceptometer under on applied magnetic field of 10000 Oe in the 5–299K temperature range. Diamagnetic corrections were made using Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_M \times T)^{1/2}$, where $\chi_M$ is the magnetic susceptibility per formula unit.

## Preparation

### *General Procedures and Materials*

All chemicals and solvents used for the synthesis were reagent grade. The quadridentate Schiff-base ligand $SalenH_2$ was prepared by mixing salicylaldehyde and ethylenediamine in a 2 : 1 molar ratio in methanol according to the literature [8, 9], $[Mn(salen)\ H_2O]\ ClO_4 \cdot H_2O$ was prepared by mixing $Mn(OAc)_3 \cdot 2H_2O$, $SalenH_2$ and $NaClO_4$ in a molar ratio of 1 : 1 : 1.5 in methanol according to the method reported previously [10].

### *Preparation of $[Mn(Salen)]_2[Ni(CN)_4] \cdot 1/2H_2O$*

A solution of $[Mn(salen)H_2O]\ ClO_4 \cdot H_2O$ (0.456 g, 1 mmol) in a mixture of methanol (30 mL) and DMF (5 mL) was added to a solution of $K_2[Ni(CN)_4] \cdot H_2O$ (0.13 g, 0.5 mmol) in water (10 mL) at room temperature. The resulting solution was filtered and the filtrate was kept a week in the dark. The resulting black pillar crystals were collected by filtration, washed with methanol and dried in air. Anal. Calcd for $C_{36}H_{29}Mn_2NiN_8O_{4.5}$ (%): C, 53.10; H, 3.59; N, 13.76; Ni, 7.21; Mn, 13.49. Found: C, 52.43; H, 3.55; N, 13.32; Ni, 7.38; Mn, 13.60. IR ($cm^{-1}$): $\nu_{C=N}$(imine):l600(s), 1634.6(*vs*); $\nu_{C\equiv N}$(cyanide): 2128.7(m).

## X-ray Data Collection, Reduction and Structure Determination

A crystal of the title complex with dimensions of 0.575 × 0.25 × 0.225 mm was stuck to the end of a glass fiber and then mounted on an Enraf -Nonius CAD4 diffractometer to perform X-ray diffraction using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined and refined by a least-squares treatment of the setting angles of 25 automatically centered reflections ($12.94 < \theta < 13.89$). The intensity data were collected by using $\omega$ -$2\theta$ scan mode in the range of $2^\circ < \theta < 26^\circ$. There was no evidence of crystal decay from three standard reflections monitored every two hours throughout the data collection. The total 3365 reflections measured were corrected for Lp effects and the absorption using $\Psi$ scan technique ($T_{max}$ and $T_{min}$ are 1.0000 and 0.9327, respectively), 1741 unique data were obtained, of which 1262 reflections with intensities $I \geq 2\ \sigma$ (I) were

TABLE I Crystallographic data for $[Mn(Salen)]_2[Ni(CN)_4] \cdot 1/2H_2O$*

| | | | |
|---|---|---|---|
| Formula | $C_{36}H_{29}Mn_2NiN_8O_{4.5}$ | V(Å$^3$) | 3614.9(10) |
| Formula weight | 814.26 | z | 4 |
| Crystal system | Tetragonal | $D_c$ (g·cm$^{-3}$) | 1.496 |
| Space group | P4/ncc | μ(cm$^{-1}$) | 12.55 |
| a(Å) | 14.604(2) | F(000) | 1660 |
| b(Å) | 14.604(2) | $R_{int}$ | 0.0555 |
| c(Å) | 16.949(3) | $R_1$ | 0.0748 |
| GOF | 1.138 | $_{w}R_2$ | 0.1861 |

* $R_1 = \sum||F_0| - |F_C||/\sum|F_0|$, $wR_2 = \sum w(F_0^2 - F_C{}^2)^2/\sum[w(F_0^2)^2]^{1/2}$, $w = [\sigma^2(F_0^2) + (0.0783P)^2 + 14.8468P]^{-1}$, where $P = (F_0^2 + 2F_C{}^2)/3$ $GOF = [\sum w(|F_0| - |F_C|)^2/(N_{obs} - N_{param})]^{1/2}$.

used in the structure solution and refinement. The structure was solved by direct methods and subsequent Fourier difference syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogen atoms were located by using a riding model. The scattering contributions of the hydrogen atoms were added to the structure factor calculations but their positions were not refined. Full matrix least-squares refinement was based on $F^2$. The number of refined parameters is 120. The final agreement factors were $R_1 = 0.0748$, $wR_2 = 0.1861$, $(\Delta/\sigma)_{max}$ on the final cycle was 0.00. The maximum and minimum residual densities on the final difference Fourier map were 0.682 and $-0.843$ e/Å$^3$, respectively. All the calculations were carried out on a microcomputer PIII-450 with the SHELXTL97 program [11]. A summary of the pertinent crystallographic data and the main results are listed in Table I.

## RESULTS AND DISCUSSION

### Crystal Structure

The ORTEP diagrams of the title complex with the atom numbering scheme is shown in Figure 1. The packing diagram projected 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 II. The molecular structure consists of one $Ni(CN)_4{}^{2-}$ anion, two $Mn(Salen)^+$ cations and one crystal water molecule. The anion and cation are linked by Ni—CN—Mn assemblies to form a two dimensional distorted square network packing structure in the {ab} plane (see Fig. 2). The Ni atom is located on the four-fold axis and coordinated by four equivalent $CN^-$ ligands with Ni—C bond lengths of 1.867(7) Å and Ni—C—N angles of 178.4(6)°. The Mn atom lies on the two-fold axis, which

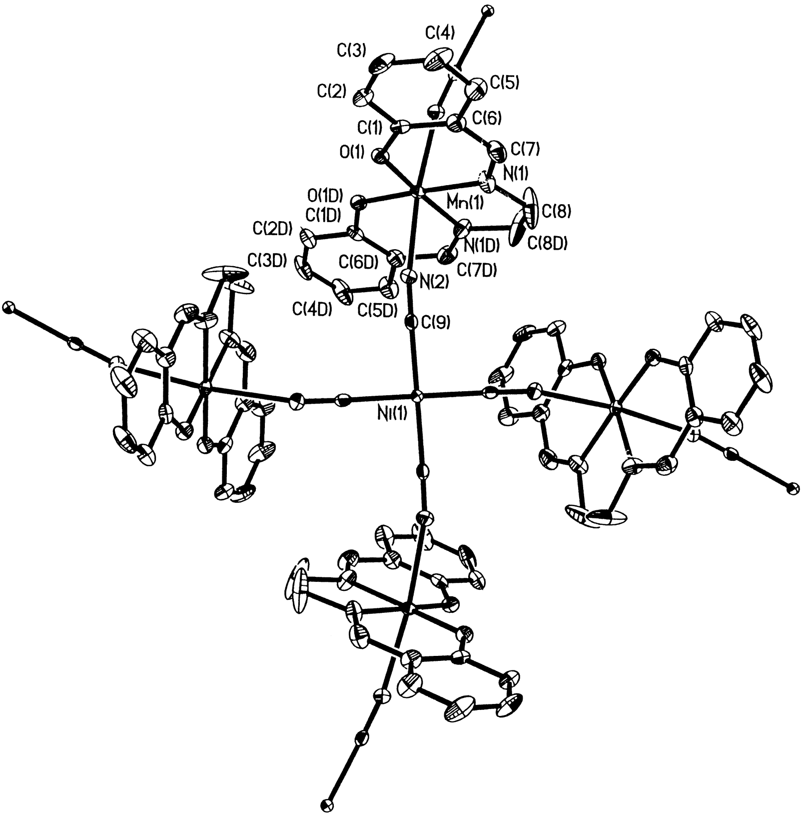

FIGURE 1 ORTEP drawing of the title complex with the atom-numbering scheme.

also crosses in the middle of —CH$_2$—CH$_2$— bond. Two CN$^-$ ligands coordinate to a Mn center by N atoms, thus constructing a slightly distorted octahedral coordination geometry for Mn in which the equatorial sites are occupied by N$_2$O$_2$ donor atoms of the quadridentate Schiff-base ligand salen and the two axial positions are occupied by two nitrogen atoms from CN$^-$ groups. The Mn ion is bound by two equally strong $\pi$-bonding CN$^-$ groups, which is different from those observed in the 2D [Mn(salen-substituted)]$^+$/[Fe(CN)$_6$]$^{3-}$ adducts [7, 12]. The Mn—N(CN) distance of 2.312(6) Å and the Mn—N—C angle of 163.8(6)° are averages of those observed in above adducts. The Mn—Ni and Mn—Mn separations along the Ni—CN—Mn linkage are 5.278 and 10.556 Å, respectively. The bonding parameters of the salen ligand with Mn are similar to those found in related complexes reported previously.

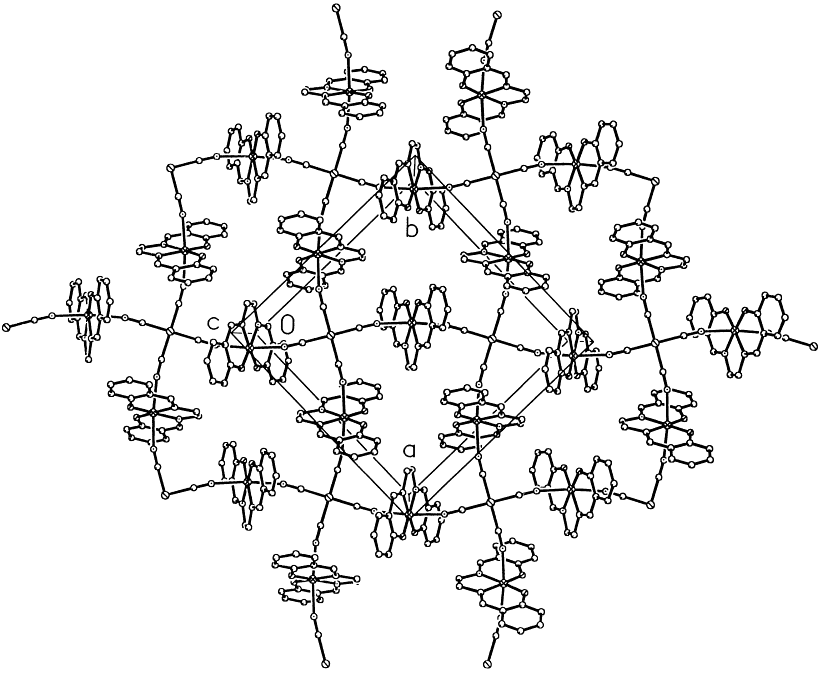

FIGURE 2 Projection along the *c*-axis for the title complex, showing a two-dimensional network structure.

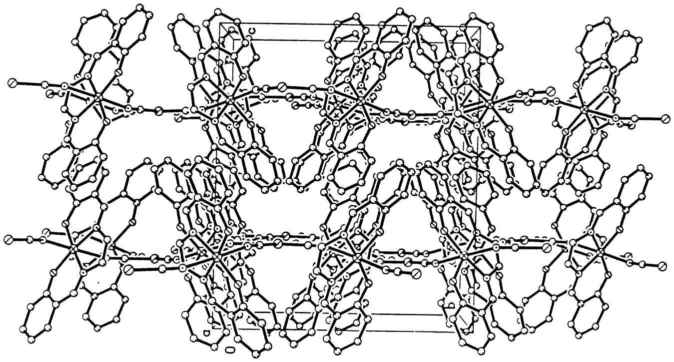

FIGURE 3 Projection along the *a*-axis for the title complex, showing a stacking of the layer structure.

As already mentioned, all the $CN^-$ ligands bridge Ni and Mn centers to give a wave-like chain (see Figs. 2 and 3). The distance between two chains is 8.747 Å. The nearest intralayer and interlayer Mn—Mn separations through

TABLE II Selected bond lengths (Å) and angles (°) for the title complex, with the estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ni(1)—C(9) | 1.867 (7) | Mn(1)—N(2) | 2.312 (6) |
| Mn(1)—O(1) | 1.892 (5) | Mn(1)—N(1) | 1.983 (6) |
| O(1)—C(1) | 1.312 (8) | N(1)—C(7) | 1.263 (9) |
| N(1)—C(8) | 1.474 (11) | N(2)—C(9) | 1.158 (9) |
| C(1)—C(6) | 1.389 (11) | C(1)—C(2) | 1.406 (10) |
| C(2)—C(3) | 1.374 (11) | C(3)—C(4) | 1.359 (15) |
| C(4)—C(5) | 1.360 (13) | C(5)—C(6) | 1.402 (10) |
| C(6)—C(7) | 1.436 (11) | C(8)—C(8)$^{\#3}$ | 1.277 (18) |
| C(9)$^{\#1}$—Ni(1)—C(9) | 89.986 (7) | C(9)$^{\#2}$—Ni(1)—C(9) | 178.2 (4) |
| O(1)—Mn(1)—O(1)$^{\#3}$ | 96.2 (3) | O(1)—Mn(1)—N(1)$^{\#3}$ | 172.3 (2) |
| O(1)—Mn(1)—N(1) | 91.2 (2) | O(1)—Mn(1)—N(2) | 93.9 (2) |
| N(1)$^{\#3}$—Mn(1)—N(1) | 81.5 (3) | O(1)$^{\#3}$—Mn(1)—N(2) | 90.2 (2) |
| N(1)—Mn(1)—N(2) | 91.4 (3) | N(1)—Mn(1)—N(2)$^{\#3}$ | 84.0 (3) |
| N(2)—Mn(1)—N(2)$^{\#3}$ | 174.0 (3) | C(1)—O(1)—Mn(1) | 128.1 (5) |
| C(7)—N(1)—Mn(1) | 126.3 (6) | C(8)—N(1)—Mn(1) | 112.7 (5) |
| C(9)—N(2)—Mn(1) | 163.8 (6) | N(2)—C(9)—Ni(1) | 178.4 (6) |

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ $-y+1/2$, $x$, $z$,
$^{\#2}$ $-x+1/2$, $-y+1/2$, $z$,
$^{\#3}$ $y+1/2$, $x-1/2$, $-z+1/2$.

space are 7.419 Å and 8.676 Å, respectively. The crystal water molecule fills the vacant position of the square net and can be regarded as a clathrated solvent molecule. No hydrogen bonds exist in this structure.

## Magnetic Properties

The variable-temperature magnetic susceptibility was measured from 5 to 299K by a SQUID magnetometer under the applied magnetic field of 10000 Oe. Plots of the magnetic susceptibility ($\chi_M$) and the effective magnetic moment ($\mu_{\text{eff}}$) *vs.* temperature ($T$) are shown in Figure 4. The $\mu_{\text{eff}}$ per $Mn_2Ni$ unit at 299K, 3.90 $\mu_B$, is much smaller than the spin-only value of 6.93 $\mu_B$ expected for the magnetically dilute high spin Mn(III) ions $[(S_{Mn}, S_{Ni}, S_{Mn}) = (2, 0, 2)]$, but is nearly equal to the value of 4.0 $\mu_B$ expected for the magnetically dilute low spin Mn(III) ions $[(S_{Mn}, S_{Ni}, S_{Mn}) = (1, 0, 1)]$, where the spin-only values were calculated by assuming $g_{Mn} = 2.00$. This suggests that the complex contains low spin Mn(III) and is different from previously characterized Mn(III) analogues [6, 7, 12], which usually involve high spin Mn(III) ions. On lowering the temperature, $\mu_{\text{eff}}$ gradually decreases to 2.50 $\mu_B$ at 23K, then reaches a plateau in the range of 238K, and finally decreases to 2.47 $\mu_B$ at 5K, which suggests the presence of an antiferromagnetic exchange interaction. As $[Ni(CN)_4]^{2-}$ is diamagnetic, the exchange interaction between Ni(II)–Mn(III) through the cyanide bridging ligand is negligible. However, the coupling between two adjacent

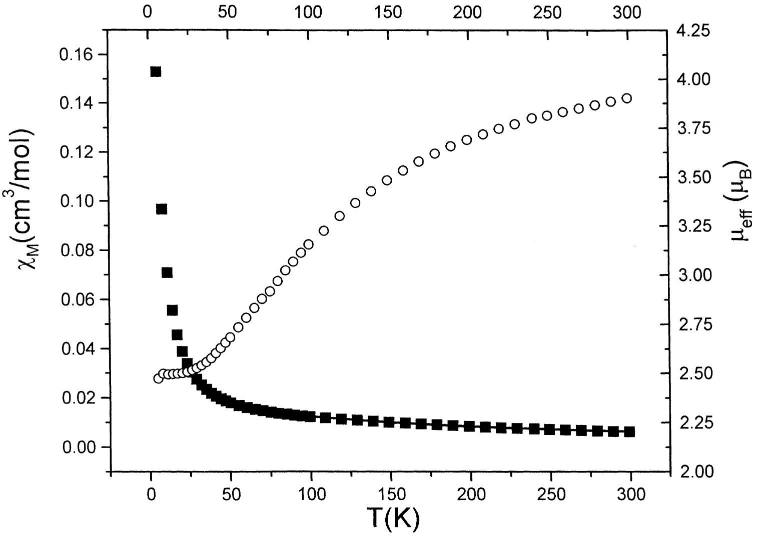

FIGURE 4 The temperature-dependence of magnetic susceptibility $\chi_M$ (■) and the effective magnetic moment $\mu_{eff}$ (○) for the title complex. The solid line represents the fit discussed in the text.

Mn(III) ions could occur through the $[Ni(CN)_4]^{2-}$ group. The linear part of the $1/\chi_M$ *vs.* T curve (T > 65 K) was fitted to the Curie-Weiss law $\chi_M = C/(T-\theta)$ (R = 0.9998) with a big negative Weiss constant of $\theta = -107$ K, indicating the existence of a fairly big antiferromagnetic interaction between Mn(III) ions.

The susceptibility data were modeled in a similar way to that reported previously [13]. The susceptibility above 23K can be approximated by Eqs. (1–4),

$$\chi_t = \frac{2Ng^2\beta^2}{3kT}\frac{15\exp(6J/kT) + 3\exp(2J/kT)}{5\exp(6J/kT) + 3\exp(2J/kT) + 1} \tag{1}$$

$$\chi_t = \frac{Ng^2\beta^2}{3kT}S_t(S_t + 1) \tag{2}$$

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\frac{1+u}{1-u} \times S_t(S_t + 1),$$
$$\text{where } u = \coth[J_cS_t(S_t + 1)/kT] - kT/J_cS_t(S_t + 1) \tag{3}$$

$$\chi_M = \frac{\chi_{chain}}{1 - \chi_{chain}(2zJ'/N g^2\beta^2)}, \quad \text{where } z = 2 \tag{4}$$

where $J_t$, $J_c$ and $J'$ stand for the exchange integrals between two $S_{Mn}$ $(S = 1)$ spins within the $Mn_2Ni$ trimer, between the $S_t$ effective spins of trimers and between the chains, respectively, and were treated as equivalent. The symbols N, g, $\beta$ and k have their usual meanings. When allowing the g and J values to vary, we obtained the best fit to the experimental data with parameters $J_t = J_c = J' = -3.2\,cm^{-1}$, $g = 1.98$ and the disagreement factor $R = 1.56 \times 10^{-3} [R = \sum(\chi_{obs} - \chi_{calc})^2/\chi^2_{obs}]$. As shown in Figure 5, the fit may be considered fairly good. The results $(J_t = J_c = J' < 0)$ show the presence of an antiferromagnetic interaction between the Mn(III) ions within each sheet through the —NC—Ni—CN— bridges. If one takes into consideration the electronic configurations of Mn(III) $(t^4_{2g})$ and $[Ni(CN)_4]^{2-}$, a $\pi$-superexchange pathway is proposed between the nearest Mn(III) ions through the $\Pi^8_9$ conjugation system of the $[Ni(CN)_4]^{2-}$ ion. The magnetic orbital $d_{xz}$ (or $d_{yz}$) of Mn(III) may overlap with the $\Pi^8_9$ system ($z$ axis is taken along the Mn—NC—Ni linkage), which transmits a magnetic interaction between adjacent Mn(III) ions and results in an antiferromagnetic interaction. Due to the symmetry, another magnetic orbital of Mn(III) cannot effectively overlap with the $\Pi^8_9$ system and there exists no coupling between these magnetic orbitals, which can perhaps account for the plateau in magnetic moment in 23 – 8 K with a value of 2.50 $\mu_B$ that corresponds to about one unpaired electron per Mn center. The decrease in magnetic moment below 8 K may be due to an intersheet antiferromagnetic interaction or an antiferromagnetic coupling between the remaining magnetic orbitals of Mn(III) ions. Further study on the magnetic behavior is underway.

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