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Cyanide-bridged Trinuclear and Ethylenediamine-bridged One-dimensional Cobalt(III)-Manganese(II) Complexes: Synthesis, Crystal Structures and Magnetic Properties

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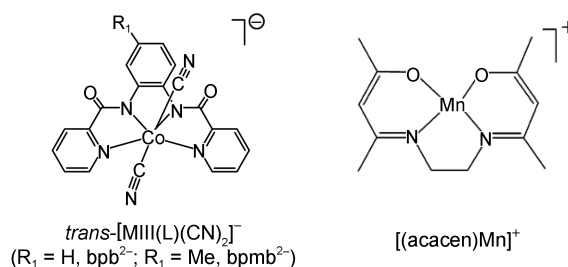*[*]E-mail: nizhonghai@cumt.edu.cn*

Two pyridinecarboxamide cobalt dicyanide building blocks and Mn(III) compounds have been employed to assemble cyanide-bridged heterometallic complexes, resulting in three trinuclear cyanide-bridged Co^{III}-Mn^{II} complexes: $\{[Mn(MeOH)_4][Co(bpb)(CN)_2]_2\}\cdot 2MeOH\cdot 2H_2O$ (**1**), $\{[Mn(MeOH)_4][Co(bpmb)(CN)_2]_2\}\cdot 2MeOH\cdot 2H_2O$ (**2**) and $\{[Mn(DMF)_2(en)_2][Co(bpb)(CN)_2]_2\}\cdot 2DMF\cdot H_2O$ (**3**) (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, $bpmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate, en = ethylenediamine). Single crystal X-ray diffraction analysis shows their similar sandwich-like structures, in which the two cyanide-containing building blocks act as monodentate ligands through one of their two cyanide groups to coordinate the Mn(II) center. For complex **3**, it was further linked into one-dimensional structure by ethylenediamine acting as bridges. Investigation of the magnetic properties of complex **3** reveals weak antiferromagnetic coupling between the neighboring Mn(II) centers through the bridging ethylenediamine molecule. A best-fit to the magnetic susceptibilities of complex **3** gave the magnetic coupling constant $J = -0.073(2)$ cm^{-1}.

Key Words : Cyanide-bridged, Heterometallic complex, Crystal structure, Magnetic property

Introduction

As one of the most important magnetic systems, cyanide-bridged complexes have received much attention in molecular magnetism field since their molecular topologies and magnetic coupling between neighboring metal centers through the cyanide bridge can be relatively easily controlled and predicted. During the past two decades, over twenty cyanide-containing precursors with or without peripheral organic ligands have been designed, synthesized, and employed in assembling into homo- or heterometallic cyanide-bridged molecular magnetic materials with various structure types, including molecular clusters, 1D chains and 2D and 3D networks.[1-11]

Recently, a series of rigid dicyanide-containing building blocks based on pyridinecarboxamide ligands, in which these relatively large equatorial in-plane ligands can efficiently decrease the dimensions of the complex formed and weaken the intermolecular magnetic coupling, have been firstly employed to synthesize cyanide-bridged heterometallic complexes by our group. Based on these *trans*-dicyanidemetalate building blocks, many cyanide-bridged magnetic complexes with various of topologies, including binuclear and arc-like tetranuclear clusters, 1D chains and nanosized molecular wheels[12-17] have been reported. In this paper, we investigated the reactions of *trans*-dicyanidecobalt(III) precursors with the manganese(III) compounds [Mn(acac)$_2$]Cl and [Mn(acacen)]ClO$_4$ (acac = acetylaceto, acacen = *N,N′*-ethylene-bis(acetylacetonylideneaminate, Scheme 1) and

trans-[MIII(L)(CN)$_2$]$^-$
(R$_1$ = H, bpb^{2-}; R$_1$ = Me, bpmb^{2-})

[(acacen)Mn]$^+$

Scheme 1

obtained three trinuclear sandwich-like heterometallic cyanide-bridged Co(III)-Mn(II) complexes, in which complex **3** was further linked into one dimensional structure by ethylenediamine molecule acting as bridges. Here, we present the synthesis, crystal structures, and magnetic properties of the three heterometallic cyanide-bridged Co(III)-Mn(II) complexes $\{[Mn(MeOH)_4][Co(bpb)(CN)_2]_2\}\cdot 2MeOH\cdot 2H_2O$ (**1**), $\{[Mn(MeOH)_4][Co(bpmb)(CN)_2]_2\}\cdot 2MeOH\cdot 2H_2O$ (**2**) and $\{[Mn(DMF)_2(en)_2][Co(bpb)(CN)_2]_2\}\cdot 2DMF\cdot H_2O$ (**3**) (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, $bpmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate, en = ethylenediamine).

Experimental

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El instrument. IR spectra of KBr pellets were recorded on a Magna-IR 750

spectrophotometer in the 4000-400 cm^{-1} region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

All the reactions were carried out under air and all chemicals and solvents used were reagent grade without further purification. K[Co^{III}(bpb)(CN)$_2$] [bpb^{2-} = 1,2-bis-(pyridine-2-carboxamido)benzenate] and its analogue were synthesized as described in the literature.[18] [Mn(acac)$_2$]Cl and [Mn(acacen)]ClO$_4$ was available from previous works.[19,20]

Preparation of Complexes 1 and 2. To a solution of [Mn(acac)$_2$]Cl (28.9 mg, 0.1 mmol) in methanol (10 mL), K[Co(bpb)(CN)$_2$] (48.2 mg, 0.10 mmol) or K[Co(bpmb)(CN)$_2$] (49.6 mg, 0.10 mmol) dissolved in methanol/water (4:1, v:v) (10 mL) was added. The resulting mixture was filtered at once and the filtrate kept undisturbed at room temperature. After one week, brown-black block crystals were collected by filtration with a yield of 0.031 g, 54.6%. Anal. Calcd. for C$_{46}$H$_{52}$Co$_2$MnN$_{12}$O$_{12}$: C, 48.56; H, 4.61; N, 14.77. Found: C, 48.71; H, 4.70; N, 14.61. Main IR bands (cm^{-1}): 2162, 2121 (s, νC≡N), 1617, 1623 (vs, νC=N).

Complex **2**: Yield 0.030g, 51.6%. Anal. Calcd. for C$_{48}$H$_{56}$Co$_2$MnN$_{12}$O$_{12}$: C, 49.45; H, 4.84; N, 14.42. Found: C, 49.52; H, 4.71; N, 14.53. Main IR bands (cm^{-1}): 2160, 2120 (s, νC≡N), 1617, 1626 (vs, νC=N).

Preparation of Complex 3. K[Co(bpb)(CN)$_2$] (48.2 mg, 0.10 mmol) dissolved in methanol/water (4:1, v:v) (10 mL) was added to a solution of [Mn(acacen)]ClO$_4$ (37.7 mg, 0.1 mmol) in methanol (10 mL), where upon dark-brown micro crystals were immediately precipitated. Single crystals suitable for X-ray diffraction were grown by slow diffusion from a DMF solution of the microcrystals, layered with ether, after about two weeks with a yield 0.031 g, 48.7%. Anal. Calcd. for C$_{54}$H$_{62}$Co$_2$MnN$_{18}$O$_9$: C, 50.67; H, 4.88; N, 19.70. Found: C, 50.73; H, 4.95; N, 19.82. Main IR bands

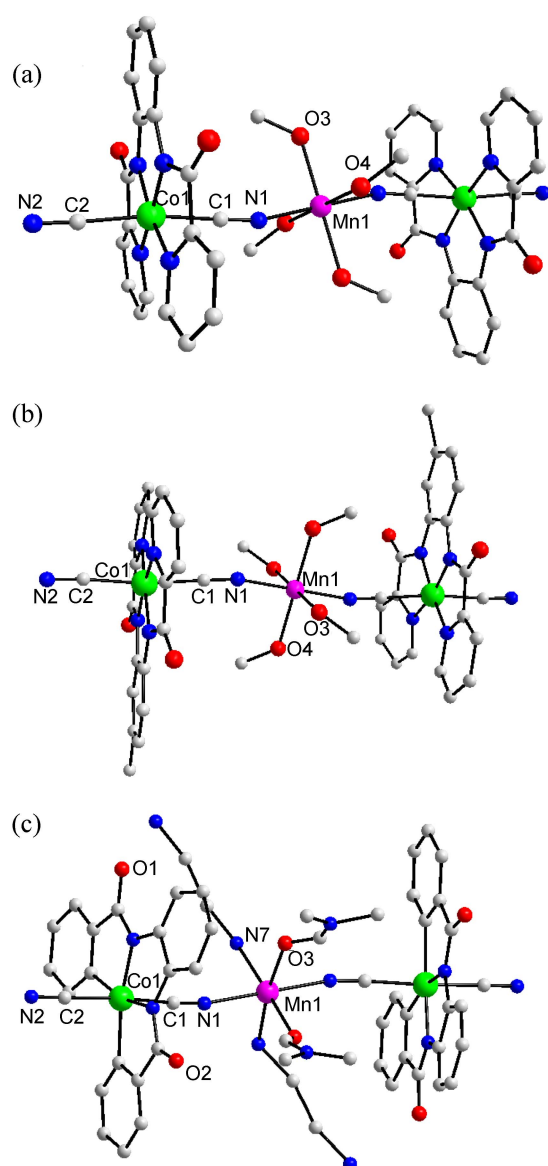(cm^{-1}): 2159, 2126 (s, νC≡N), 1614, 1627 (vs, νC=N).

X-ray Data Collection and Structure Refinement. Single crystals of all the complexes with suitable dimensions for X-ray diffraction analyses were mounted on glass rods and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoKα sealed tube (λ = 0.71073 Å) at 293 K, using ω scan mode. The structures were solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All of the non-hydrogen atoms, except the disordered ones, were refined with anisotropic displacement coefficients. For the disordered contents, the partially occupied atoms were refined isotropically. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C), and their coordinates were allowed to ride on their respective carbons using SHELXL97, except some of the H atoms of the solvent molecules. These H atoms were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. CCDC 827303, 827304 and 827305 for complexes **1-3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of the crystal parameters, data collection, and refinement are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. In our recent works,[12-17] pyridinecarboxamide *trans*-dicyanidemetalate building blocks have been successfully employed to construct cyanide-bridged heterometallic complexes with various structures by using Mn(III) compounds of salen type Schiff Base ligands, seven-coordinate macrocyclic manganese(II) compounds or polyaza-Ni(II) complexes as as-

Table 1. Crystallographic data for complexes **1-3**

	1	**2**	**3**
chemical formula	C$_{46}$H$_{52}$Co$_2$Mn N$_{12}$O$_{12}$	C$_{48}$H$_{56}$Co$_2$ MnN$_{12}$O$_{12}$	C$_{54}$H$_{62}$Co$_2$ MnN$_{18}$O$_9$
Fw	1137.80	1165.85	1280.02
crystal system	monoclinic	monoclinic	orthorhombic
Space group	*P*2(1)/*n*	*P*2(1)/*n*	*Pbcn*
a/Å	8.6138(13)	8.610(3)	25.321(3)
b/Å	11.7258(18)	11.972(4)	15.0247(16)
c/Å	25.467(4)	24.988(9)	15.5350(17)
α/deg	90	90	90
β/deg	91.439(2)	90.02	90
γ/deg	90	90	90
V/Å^3	2571.5(7)	2575.8(15)	5910.1(11)
Z	2	2	4
F(000)	1174	1206	2652
GOF	1.059	1.013	1.015
$R_1[I>2s(I)]$	0.0349	0.0506	0.0672
wR_2 (all data)	0.0984	0.1209	0.2024

Figure 1. The trinuclear structure of complexes **1**(a), **2**(b), **3**(c). The solvent molecules and all the H atoms have been omitted for clarity.

sembling segments, indicating that these types of cyanide precursors are good candidates for the synthesis of low-dimensional cyanide-bridged complexes. In the present study, complexes **1-3** were obtained by the reactions of *trans*-$[Co(L)(CN)_2]^-$ with the Mn(III) compounds $[Mn(acac)_2]Cl$ or $[Mn(acacen)]ClO_4$, in the form of stable heterometallic trinuclear cyanide-bridged Co(III)-Mn(II)-Co(III) systems. For complex **3**, the initial acacen ligand was decomposed, therefore forming a cyanide and ethylenediamine mix-bridged one dimensional structure.

In the IR spectra of complexes **1-3**, two sharp peaks due to the cyanide stretching vibration were observed at about 2120 and 2160 cm^{-1}, respectively, indicating the presence of both bridging and non-bridging cyanide ligands in these complexes. For complex **3**, there exhibits two strong peaks at about 3420 and 3450 cm^{-1}, which can be assigned the vibration of N-H bond.

Crystal Structures of Complexes 1-3. Some important structural parameters for complexes **1-3** are collected in Table 2. Their neutral trinuclear structures are shown in Figure 1. For complex **3**, its ethylenediamine-bridged one-diemnsional structure is given in Figure 2.

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1-3**

	1	2	3
Mn1-N1	2.159(2)	2.150(3)	2.200(6)
Mn1-O3	2.212(2)	2.192(3)	2.193(6)
Mn1-O4/N7	2.2025(19)	2.209(3)	2.170(4)
Co1-C1	1.920(2)	1.915(4)	1.968(6)
Co 1-C2	1.926(2)	1.917(4)	1.983(6)
Co 1-N3	1.8976(19)	1.891(3)	1.891(4)
Co 1-N4	1.895(2)	1.879(3)	1.889(4)
Co 1-N5	1.982(2)	1.962(3)	1.990(4)
Co 1-N6	1.9770(19)	1.959(3)	2.000(4)
Mn1-N1-C1	167.2(2)	167.5(3)	167.5(5)
C1-Co1-C2	177.80(10)	178.22(16)	171.3(2)
Co1-C1-N1	179.1(2)	178.7(4)	175.6(5)
Co1-C2-N2	178.2(2)	177.9(4)	178.1(5)
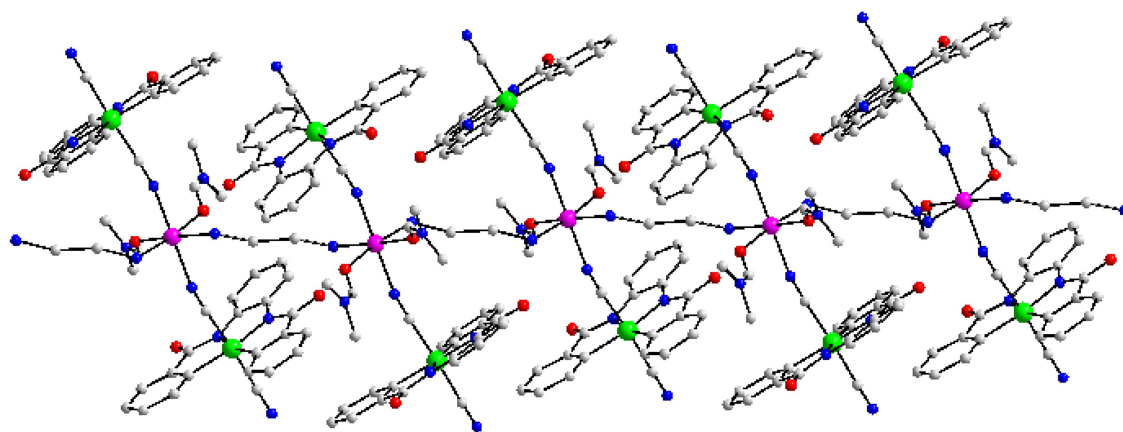
Figure 2. The one-dimensional structure for complex **3** formed by ethylenediamine. acting as bridges. The solvent molecules and all the H atoms have been omitted for clarity.
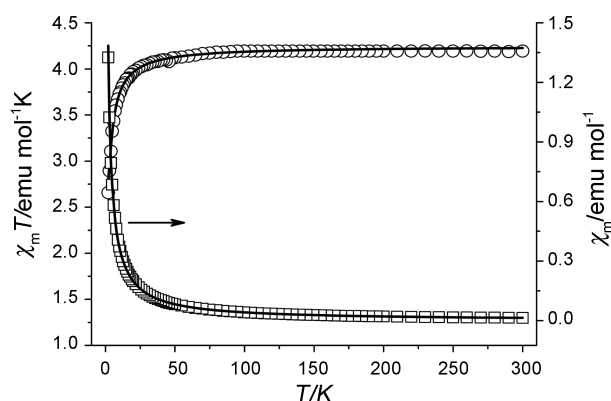
Figure 3. Temperature dependences of $\chi_m T$ for complex **3** (the solid line represents the best fit based on the parameters discussed in the text).

As can be seen, complexes **1-3** possess similar trinuclear sandwich-like structures comprising of two *trans*-[Co(L)(CN)$_2$]$^-$ units with the Mn(II) center in the middle. Complexes **1** and **2** crystallize in the monoclinic *P*2(1)/*n* group, while complex **3** crystallizes in the orthorhombic *Pbcn* group. In these three complexes, two [Co(L)(CN)$_2$]$^-$ units, acting as a mono-dentate ligand through one of its its two cyanide groups, connect the central Mn(II). The Co atom is coordinated by four N atoms of the chelating ligands in the equatorial plane and two C atoms from the cyanide ligands in *trans* positions, forming a slightly distorted octahedral geometry. The Co-N bond lengths are in the very narrow range of 1.879(3)-1.8976(19) Å for these complexes and the Co-C$_{cyanide}$ bond lengths are distributed to the range of 1.915(4)-1.983(6) Å. As listed in Table 2, the Co-C≡N bond angles in the realm of 175.6(5)-179.1(2)^o clearly indicate that the three atoms are in a very good linear configuration.

The coordination sphere for the Mn(II) atom in these complexes is also a octahedron, in which the four equatorial positions are occupied by four O atoms from methanol in complexes **1** and **2** and by two O atoms of coordinated DMF and two N atoms of two ethylenediamine ligands in complex **3**, and the axial positions are occupied by the N atoms of the bridging cyanide groups. As shown in Table 2, the distances between the Mn atom and the O atoms of the solvent ligands, the N atom of ethylenediamine ligand are 2.212(2), 2.2025(19) Å (**1**), 2.192(3), 2.209(3) Å (**2**) and 2.193(6), 2.170(4) Å (**3**), while the Mn-N$_{cyanide}$ bond lengths are 2.159(2), 2.150(3) and 2.200(6) Å for complexes **1**, **2** and **3**, respectively. The C1≡N1-Mn1 angles in these three complexes are 167.2(2), 167.5(3) and 167.5(5)°, respectively, indicating that these three atoms deviate slightly from a linear configuration. The intramolecular Mn^{II}-Mn^{II} separation through the bridging cyanide precursor is 10.38, 10.36 and 10.48 Å for complexes **1**, **2** and **3**, respectively. Foe complex **3**, the distance between the Mn(II) ions bridged by ethylenediamine is 8.17 Å.

Magnetic Properties of Complex 3. The magnetic properties for complex **3** have been investigated, and its mag-

netic susceptibilities measured in the temperature range of 2-300 K at an applied field of 2000 Oe is given in Figure 3. The room temperature $\chi_m T$ values is 4.20 emu K mol^{-1}, slightly lower than the spin only value of 4.375 emu K mol^{-1} for the isolated high spin Mn(II) (S = 5/2). With the temperature decreasing, the $\chi_m T$ value remains almost constant from 300 to about 50 K. After this, the $\chi_m T$ value starts to decrease rapidly and reaches their lowest peak with the value of 2.65 emu K mol^{-1} at 2 K. The magnetic susceptibility of complex **1** conforms well to Curie-Weiss law in a range of 2-300 K and gives the negative Weiss constant θ = −1.13 K and Curie constant C = 4.22 emu K mol^{-1}. These results primarily show the antiferromagnetic magnetic coupling between the two Mn(II) centers bridged by ethylenediamine molecule.

The magnetic data are analyzed by using the Hamiltonian: $\hat{H} = -2\Sigma J\hat{S}_i\hat{S}_{i+1}$. The temperature dependence of the magnetic susceptibility is given by the equation:[21]

$$\chi_M^{chain} = Ng^2\beta^2\{S_{Mn}(S_{Mn}+1)/3kT\}\{(1+\mu)/(1-\mu)\} \quad (1)$$

(Fisher's infinite chain model) with:

$$\mu = \coth[JS_{Mn}(S_{Mn}+1)/KT] - [KT/JS_{Mn}(S_{Mn}+1)] \quad (2)$$

The least-squares fit to the data leads to J = −0.073(2) cm^{-1}, g = 1.99(4), R = 1.35 × 10^{-5}. The small J value suggests the overall very weak magnetic coupling between the Mn(II) ions with a long separation.

Conclusion

In summary, two *trans*-dicyanidecobalt(III) precursors K[Co(L)(CN)$_2$] were used as building blocks to assemble three trinuclear cyanide-bridged heterometallic Co(III)-Mn(II) complexes with sandwich-like structures. Due to the decomposition of the initial Schiff-Base ligand, one of them is further linked into one-dimensional structure by the coordinated ethylenediamine molecules acting as bridges. Investigation of the magnetic properties of complex **3** reveals weak antiferromagnetic interaction between the ethylenediamine-bridged Mn(II) centers.

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