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

Jingwen Shi,1 Chongchong Xue,1 Lingqian Kong2 and Daopeng Zhang1,*

1 College of Chemical Engineering, Shandong University of Technology, Zibo 255049, China
2 Dongchang College, Liaocheng University, Liaocheng 252059, P.R. China
* Corresponding author: E-mail: dpzhang73@126.com

Received: 13-12-2016

Abstract

Abstract: Three tetracyanide-containing building blocks $K_2[M(CN)_4]$ ($M = \text{Ni, Pd, Pt}$) and one semi-closed macrocyclic seven-coordinated manganese(II) compound have been employed to assemble cyanide-bridged heterometallic complexes, resulting in three cyanide-bridged $M^{II}$-$Mn^{II}$ complexes: $[\text{Mn(L)}][\text{Ni(CN)}_4] \cdot 2\text{H}_2\text{O}$ (1) $[\text{Mn(L)}][\text{Pd(CN)}_4]$ (2) and $[\text{Mn(L)}][\text{Pt(CN)}_4]$ (3) ($L = 2,6$-$\text{bis}[1-(2-(N$-$\text{methylamino)ethylimino)ethyl]pyridine}$). Single-crystal X-ray diffraction analysis shows their similar one-dimensional structure consisting of the alternating $[\text{Mn(L)}]^{2+}$ species and $[\text{M(CN)}_4]^{2-}$ 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 $-0.14 \text{ cm}^{-1}$, 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 cyanide-containing 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-diacetylpipidine and polyamine, which are usually coordinated to the equatorial plane of metal ions with only two trans replaceable sites weakly bonded to other ligands,24–31 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 ($L = 2,6$-$\text{bis}[1-(2-(N$-$\text{methylamino)ethylimino)ethyl]pyridine}$) with three teta-cyanometallates
Shi et al.: Three 1D cyanide-bridged M(Ni, Pd, Pt)-Mn(II) ...
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 pendent 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 macrocyclic 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 packing 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).

As can be found, complexes 1–3 possess similar one dimensional neutral single chain structure comprising of repeating [-NC–M(CN)5–CN–Mn(L)–] (M = Ni, Pd, Pt) unit. In these three complexes, each [M(CN)5]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')][Fe(1-MeIm)(CN)2]}₈, but different from {([Mn(L')(H₂O)][Mn(L')][Fe(CN)₅]₁₈, n(CH₃)₂O) · 3.5nH₂O] and {([Mn(L')(H₂O)][Mn(L')][M'C(N₅)]₈, 4nH₂O} for the latter which can be structurally characterized as one-dimensional zig-zag chain structure.

| 1                | 2                  | 3                  |
|------------------|--------------------|--------------------|
| Formula          | C₁₁₂H₁₇MnN₁₉NiO₂   | C₁₁₂H₁₉MnN₁₉Pd    | C₁₁₂H₁₉MnN₁₉Pt    |
| $M$              | 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)         |
| $\alpha$/°       | 90                 | 90                 | 90                 |
| $\beta$/°        | 93.440(3)          | 91.187(6)          | 91.305(4)          |
| $\gamma$/°       | 90                 | 90                 | 90                 |
| V/Å³             | 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              |
| $R_l$/$R_w$ (all data) | 0.0350            | 0.0303             | 0.0332             |
| $wR_f$ (all data) | 0.0834             | 0.0751             | 0.0701             |

As can be known, 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 macrocyclic 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 packing 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)5–CN–Mn(L)–] (M = Ni, Pd, Pt) unit. In these three complexes, each [M(CN)5]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')][Fe(1-MeIm)(CN)2]}₈, but different from {([Mn(L')(H₂O)][Mn(L')][Fe(CN)₅]₁₈, n(CH₃)₂O) · 3.5nH₂O] and {([Mn(L')(H₂O)][Mn(L')][M'C(N₅)]₈, 4nH₂O} for the latter which can be structurally characterized as one-dimensional zig-zag chain structure.

| 1                | 2                  | 3                  |
|------------------|--------------------|--------------------|
| Formula          | C₁₁₂H₁₇MnN₁₉NiO₂   | C₁₁₂H₁₉MnN₁₉Pd    | C₁₁₂H₁₉MnN₁₉Pt    |
| $M$              | 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)         |
| $\alpha$/°       | 90                 | 90                 | 90                 |
| $\beta$/°        | 93.440(3)          | 91.187(6)          | 91.305(4)          |
| $\gamma$/°       | 90                 | 90                 | 90                 |
| V/Å³             | 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              |
| $R_l$/$R_w$ (all data) | 0.0350            | 0.0303             | 0.0332             |
| $wR_f$ (all data) | 0.0834             | 0.0751             | 0.0701             |

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 N₈ 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–Ncyanide bond lengths in all these complexes are 2.257(2), 2.236(2)
and 2.225(5) Å, respectively, slightly shorter than the Mn–N<sub>equatorial</sub> 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)<sup>°</sup>, respectively, indicating the good linear configuration of these three atoms. However, the Mn–C≡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 1.** The representative neutral binuclear independent unit of complex 1. All hydrogen atoms and solvent molecules have been omitted for clarity.

**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.

---

Shi et al.: Three 1D cyanide-bridged M(Ni, Pd, Pt)-Mn(II) ...
The magnetic data are analyzed by using the Hamiltonian: $\hat{H} = -2\sum J S_i S_{i+1}$. The temperature dependence of the magnetic susceptibility is given by the equation:\cite{37,38}

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

(Fisher’s infinite chain model) with:

$$\mu = \coth[JS_{\text{eff}}(S_m+1)/KT] - [KT/JS_{\text{eff}}(S_m+1)]$$

(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 1, $J = -0.103$ cm$^{-1}$, $g = 1.99$, $R = 1.23 \cdot 10^{-5}$ for 2 and $J = -0.14$ cm$^{-1}$, $g = 1.98$, $R = 2.12 \cdot 10^{-5}$ for 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 found in the reported complexes assembled from the closed macrocyclic manganese compounds and other diamagnetic cyanometallates.\cite{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 assembly segment. The magnetic studies demonstrate the weak antiferromagnetic interaction between the Mn(II) ions through $[\text{–NC–M–CN–}]$ unit in all the three complexes. The current results and those reported recently\cite{28,29} indicate that the semi-closed macrocycle manganese(II) compound employed here is good candidate for assembling cyanide-bridged heterometallic complexes with low dimensional structures and sometime interesting magnetic properties.
5. Acknowledgement

This work was supported by the Natural Science Foundation of China (21171107 and 21671121).

6. References:

1. S. Ferlay, T. R. Mallah, P. Ouahès, M. V. Veillet, Nature 1995, 378, 701–703.
2. W. R. Entley, G. S. Girolami, Science 1995, 268, 397–400.
3. J. N. Rebilly, T. Mallah, Struct. Bond. 2006, 122, 103–131.
4. R. Lescouezec, L. M. Toma, J. Vaissermann, M. Verdaguer, F. S. Delgado, C. Ruiz-Perez, F. Lloret, M. Julve, Coord. Chem. Rev. 2005, 249, 2691–2729.
5. H. Miyasaka, A. Saitoh, S. Abe, Coord. Chem. Rev. 2007, 251, 2622–2664 and references therein.
6. O. Sato, T. Kawakami, M. Kimura, S. Hishiya, S. Kubo, Y. Einaga, J. Am. Chem. Soc. 2004, 126, 13176–13177.
7. L. M. Toma, R. Lescouezec, L. D. Toma, F. Lloret, M. Julve, J. Vaissermann, M. J. Andruh, J. Chem. Soc., Dalton Trans. 2002, 3171–3176.
8. L. M. C. Beltran, J. R. Long, Acc. Chem. Res. 2005, 38, 325–334.
9. S. S. Kaye, J. R. Long, J. Am. Chem. Soc. 2005, 127, 6506–6507.
10. K. W. Chapman, P. D. Southon, C. L. Weeks, C. J. Kepert, Chem. Commun. 2005, 3322–3324.
11. L. Jiang, X. L. Feng, T. B. Lu, S. Gao, Inorg. Chem. 2006, 45, 5018–5026.
12. J. Kim, H. S. Yoo, E. K. Koh, H. C. Kim, C. S. Hong, Inorg. Chem. 2007, 46, 8481–8483.
13. L. Jiang, H. J. Choi, X. L. Feng, T. B. Lu, J. R. Long, Inorg. Chem. 2007, 46, 2181–2186.
14. H. Miyasaka, A. Saitoh, S. Abe, Coord. Chem. Rev. 2007, 251, 2622–2644 and references therein.
15. K. R. Dunbar, R. A. Heintz, Prog. Inorg. Chem. 2009, 56, 155–334.
16. S. Wang, X. H. Ding, J. L. Zuo, X. Z. You, W. Huang, Coord. Chem. Rev. 2011, 255, 1713–1732.
17. S. Wang, X. H. Ding, Y. H. Li, W. Huang, Coord. Chem. Rev. 2012, 256, 439–464.
18. Y. H. Li, W. R. He, X. H. Ding, S. Wang, L. F. Cui, W. Huang, Coord. Chem. Rev. 2012, 256, 2795–2815.
19. T. Senapati, C. Pichon, R. Ababei, C. Mathonie`re, R. Cleirac, Inorg. Chem. 2012, 51, 3796–3812.
20. A. Panja, P. Guionneau, I. R. Jeon, S. M. Holmes, R. Cleirac, C. Mathonie`re, Inorg. Chem. 2012, 51, 12350–12359.
21. R. Ababei, C. Pichon, O. Roubou, Y. G. Li, N. Breìfuel, L. Buissong, P. Guionneau, C. Mathonie`re, R. Cleirac, J. Am. Chem. Soc. 2013, 135, 14840–14853.
22. D. P. Zhang, S. P. Zhuo, H. Y. Zhang, P. Wang, J. Z. Jiang, Dalton Trans. 2015, 44, 4655–4664.
23. D. P. Zhang, L. Q. Kong, H. Y. Zhang, Acta. Chim. Slov. 2015, 62, 219–224.
24. M. Mousavi, V. Beireau, C. Desplanches, C. Duhayonab, J. P. Sutter, Chem. Commun. 2010, 46, 7519–7521.
25. T. S. Venkatakrisman, S. Sahoo, N. Breìfuel, C. Duhayon, C. Paulsen, A. L. Barra, S. Ramasesha, J. P. Sutter, J. Am. Chem. Soc. 2010, 132, 6047–6056.
26. C. Parasciv, M. Andruh, Y. Journaux, Z. Za^k, N. Kyritsa-kas, L. Ricard, J. Mater. Chem. 2006, 16, 2660–2668.
27. G. Rombaut, S. Golhen, L. Ouahab, C. Mathonie`, O. Kahn, J. Chem. Soc, Dalton Trans. 2000, 3609–3614.
28. K. Qian, X. C. Huang, C. Zhou, X. Z. You, X. Y. Wang, K. R. Dunbar, J. Am. Chem. Soc. 2013, 135, 13302–13305.
29. S. L. Zhang, X. H. Zhao, X. Y. Wang, Dalton Trans. 2015, 44, 15189–15197.
30. F. Bonadio, M. C. Senna, J. Ensling, A. Sieber, A. Neels, H. Stockecll-Evans, S. Decurtins, Inorg. Chem. 2005, 44, 969–978.
31. D. P. Zhang, W. J. Si, P. Wang, X. Chen, J. Z. Jiang, Inorg. Chem. 2014, 53, 3494–3502.
32. D. P. Zhang, H. L. Wang, Y. T. Chen, Z. H. Ni, L. J. Tian, J. Z. Jiang, Inorg. Chem. 2009, 48, 5488–5496.
33. D. P. Zhang, H. L. Wang, L. J. Tian, J. Z. Jiang, Z. H. Ni, CryEngComm. 2009, 11, 2447–2451.
34. D. P. Zhang, Z. D. Zhao, P. Wang, X. J. Chen, J. Coord. Chem. 2012, 65, 2549–2560.
35. D. P. Zhang, Z. D. Zhao, P. Wang, X. Chen, Bull. Korean Chem. Soc. 2012, 33, 1581–1585.
36. H. Y. Zhang, C. C. Xue, J. W. Shi, H. Liu, Y. H. Dong, Z. D. Zhao, D. F. Zhang, J. Z. Jiang, Cryst. Growth Des. 2016, 16, 5753–5761.
37. O. Kahn, Molecular Magnetism, VCH, New York, 1993, 258.
38. M. E. Fisher, Am. J. Phys. 1964, 32, 343–346.

Povzetek

Tri strukturne motive s štirimi ciano skupinami $K_2[M(CN)_4]$ ($M = Ni, Pd, Pt$) in mangano(II) spojino s koordinacijskim številom sedem, ki vsebuje polzaprti makrociklični ligand, smo uporabili za pripravo mostovnih ciano heterokompleksov $[Mn(L)(Ni(CN)_4)]_2 \cdot 2H_2O$ (1) $[Mn(L)][Pd(CN)_4]_2$ (2) in $[Mn(L)][Pt(CN)_4]_2$ (3) (3 = 2,6-bis[1-(2-(N-metilamino)etilimino)etil]piridin). Monokristalna rentgenska strukturanaliza razkrije podobno enodimenzionalno strukturo pri vseh treh spojinah zgrajeno iz izmeničnih $[Mn(L)]^{2+}$ in $[Mn(CN)_4]^{2–}$ 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 duškovima 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 sodestojnimi Mn(II) ioni, ki so povezani preko dveh NL–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$^{-1}$.

Shi et al.: Three 1D cyanide-bridged M(Ni, Pd, Pt)-Mn(II) ...