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Coordination Polymers Constructed from $[Mn(N)(CN)_4]^{2-}$: Synthesis, Structures, and Magnetic Properties

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The dimetallic complexes $[\{Ni(cyclen)\}\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (cyclen = 1,4,7,10-tetraazacyclododecane) (**1**), $[\{Cu(cyclen)\}\{Mn(N)(CN)_4\}]_n$ (**2**), and $[\{Mn(5,5'\text{-}Me_2salen)\}_2\{Mn(N)(CN)_4\cdot CH_3OH]_n$ [5,5′-Me$_2$salen = *N*,*N*′-bis(5,5′-dimethylsalicylidene)-*o*-ethylenediimine] (**3**) have been synthesized and structurally characterized. Compounds **1** and **2** have one-dimensional chain structures, while compound **3** has a two-dimensional sheet-like network structure. Magnetic studies of **1** and **3** show that there is no significant magnetic coupling between the paramagnetic metal centers.

Introduction

Hexacyanometalates $\{[M(CN)_6]^{n-}$, M = 3d metal} have long been used as building blocks for Prussian Blue (PB)-type compounds, many of which have remarkable properties.[1,2] In 1998, Wieghardt reported the synthesis of the high-valent cyanido nitrido complexes $[M^V(N)(CN)_x]^{2-x}$ (M = Cr, Mn; x = 4, 5),[3,4] which may serve as building blocks for new coordination polymers. Indeed, in 2003 Miller reported a series of coordination polymers with the general formula $[M^{II}\{Cr^V(N)(CN)_4\}]\cdot MeCN$ (M^{II} = Cr, Mn, V, Fe, Co, Ni, V) using $[Cr(N)(CN)_4]^{2-}$ as the building block.[5] $[V^{II}\{Cr^V(N)(CN)_4\}]\cdot MeCN$ is an antiferromagnet at T_c = 10.0 K and $[M^{II}\{Cr^V(N)(CN)_4\}]\cdot MeCN$ (M = Cr, Mn, Fe, Co and Ni) are weak ferromagnets (canted antiferromagnets). However, the crystal structures of these polymers have not been reported.

We have also been working on coordination polymers based on $[Cr(N)(CN)_4]^{2-}$, although our attempts at growing crystals of polymers suitable for X-ray crystallography have also been unsuccessful. We thus turned our attention to the building block $[Mn(N)(CN)_4]^{2-}$, which is isostructural with $[Cr(N)(CN)_4]^{2-}$. Although the Mn^V center is diamagnetic, it may still combine with paramagnetic metal centers to form compounds with interesting structural and magnetic properties. For example, the single molecule magnet (SMM) $[(CH_3OH)_{24}Co_9W_5Re(CN)_{48}]$ has been constructed using the diamagnetic building block $[Re(CN)_8]^{3-}$ in conjunction with paramagnetic metal ions,[6] and $[\{Ni(tn)_2\}_2\{Co(CN)_6\}NO_3]\cdot 2H_2O$ (tn = 1,3-diaminopropane), which has a two-dimensional grid-like structure, exhibits $Ni^{II}\cdots Ni^{II}$ ferromagnetic interactions through the diamagnetic NC–Co–NC bridges.[7] Herein we report the synthesis and structures of three new coordination polymers based on $[Mn^V(N)(CN)_4]^{2-}$, namely $[\{Ni(cyclen)\}\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (**1**), $[\{Cu(cyclen)\}\{Mn(N)(CN)_4\}]_n$ (**2**), and $[\{Mn(5,5'\text{-}Me_2salen)\}_2\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (**3**). The magnetic properties of **1** and **3** are also reported.

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Results and Discussion

Synthesis and IR Spectra

The reaction of $Ni(OAc)_2\cdot 4H_2O$ and cyclen with $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$[3] in methanol and H_2O results in the formation of $[\{Ni(cyclen)\}\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (**1**). The IR spectrum of **1** shows ν_{CN} absorptions at $\tilde{\nu}$ = 2135(s) and 2114(m) cm^{-1}.

The reaction of $CuSO_4\cdot 5H_2O$ and cyclen with $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ in methanol and water results in the formation of $[\{Cu(cyclen)\}\{Mn(N)(CN)_4\}]_n$ (**2**). The IR spectrum of **2** shows three peaks at $\tilde{\nu}$ = 2142(m), 2124(m) and 2107(s) cm^{-1}, which are attributed to cyanide stretches.

The reaction of $[Mn(5,5'\text{-}Me_2salen)]PF_6$[8] with $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ in methanol yields the complex $[\{Mn(5,5'\text{-}Me_2salen)\}_2\{Mn(N)(CN)_4\}\cdot CH_3OH\}_n$ (**3**). The IR spectrum of **3** shows one ν_{CN} stretch at 2140(m) cm^{-1}.

In all three compounds the cyanide stretches occur at higher frequencies than in $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ ($\tilde{\nu}$ = 2126 and 2115 cm^{-1}), which indicates coordination of the cyanide to a second metal.

X-ray Crystal Structures

Selected bond lengths and angles for compounds **1**–**3** are listed in Tables 1, 2, and 3, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Ni1–N1	2.0882(16)	Ni1–N6	2.1094(15)
Ni1–N5	2.127(2)	Ni1–N7	2.131(2)
Mn1–N4	1.512(2)	Mn1–C2	1.977(3)
Mn1–C1	1.9785(19)	Mn1–C3	1.984(3)
N1–C1	1.150(2)		
N1–Ni1–N1#1	91.17(8)	N1–Ni1–N6#1	83.74(6)
N1–Ni1–N6	174.91(6)	N6#1–Ni1–N6	101.35(9)
N1–Ni1–N5	98.85(7)	N6–Ni1–N5	81.94(6)
N1–Ni1–N7	98.81(6)	N6–Ni1–N7	82.08(6)
N5–Ni1–N7	154.66(10)	N4–Mn1–C2	100.02(13)
N4–Mn1–C1	101.65(5)	C2–Mn1–C1	85.95(5)
C1#2–Mn1–C1	156.33(11)	N4–Mn1–C3	100.28(13)
C2–Mn1–C3	159.71(11)	C1–Mn1–C3	89.97(5)
N1–C1–Mn1	172.31(16)	C1–N1–Ni1	153.04(14)

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, –*y* + 1, *z*; #2 *x*, –*y*, *z*.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.[a]

Cu–N1	2.127(5)	Mn–C4	2.014(6)
Cu–N6	1.989(6)	Mn–C2	2.016(6)
Cu–N7	2.033(6)	Mn–N2#1	2.291(5)
Cu–N8	2.057(6)	N1–C1	1.154(7)
Cu–N9	2.033(6)	N2–C2	1.145(7)
Mn–N5	1.538(5)	N3–C3	1.152(7)
Mn–C3	1.987(6)	N4–C4	1.148(7)
Mn–C1	1.992(5)		
N6–Cu–N1	99.6(2)	C3–Mn–C1	168.3(2)
N7–Cu–N1	115.1(2)	N5–Mn–C4	93.5(3)
N8–Cu–N1	113.2(2)	C3–Mn–C4	90.1(2)
N9–Cu–N1	95.9(2)	C1–Mn–C4	89.2(2)
N6–Cu–N7	86.8(3)	N5–Mn–C2	93.4(2)
N6–Cu–N8	146.7(3)	C3–Mn–C2	88.9(2)
N6–Cu–N9	86.2(3)	C1–Mn–C2	90.4(2)
N7–Cu–N8	84.2(2)	C4–Mn–C2	173.2(2)
N7–Cu–N9	148.9(2)	N5–Mn–N2#1	178.2(2)
N9–Cu–N8	85.3(2)	C3–Mn–N2#1	85.4(2)
N5–Mn–C3	95.6(2)	C1–Mn–N2#1	82.94(19)
N5–Mn–C1	96.1(2)	C4–Mn–N2#1	85.0(2)
C2–Mn–N2#1	88.18(18)	C1–N1–Cu	133.6(4)
N1–C1–Mn	176.7(5)	N2–C2–Mn	170.3(5)
C2–N2–Mn#2	172.9(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 *x* – 1/2, –*y* + 1/2, –*z*; #2 *x* + 1/2, –*y* + 1/2, –*z*.

Table 3. Selected bond lengths [Å] and angles [°] for **3**.[a]

Mn1–N2	1.515(5)	Mn2–O1	1.8899(19)
Mn1–C	1.977(3)	Mn2–N3	2.004(2)
Mn1–O2	2.402(5)	Mn2–N1	2.252(3)
N1–C1	1.148(4)		
N2–Mn1–C	98.32(9)	O1A–Mn2–N1	90.20(9)
N2–Mn1–O2	180.000(1)	O1–Mn2–N1	94.32(9)
C1B–Mn1–C1	88.80(3)	N3–Mn2–N1	87.94(9)
C1–Mn1–C1A	163.36(18)	N3A–Mn2–N1	86.91(9)
C–Mn1–O2	81.68(9)	N1–Mn2–N1D	173.21(14)
C1–N1–Mn2	159.0(2)	N1–C1–Mn1	178.6(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x* + 1/2, *y*, *z*; #2 –*x* + 1/2, –*y* + 1/2, *z*; #3 *x*, –*y* + 1/2, *z*; #4 *x* + 1/2, *y* – 1/2, –*z* + 1/2.

The crystal structure (Figure 1) of **1** shows that it has a one-dimensional zig-zag chain structure with each $[Mn(N)(CN)_4]^{2-}$ unit connected to two $[Ni(cyclen)]^{2+}$ units through its *trans* cyano groups. Each Ni^{II} center is octahedrally coordinated to the four nitrogen atoms of cyclen and two nitrogen atoms of cyano groups in a *cis* configuration. The Ni–N(cyclen) [2.1094(15)–2.131(2) Å] and Ni–N(cyanido) bond lengths [2.0882(16) Å] in compound **1** are comparable to those in $[Ni(cyclen)]_2[Pt(CN)_4]_2\cdot 6H_2O$.[9] The Ni–N≡C unit is bent with an angle of 153.04(14)°. The bridging $[Mn(N)(CN)_4]^{2-}$ unit remains as a slightly distorted square pyramid. The Mn–C [1.977(3)–1.984(3) Å] and Mn–N(nitrido) [1.512(2) Å] bond lengths are similar to those of the monomeric complexes $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ [Mn–C = 1.982 Å, Mn–N(nitrido) = 1.507(2) Å][3] and $[Rh(en)_3][Mn(N)(CN)_5]\cdot H_2O$ [Mn–C^{cis} = 1.985(6)–2.001(7) Å, Mn–N(nitrido) = 1.499(8) Å].[4] The C≡N bond lengths [1.150(2)–1.156(4) Å] are also similar to that of the monomeric complex [1.159(2)–1.162(2) Å]. The Mn–C≡N angles for terminal [179.1(3)–179.3(3)°] and bridging cyano groups [172.3(16)°] are close to linear.

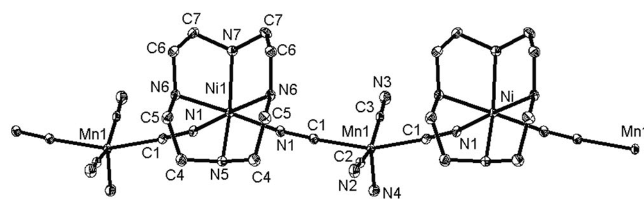

Figure 1. An ORTEP view of compound **1** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvated methanol molecules have been omitted for clarity.

Each 1D zig-zag chain stacks with another 1D chain to form a double chain structure with an intermolecular closest Ni···Ni distance of 5.147 Å; the intrachain Ni···Ni distance is 9.035 Å (Figure 2).

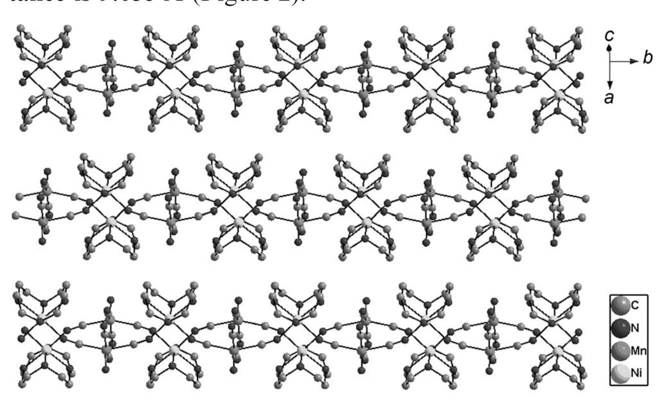

Figure 2. A view of the 1D chains in **1**. Hydrogen atoms and solvated methanol molecules have been omitted for clarity.

The crystal structure of **2** (Figure 3) shows that the $[Mn(N)(CN)_4]^{2-}$ units are linked together by cyanido bridges to form an $Mn(N)(CN)_3$-(μ-CN)-$Mn(N)(CN)_3$ 1D zig-zag chain with a C2–Mn–N2A bond angle of 88.18(18)°. Each manganese atom is also connected to a $[Cu(cyclen)]^{2+}$ unit through one of its cyano groups. The manganese atom has a distorted octahedral environment and is coordinated to four cyanido carbon atoms in the equatorial plane, one terminal nitrido ligand, and one cyanido nitrogen atom. The Mn–C [1.987(6)–2.106(6) Å], Mn≡N [1.538(5) Å], and C≡N bond lengths [1.145(7)–1.154(7) Å] are comparable to those in compound **1** and $[Rh(en)_3][Mn(N)(CN)_5]\cdot H_2O$.[4] The Mn–N(cyanido) bond length is 2.291(5) Å. The Mn–C≡N angles for terminal [173.1(5)–175.7(5)°] and bridging cyano groups [170.3(5)–176.7(5)°] and the Mn–N≡C angle [172.9(4)°] are close to linear. The copper center has a distorted square-pyramidal geometry and is coordinated to the four nitrogen atoms of a cyclen ligand with a cyanido nitrogen atom in the apical position. The average Cu–N(cyclen) (2.028 Å) and Cu–N(cyanido) [2.127(5) Å] bond lengths in compound **2** are comparable to those found in Cu(cyclen)$[Au(CN)_2]_2$ [2.003 and 2.10(3) Å respectively].[10] The Cu–N≡C unit is bent, with an angle of 133.6(4)°. The shortest interchain Cu···Cu distance between adjacent chains is 6.707 Å and the shortest intrachain Cu···Cu distance is 7.627 Å (Figure 4).

The X-ray structure of **3** shows that each $[Mn^{V}(N)(CN)_4]^{2-}$ unit is coordinated to four $[Mn^{III}(5,5'\text{-}Me_2\text{-}salen)]^+$ units through the cyano groups to form a 2D sheet-like network structure (Figures 5 and 6). Each Mn^{V} center has a distorted octahedral environment comprising four carbon atoms from cyanido ligands, one terminal nitrido ligand, and one oxygen atom of a methanol molecule (dis-

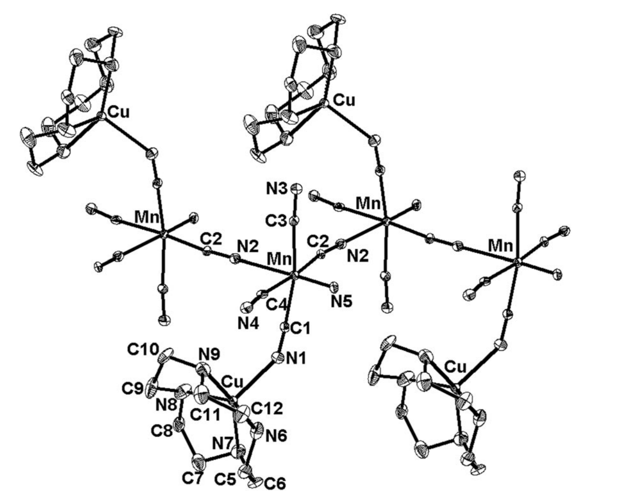

Figure 3. An ORTEP view of compound **2** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

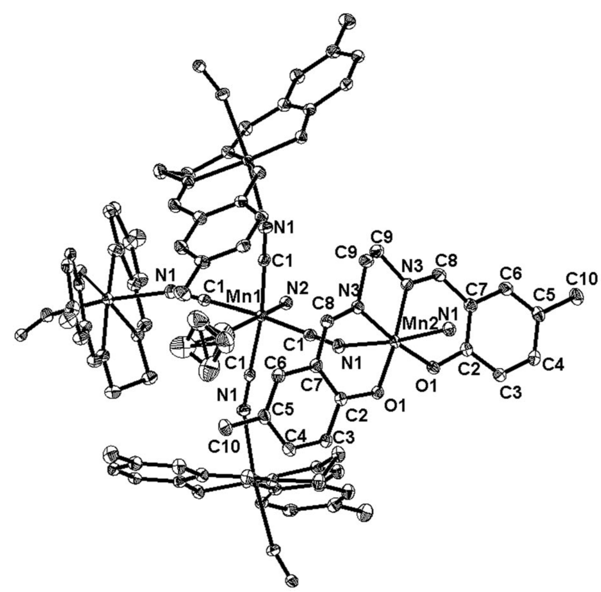

Figure 5. An ORTEP view of compound **3** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

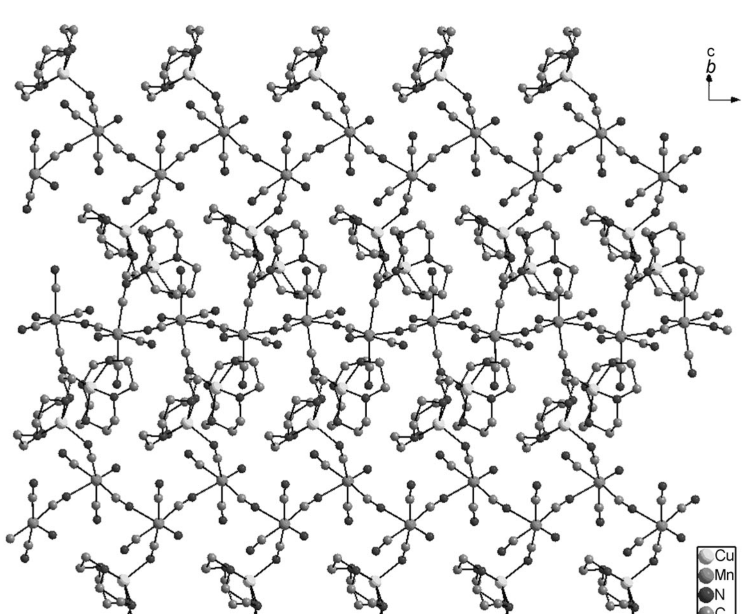

Figure 4. A view of the 1D zig-zag chain in **2**.

ordered). The average Mn–C [1.977(3) Å], the Mn≡N [1.515(5) Å], and the C≡N bond lengths [1.148(4) Å] at the Mn^V center are comparable to those in compounds **1** and **2**. The Mn–O(methanol) bond *trans* to the nitrido ligand is elongated, with a length of 2.402(5) Å. The Mn–C≡N angles [178.6(3)°] for the bridging cyano groups are close to linear. The Mn^{III} ions are coordinated equatorially by the N_2O_2 donors of the tetradentate Schiff base ligand [Mn2–O1 = 1.8899(19) Å and Mn2–N3 = 2.004(2) Å] and axially by two cyanido nitrogen atoms of $[Mn(N)(CN)_4]^{2-}$ [Mn2–N1 = 2.252(3) Å], which gives rise to a distorted octahedral coordination geometry. The bridging cyanido ligands coordinate to the Mn^{III} ions in a bent fashion with C1–N1–Mn2 angles of 159.0(2)°. The N1–Mn2–N1D unit is nearly linear [173.21(14)°]. The shortest intralayer $Mn^{III}\cdots Mn^{III}$ distance is 7.189 Å and the shortest interlayer $Mn^{III}\cdots Mn^{III}$ distance is 10.431 Å.

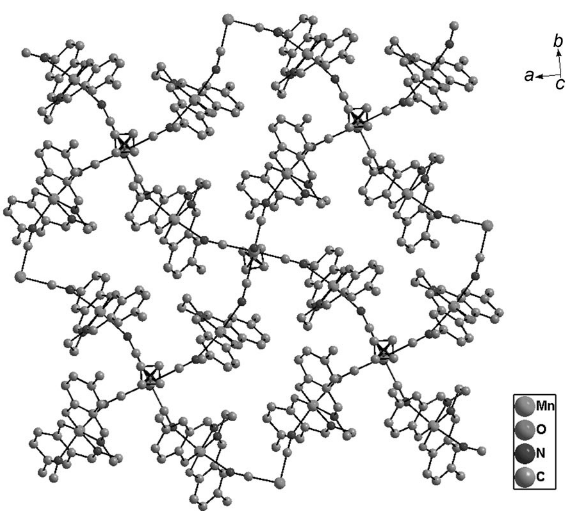

Figure 6. A view of the 2D sheet-like network in **3**. Hydrogen atoms have been omitted for clarity.

Magnetic Properties

The magnetic behavior of **1** was studied in the temperature range 2–300 K. (Figure 7) The $\chi_m T$ value at 300 K is 1.19 $cm^3 mol^{-1} K$, which is slightly larger than the expected uncoupled value of 1.00 $cm^3 mol^{-1} K$ for a high-spin Ni^{II} center in an octahedral environment. The molar magnetic susceptibility data of compound **1** can be fitted using the Curie–Weiss law [$\chi_m = C/(T - \theta)$] in the temperature range 2–300 K, which gives C = 1.19 $cm^3 mol^{-1} K$ and θ = –0.02 K. This value of C is also consistent with non-interacting Ni^{II} systems ($C_{calcd.}$ = 1.19 $cm^3 mol^{-1} K$) and the very small Weiss constant of –0.02 K again suggests that there is no significant magnetic coupling between Ni^{II} ions. The field dependence of the magnetization at about 2.0 K for **1** is shown in Figure 8. The $M(H)$ curve is consistent with the paramagnetic state of the Ni^{II} ions (S = 1; g = 2) and reaches 2.12 $N\beta mol^{-1}$ at 50 kOe, which is close to the expected saturation value of 2.0 $N\beta mol^{-1}$.

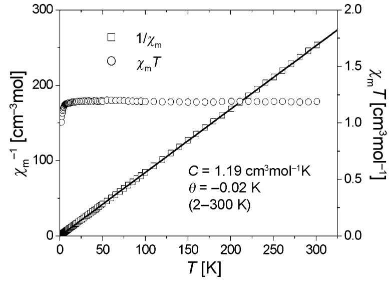

Figure 7. Temperature dependence of $\chi_M T$ (circles) and χ_M^{-1} (squares) for compound **1**.

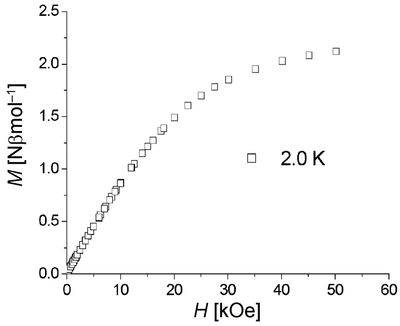

Figure 8. Field dependence of the magnetization for compound **1**.

The magnetic behavior of **3** was also studied in the temperature range 2–300 K (Figure 9). The $\chi_m T$ value at 300 K is 6.04 $cm^3 mol^{-1} K$, which is slightly larger than the expected uncoupled value of 6.00 $cm^3 mol^{-1} K$ for two uncoupled high-spin Mn^{III} centers with S = 2 and one diamagnetic Mn^V center with S = 0. The plot of χ_m^{-1} vs. T for complex **3** obeys the Curie–Weiss law well in the 15–300 K range, with a Curie constant of 6.04 $cm^3 K mol^{-1}$ and a small Weiss constant of 0.03 K. The value of C is consistent with non-interacting Mn^{III} systems ($C_{calcd.}$ = 6.04 $cm^3 mol^{-1} K$) and the very small Weiss constant of 0.03 K also suggests that there is no significant magnetic coupling between the Mn^{III} centers through the diamagnetic $[Mn^VN(CN)_4]^{2-}$ bridges. The $\chi_m T$ vs. T curve decreases below 15 K, most probably because of a zero-field splitting effect, which is characteristic for Mn^{III}. The field dependence of the magnetization at about 2.0 K for **3** is

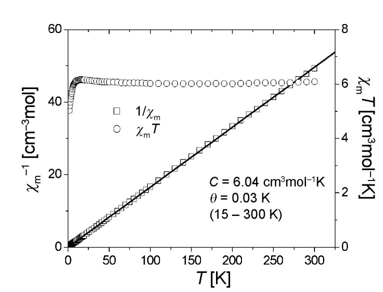

Figure 9. Temperature dependence of $\chi_M T$ (circles) and χ_M^{-1} (squares) for compound **3**.

shown in Figure 10. The $M(H)$ curve reaches 6.15 $N\beta$ mol^{-1} at 50 kOe, which is smaller than the expected saturation value of 8.0 $N\beta$ mol^{-1} for the sum of two Mn^{III} magnetic moments ($S_{total} = S_{Mn} + S_{Mn} = 4$; $g = 2.0$).

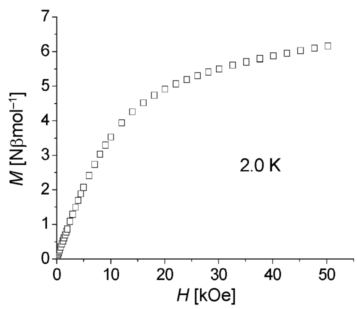

Figure 10. Field dependence of the magnetization for compound **3**.

The magnetic behavior of **2** was not investigated since the Cu···Cu distances are very long and no significant magnetic coupling between Cu^{II} centers was expected.

Conclusions

The square-pyramidal $[Mn(N)(CN)_4]^{2-}$ ion is a useful building block for the construction of coordination polymers with interesting structures. In principle, both the cyano and nitride groups can function as bridging ligands. However, only cyanido bridging is observed in the three compounds described here, which suggests that the nitrido ligand in $[Mn(N)(CN)_4]^{2-}$ is not nucleophilic. Although paramagnetic centers bridged by diamagnetic metal units may also exhibit interesting magnetic behavior, no significant magnetic interaction between the paramagnetic metal centers in compounds **1** and **3** is observed.

Experimental Section

Materials and Physical Measurements: All chemicals and solvents were of reagent grade and were used as received. $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ and $[Mn(5,5'\text{-}Me_2salen)](PF_6)$ were synthesized by literature methods.[3,8] Elemental analyses were performed with a Vario EL III Elemental analyzer. IR spectra were recorded with a Nicolet 360 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

Preparation of $[\{Ni(cyclen)\}\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (1): A methanol solution (20 mL) of $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ (100 mg, 0.11 mmol) was added to 10 mL of an aqueous solution of $Ni(CH_3COO)_2\cdot 4H_2O$ (28 mg, 0.11 mmol) and cyclen (19.5 mg, 0.11 mmol). The resulting red solution was allowed to stand in the dark at room temperature (23 °C). After three weeks, the red block crystals were filtered, washed with a little ice-cold water, and then with diethyl ether. Yield: 30 mg (52 %). $C_{13}H_{24}MnN_9NiO$ (436.06): calcd. C 31.86, H 6.17, N 25.72; found C 32.16, H 6.02, N 25.63. IR (KBr): $\tilde{\nu}$ = 2135 and 2114 cm^{-1} ($\nu_{C\equiv N}$).

Preparation of $[\{Cu(cyclen)\}\{Mn(N)(CN)_4\}]_n$ (2): $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ (50 mg, 0.051 mmol), $CuSO_4\cdot 5H_2O$ (12.8 mg, 0.051 mmol) and cyclen (8.83 mg, 0.051 mmol) were placed in three separate 10-mL sample tubes in a 150-mL beaker. The sample tubes and beaker were carefully filled with methanol to minimize turbulence and the beaker was then wrapped with paraffin film. Well-defined red, needle-shaped crystals were obtained after leaving the beaker undisturbed at room temperature for two weeks; these were collected, washed with methanol, and dried in air. Yield: 8 mg (35 %). $C_{12}H_{20}CuMnN_9$ (408.85): calcd. C 35.22, H 4.93, N 30.83; found C 35.46, H 5.34, N 30.62. IR (KBr): $\tilde{\nu}$ = 2142, 2124, 2107 cm^{-1} ($\nu_{C\equiv N}$).

Preparation of $[\{Mn(5,5'\text{-}Me_2salen)\}_2\{Mn(N)(CN)_4\}\cdot CH_3OH]_n$ (3): A solution of $(Ph_4P)_2[Mn(N)(CN)_4]\cdot 2H_2O$ (50 mg, 0.056 mmol) in 10 mL of methanol was added to a solution of $[Mn(5,5'\text{-}Me_2salen)]PF_6$ (55.8 mg, 0.112 mmol) in 15 mL of methanol. The dark brown cubic crystals obtained by slow evaporation of the resulting solution were collected, washed with CH_3CN, and dried in air. Yield: 20 mg (38 %). $C_{41}H_{40}Mn_3N_9O_5$ (903.64): calcd. C 54.50, H

Table 4. Summary of the crystallographic data for **1**–**3**.

	1	**2**	**3**
Formula	$C_{13}H_{24}MnN_9NiO$	$C_{12}H_{20}CuMnN_9$	$C_{41}H_{40}Mn_3N_9O_5$
Formula mass	436.06	408.85	903.64
Crystal system	monoclinic	orthorhombic	tetragonal
Space group	$C2/m$	$P2_12_12_1$	$P4/ncc$
a [Å]	18.0492(9)	7.6274(1)	14.2573(3)
b [Å]	9.0353(5)	12.8092(2)	14.2573(3)
c [Å]	13.4953(7)	17.0868(3)	20.0449(5)
α [°]	90	90	90
β [°]	125.088(1)	90	90
γ [°]	90	90	90
V [Å^3]	1800.86(16)	1669.40(4)	4074.54(16)
Z	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.608	1.627	1.473
T [K]	150(2)	150(2)	150(2)
μ [mm^{-1}]	1.769	2.043	0.971
$F(000)$	904	836	1856
Data/restraints/parameters	2205/0/136	3800/0/208	2353/1/142
GOF on F^2	1.046	1.043	1.023
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0307, 0.0777	0.0523, 0.1296	0.0441, 0.1146
$R1$, $wR2$ (all data)	0.0337, 0.0795	0.0678, 0.1374	0.0731, 0.1270

4.46, N 13.95; found C 54.29, H 4.54, N 14.10. IR (KBr): $\tilde{\nu}$ = 2140 cm^{-1} ($\nu_{C\equiv N}$).

Magnetic Measurements: Magnetic measurements for all crystalline samples were performed with a Quantum Design MPMS-XL5 SQUID magnetometer. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms (Pascal's tables).

X-ray Structure Determination: The crystal structures were determined with a Bruker Smart APEX CCD area-detector diffractometer (**1**) and a NONIUS KappaCCD diffractometer (**2** and **3**) using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150 K. The structures were solved by direct methods with SHELXL-97[11] and refined by full-matrix least-squares on F^2. Hydrogen atoms were added geometrically and refined as riding atoms with a uniform value of U_{iso}. Final crystallographic data and values of $R1$ and wR are listed in Table 4. The methanol solvent in complex **3** was disordered.

CCDC-653542 (**1**), -653541 (**2**) and -653540 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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