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Three 1D cyanide-bridged M(Ni, Pd, Pt)-Mn(II) Coordination Polymer: Synthesis, Crystal Structure and Magnetic Properties

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Abstract

Abstract: Three tetracyanide-containing building blocks $K_2[M(CN)_4]$ (M=Ni, Pd, Pt) and one semi-closed macrocycle seven-coordinated manganese(II) compound have been employed to assemble cyanide-bridged heterometallic complexes, resulting in three cyanide-bridged M^{II} - Mn^{II} complexes: $[Mn(L)][Ni(CN)_4] \cdot 2H_2O(1)[Mn(L)][Pd(CN)_4]$ (2) and $[Mn(L)][Pt(CN)_4]$ (3) (L=2,6-bis[1-(2-(N-methylamino)ethylimino)ethylipyridine). Single-crystal X-ray diffraction analysis shows their similar one-dimensional structure consisting of the alternating $[Mn(L)]^{2+}$ species and $[M(CN)_4]^{2-}$ building blocks, generating a cyanide-bridged neutral polymeric chain. In all three isostructural complexes the coordination geometry of manganese ion is a slightly distorted pentagonal-bipyramidal with the two cyanide nitrogen atoms at the *trans* positions and N5 coordinating mode at the equatorial plane from ligand L. Investigation over magnetic properties of these complexes reveals very weak antiferromagnetic interaction between neighboring Mn(II) ions bridged by the long NC-M-CN unit. A best-fit to the magnetic susceptibility of complexes 1-3 leads to the magnetic coupling constant of J=0.081, -0.103 and -0.14 cm⁻¹, respectively.

Keywords: Cyanide-bridged, heterometallic complex, crystal structure, magnetic property

1. Introduction

In the past several decades, the ultimate goal of crystal engineering is to directional design and construction of molecular crystals with new structures, properties and functions. During which, many effective strategies have been developed to rationally designing and controlling assembly of metal complexes with diversified topological structures and interesting properties. Among the various transition metal coordination systems, the rational design of the cyanide-bridged heterometallic complexes with target structure types have been given intense attention because not only the structures and the nature of the magnetic, optic and electric properties of corresponding complexes can be readily controlled and anticipated, but also the excellent stabilizing ability of cyanide group for many transition metal centers and oxidation states with or without the peripheral ligands. 1–23

As has been known, except the several factors from the cyanide precursor such as the number and position of cyanide group, number and nature of charge of cyanidecontaining building block, and steric effect of reactants that can be used to tune the structure of the cyanide-bridged complexes formed, the ancillary ligands attached to the counterpart assembling cations also play a crucial role for constructing cyanide-bridged complexes with different structures. The polyaza macrocyclic ligands with some rigid character obtained by condensation of 2,6-diacetylpyridine and polyamine, which are usually coordinated to the equatorial plane of metal ions with only two trans replaceable sites weakly bonded to other ligands, have proved to be good ancillary ligands to assemble low-dimensional structural cyanide-bridged complexes. ^{24–31} Interested also in these types of ligands, we have reported many cyanide-bridged bimetallic complexes by using cyanide precursors containing different cyanide groups. 32-36 Here, we investigated the reactions the Mn(II) compound based-on a semi-closed macrocyclic ligand L (L = 2,6-bis[1-(2-(N-methylamino)ethylimino)ethyl]pyridine) with three tetra-cyanometallates

$$\begin{array}{c|c}
N & & & \\
N & & \\
N$$

Scheme 1. The semi-closed macrocycle ligand and the cyanide precursors used to synthesize the complexes 1–3.

(Scheme 1), and obtained three one-dimensional cyanide-bridged heterobimetallic complexes with the formula $[Mn(L)][Ni(CN)_4] \cdot 2H_2O$ (1) $[Mn(L)][Pd(CN)_4]$ (2) and $[Mn(L)][Pt(CN)_4]$ (3). It should be mentioned that current complexes are the first one-dimensional example assembled from the semi-closed macrocyclic manganese compound. The synthesis, crystal structure and magnetic properties of all the three complexes are described in this paper.

2. Experimental Section

2. 1. Instruments

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed 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).

2. 2. General Procedures and Materials

All the reactions were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification. The [Mn(L)(H₂O)₂]Cl₂ were prepared by using the reported method for similar manganese macrocycle complex.³³

Caution! The cyanide compounds are hypertoxic and hazardous and they should be handled in small quantities with care.

2. 3. Preparation of Complexes 1–3

These three complexes were prepared using one similar three layers diffusion procedure, therefore only the synthesis of **1** is reported as a typical representative. A solution containing $K_2[Ni(CN)_4]$ (0.10 mmol, 24.1 mg) dis-

solved in 5 mL of water was laid in the bottom of a tube, upon which a mixture solvent of water and methanol with a ratio of 1:1 was carefully added. Then, a solution of $[Mn(L)]Cl_2$ (0.10 mmol, 40.1 g) in 5 mL of methanol was carefully added to the top of the mixture solvent layer above formed. About two weeks later, single yellow crystals suitable for X-ray diffraction were obtained from the interface, collected by filtration and dried in air. Yield: 35.5 mg, 67.1%. Anal. Calcd. for $C_{19}H_{29}MnN_9NiO_2$: C, 43.13; H, 5.52; N, 23.82. Found: C, 43.01; H, 5.45; N, 24.01. Main IR bands (cm⁻¹): 3255(s), 2915(m), 2845(m), 2153(s), 2125(s), 1650(m), 1594(m), 1455(m), 1370(m), 1190(m), 965(m).

Complex **2**: Yield: 30.8 mg, 57.1%. Anal. Calcd. for $C_{19}H_{25}MnN_9Pd$: C, 42.20; H, 4.66; N, 23.31. Found: C, 42.10; H, 4.61; N, 23.15. Main IR bands (cm⁻¹): 3257(s), 2910(m), 2850(m), 2150(s), 2120(s), 1652(m), 1590(m), 1458(m), 1377(m), 1197(m), 961(m).

Complex 3: Yield: 40.1 mg, 63.6%. Anal. Calcd. for $C_{19}H_{25}MnN_9Pt$: C, 36.25; H, 4.00; N, 20.02. Found: C, 36.14; H, 3.85; N, 19.81. Main IR bands (cm⁻¹): 3260(s), 2900(m), 2853(m), 2155 (s), 2123(s), 1658(m), 1597(m), 1452(m), 1375(m), 1191(m), 959(m).

2. 4. X-ray Data Collection and Structure Refinement

Single crystals of all complexes for X-ray diffraction analysis with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoK_α sealed tube ($\lambda = 0.71073 \text{ Å}$) at 293 K using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package. All the non-hydrogen atoms were refined with anisotropic displacement coefficients. 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 that were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. CCDC 1521398-1521400 for these three complexes contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via . Details of the crystal parameters, data collection, and refinement are summarized in Table 1.

3. Results and Discussion

3. 1. Synthesis and General Characterization

As has been known, the closed macrocycle ligand 3,6-diazaoctane-1,8-diamine and 3,6-dioxaoctano-1,8-

Table 1. Crystallographic data for complexes 1-3.

	1	2	3
Formula	$C_{19}H_{29}MnN_9NiO_2$	$C_{19}H_{25}MnN_9Pd$	$C_{19}H_{25}MnN_9Pt$
M	529.16	540.82	629.51
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c	C2/c
a/Å	18.1273(5)	11.3312(7)	11.3015(6)
b/Å	16.7829(5)	11.2415(6)	11.2472(6)
c/Å	7.7459(2)	17.4718(9)	17.4485(8)
α / °	90	90	90
!b/°	93.440(3)	91.187(6)	91.305(4)
γ / $^{\circ}$	90	90	90
V/Å ³	2352.28(11)	2225.1(2)	2217.3(2)
Z	4	4	4
F(000)	1100	1092	1220
GOF	1.038	1.049	0.995
$R_1[I > 2\sigma(I)]$	0.0350	0.0303	0.0332
wR_2 (all data)	0.0834	0.0751	0.0701

diamine are good auxiliary ligands for assembling cyanide-bridged magnetic complexes by incorporating some paramagnetic metal ions such as Mn(II), Fe(II) and Co(II), etc.^{24–31} With comparison to the above two macrocyclic ligands, the semi-closed pentadentate macrocycles ligand used here (Scheme 1) may have more flexibility due to its semi-open nature and the two pendulous methyl groups, which is maybe beneficial to produce single axial magnetic anisotropy for paramagnetic metal ions. As has been known, the Mn(II) ion in some complexes based-on aliphatic amines ligands can be easily oxidized to Mn(III) ion. However, the seven-coordinated Mn(II) species obtained by incorporating Mn(II) ion into these types of macrocyclic ligands are very robust and can be handled in air and in aqueous solution without being oxidized. Furthermore, the large equatorial steric effect from the macrocyclic ligand can effectively lower the dimensionality of the complexes formed, thus far more favoring of constructing functional complexes with low dimensional structure through replacing the two weakly bonded and replaceable ligands at the two trans positions. The reactions between the manganese(II) compound with the semi-closed macrocycle acting as auxiliary ligand and three tetra-cyanidemetallates result in three isostructural one-dimensional cyanide-bridged complexes. In the IR spectra of complexes 1-3 two sharp peaks due to the cyanide-stretching vibration were observed at about 2120 and 2150 cm⁻¹, respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes.

3. 2. Crystal Structures of Complexes 1–3.

Some important structural parameters for complexes **1–3** are collected in Table 2. The neutral binuclear independent unit, one-dimensional structure and the cell pac-

king diagram of compound 1 are shown in Figures 1–3, respectively, and the other compounds show similar structures. The calculated and measured partner of XPRD data for these three complexes is given in Figures S1–S3 (Supporting Information), respectively.

As can be found, complexes 1–3 possess similar one dimensional neutral single chain structure comprising of repeating $[-NC-M(CN)_2-CN-Mn(L)-]$ (M = Ni, Pd, Pt) unit. In these three complexes, each [M(CN)₄]²⁻ unit, acting as a bidentate ligand through it's a pair of trans cyanide groups, connects the Mn(II) ion of two independent semi-closed macrocyclic manganese units. The structure of these three complexes is very similar to the reported 1D linear chain complex $\{[Mn(L^1)][Fe(1-MeIm)(CN)_5]\}_n$, but different from $\{[Mn(L^1)(H_2O)][Mn(L^1)][Fe(CN)_6]\}_n$. $n(CH_4O)\cdot 3.5nH_2O$ and $\{[Mn(L^1)(H_2O)][Mn(L^1)][M'$ $(CN)_{8}$]_n · 4nH₂O, ³⁶ for the latter which can be structurally characterized as one-dimensional zig-zag chain structure. $(L^1 = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]$ octadeca-1(18),2,12,14,16-pentaene), M' = Mo, W). The $M\!\!-\!\!C_{bridged\text{-}CN}$ bond lengths and the $M\!\!-\!\!C\!\!\equiv\!\!N_{bridge}$ bond angles are almost equal to those corresponding parameters found in other non-bridged cyanide groups, demonstrating that the coordination or non-coordination of the N atom to the metal atom has no obvious influence on the geometry of the cyanide precursor.

The Mn(II) ion in complexes **1–3** is seven-coordinated forming a slightly distorted pentagonal-bipyramidal coordination geometry in which the five equatorial positions are occupied by N_5 unit coming from the semi-closed macrocyclic ligand and the two axial ones coordinated by two N atoms of cyanide groups. The distances between Mn ion and the equatorial N atoms in complexes **1–3** are almost equal to each other within the very narrow range 2.322(5)-2.383(2) Å (Table 2). The average Mn– $N_{cyanide}$ bond lengths in all these complexes are 2.257(2), 2.236(3)

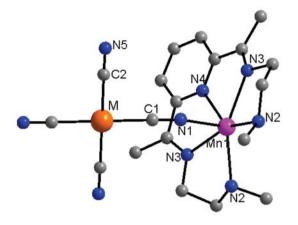


Figure 1. The representative neutral binuclear independent unit of complex **1**. All hydrogen atoms and solvent molecules have been omitted for clarity.

and 2.225(5) Å, respectively, slightly shorter than the Mn–N_{equatorial} bond lengths. As tabulated in Table 2, the bond angle of N1–Mn1–N2 are 176.74(9), 177.42(16) and 177.6(3)°, respectively, indicating the good linear configuration of these three atoms. However, the Mn–C \equiv N bond angle is somewhat bent with the values about 155°. The intramolecular Mn···Mn separation through the diamagnetic bridging cyanide precursor in **1–3** is 9.926, 10.476 and 10.450 Å, respectively.

3. 3. Magnetic Properties of Complexes 1–3.

The temperature dependence of magnetic susceptibility for complex 1 measured in the range of 2–300 K under the external magnetic field of 2000 Oe is showed in Fig. 4. For complexes 2 and 3 their temperature dependen-



Figure 2. The representative 1D structure of complex 1. All hydrogen atoms and solvent molecules have been omitted for clarity.

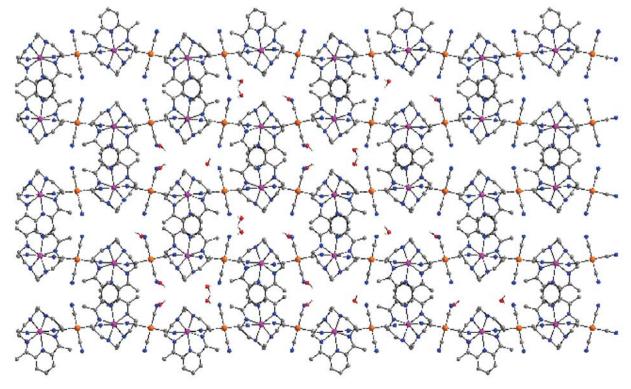


Figure 3. The cell packing diagram along b for complex 1. All the non-solvent hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

	1 (M = Ni)	2 (M = Pd)	3 (M = Pt)
Mn(1)–N(1)	2.257(2)	2.236(3)	2.225(5)
Mn(1)-N(2)	2.359(2)	2.322(5)	2.367(5)
Mn(1)-N(3)	2.366(2)	2.338(3)	2.342(6)
Mn(1)-N(4)	2.383(2)	2.378(3)	2.325(8)
M(1)– $C(1)$	1.871(3)	1.989(4)	2.007(6)
M(1)–C(2)	1.858(3)	1.996(5)	1.999(8)
C(1)–N(1)–Mn(1)	156.4(2)	155.2(3)	154.6(5)
N(1)-C(1)-M(1)	178.0(3)	177.6(3)	178.3(6)
$N(1)^{i}$ – $Mn(1)$ – $N(1)$	176.74(9)	177.42(16)	177.6(3)

Symmetry code: (i) -x + 3/2, -y + 3/2, -z + 1.

ce of magnetic susceptibilities is given in Figure S4 (Supporting Information). The changing tendency of $\chi_m T$ for these three complexes is comparatively similar. The $\chi_m T$ value at room temperature is 4.31, 4.30 and 4.29 emu K mol⁻¹ for complexes **1–3**, respectively, 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 $\chi_{\rm m}T$ value is with no obvious change from 300 to about 50 K. Below this temperature the $\chi_m T$ begins to decrease rapidly and reaches their lowest value of 1.73 for 1, 1.85 for 2 and 2.72 for 3 at 2 K, respectively. The magnetic susceptibility for these three complexes conforms well to Curie-Weiss law in a range of 2–300 K (the inset of Fig. 4) and gives the negative Weiss constant $\theta = -3.38$ K and Curie constant C = 4.17 emu K mol⁻¹ for 1, $\theta = -4.75$, C =4.20 emu K mol⁻¹ for **2** and $\theta = -1.16$, C = 3.99 emu K mol⁻¹ for 3. These results primarily show the antiferromagnetic magnetic coupling between the two Mn(II) centers bridged by [-NC-M-CN-] unit in these three complexes.

The magnetic data are analyzed by using the Hamiltonian: $\hat{H} = -2\sum J \hat{S}_i \hat{S}_{i+1}$. The temperature dependence of the magnetic susceptibility is given by the equation:^{37,38}

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

(Fisher's infinite chain model) with:

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

The least-squares fit to the data leads to J = -0.081 cm⁻¹, g = 1.99, $R = 1.19 \cdot 10^{-5}$ for $\mathbf{1}$, J = -0.103 cm⁻¹, g = 1.99, $R = 1.23 \cdot 10^{-5}$ for $\mathbf{2}$ and J = -0.14 cm⁻¹, g = 1.98, $R = 2.12 \cdot 10^{-5}$ for $\mathbf{3}$, respectively. These results reveal also the antiferromagnetic coupling between adjacent manganese ion bridged by the cyanide precursor and the small J value can be attributed to the long distance separated by the diamagnetic bridging unit. Both of the thermal magnetic behavior and the theoretical simulation results of the above three complexes are basically consistent with those

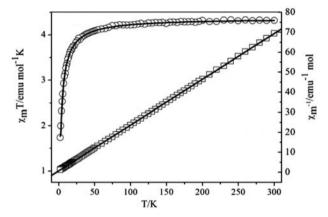


Figure 4. Temperature dependences of $\chi_m T$ -T (the solid line represents the best fit based on the parameters discussed in the text) for complex 1. Inset: Temperature dependences χ_m^{-1} -T (the solid line was calculated from the Curie-Weiss law).

found in the reported complexes assembled from the closed macrocyclic manganese compounds and other diamagnetic cyanometallates. 33,36

4. Conclusion

In summary, three new cyanide-bridged M(II)-Mn(II) (M = Ni, Pd, Pt) complexes structurally characterized as one-dimensional single chain have been synthesized with tetracyanide-containing precursor $K_2[M(CN)_4]$ as building blocks and semi-closed macrocycle ligand based manganese(II) compound as assemble segment. The magnetic studies demonstrate the weak antiferromagnetic interaction between the Mn(II)ions through [-NC-M-CN-] unit in all the three complexes. The current results and those reported recently 28,29 indicate that the semi-closed macrocycle mangaese(II) compound employed here is good candidate for assembling cyanidebridged heterometallic complexes with low dimensional structures and sometime interesting magnetic properties.

5. Acknowledgement

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Povzetek

Tri strukturne motive s štirimi ciano skupinami $K_2[M(CN)_4]$ (M=Ni, Pd, Pt) in manganovo(II) spojino s koordinacijskim številom sedem, ki vsebuje polzaprti makrociklični ligand, smo uporabili za pripravo mostovnih ciano heterokovinskih kompleksov in tako pripravili tri M^{II} — Mn^{II} komplekse s mostovno ciano skupino: $[Mn(L)][Ni(CN)_4] \cdot 2H_2O(1)$ $[Mn(L)][Pd(CN)_4]$ (2) in $[Mn(L)][Pt(CN)_4]$ (3) (L=2,6-bis[1-(2-(N-metilamino)etilimino)etilipiridin). Monokristalna rentgenska strukturna analiza razkrije podobno enodimenzionalno strukturo pri vseh treh spojinah zgrajeno iz izmeničnih $[Mn(L)]^{2+}$ in $[M(CN)_4]^{2-}$ strukturnih motivov, ki so povezani preko ciano mostov. Pri vseh treh izostrukturnih kompleksih je koordinacijska geometrija manganovega iona v obliki rahlo popačene pentagonalne bipiramide z dvema ciano dušikovima atomoma v *trans* položaju in z N5 koordinacijo liganda L v ekvatorialni legi. Raziskave magnetnih lastnosti teh kompleksov so razkrile zelo šibko antiferomagnetno interakcijo med sosednjimi Mn(II) ioni, ki so povezani preko daljših NC-M-CN enot. Na podlagi magnetne susceptibilnosti smo določili magnetne sklopitvene konstante za komplekse 1-3, ki so J = -0.081, -0.103 in -0.14 cm $^{-1}$.