

## Trinuclear Mn<sup>III</sup>-NC-Fe<sup>III</sup>-CN-Mn<sup>III</sup> Ferromagnetic System

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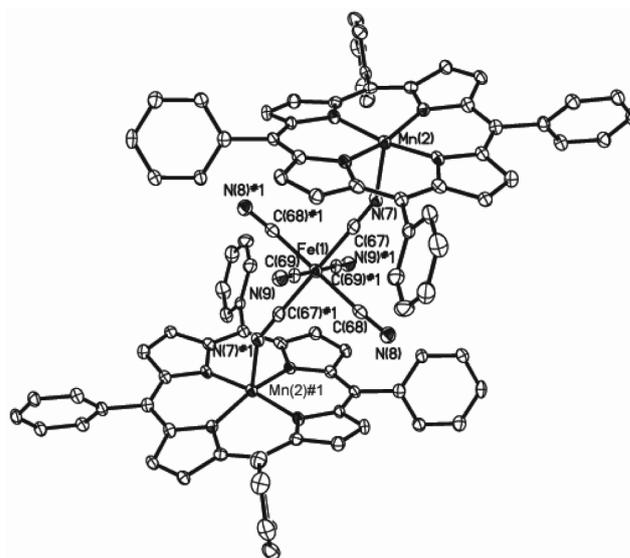
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Extended structures of magnetic centers linked by cyanides are of great importance in search of high-temperature ordering magnetic materials.<sup>1</sup> Transition metal cyanides are generally employed to produce various 1D, 2D and 3D magnetic structures.<sup>2</sup> Magnetic properties of metalloporphyrins coupled with numerous organic polynitrile bridges have been extensively studied by Miller *et al.*<sup>3</sup> However, metalloporphyrin systems bridged by metalloacyanides are unknown. Recently magnetic bimetallic coordination polymers containing metalloacyanide bridges have been reviewed.<sup>4</sup> The M<sub>A</sub>-CN-M<sub>B</sub>-NC- linkages turned out to be very useful for designing high *T<sub>c</sub>* complex-based magnets. Herein we describe the synthesis, characterization and temperature dependent magnetic study of new heterometallic trimer systems consisted of two cationic Mn(TPP)<sup>+</sup> centers connected by anionic Fe(CN)<sub>6</sub><sup>3-</sup> or Pd(CN)<sub>4</sub><sup>2-</sup>, where TPP is a 5,10,15,20-tetraphenylporphyrine.

The reaction between equimolar amounts of K<sub>3</sub>[Fe(CN)<sub>6</sub>] and [Mn(TPP)]ClO<sub>4</sub> only afforded a discrete trimer with a [Mn(TPP)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> countercation monomer, [Mn(TPP)(H<sub>2</sub>O)<sub>2</sub>][{Mn(TPP)}<sub>2</sub>{Fe(CN)<sub>6</sub>}]·8H<sub>2</sub>O·2CH<sub>3</sub>COCH<sub>3</sub> **1**<sup>5</sup>, instead of a variety of possible chain structures. No 1D polymer was observed in repeated experiments. Similar reaction between [Mn(TPP)]ClO<sub>4</sub> and K<sub>2</sub>[Pd(CN)<sub>4</sub>] produced [Mn(TPP)(H<sub>2</sub>O)<sub>2</sub>][Pd(CN)<sub>4</sub>]<sup>2-</sup>·2H<sub>2</sub>O·2CH<sub>3</sub>COCH<sub>3</sub> **2**<sup>6</sup>. The different products are raised by different anionic charge between Fe(CN)<sub>6</sub><sup>3-</sup> and Pd(CN)<sub>4</sub><sup>2-</sup>. However, the trinuclear structural motifs are same. Unlike organic nitrile bridging ligands, both Fe(CN)<sub>6</sub><sup>3-</sup> and Pd(CN)<sub>4</sub><sup>2-</sup> ions bridge two Mn(TPP)<sup>+</sup> moieties resulted in discrete heterometallic trinuclear complexes.

Both complexes were characterized by spectroscopic methods and X-ray crystallography. The IR spectra of **1** and **2** show ν(CN) bands at 2105 and 2136 cm<sup>-1</sup>, respectively. These values are shifted to lower wavenumbers relative to those of K<sub>3</sub>[Fe(CN)<sub>6</sub>] and K<sub>2</sub>[Pd(CN)<sub>4</sub>], which show 2117 and 2143 cm<sup>-1</sup>, respectively. These shifts indicate successful coordinations of the metalloacyanide ligands.<sup>7</sup> The molecular structure of the anionic moiety of **1**, [{Mn(TPP)}<sub>2</sub>{Fe(CN)<sub>6</sub>}]<sup>-</sup>, revealed by X-ray crystallography is shown in Figure 1. Because the trimer unit of **1** is a negatively

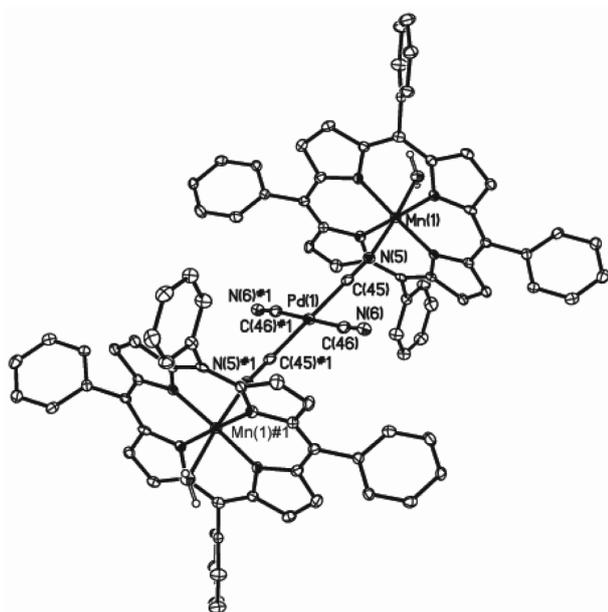


**Figure 1.** Crystal structure of an anionic trimer of **1** (30% probability). Selected bond lengths (Å) and angles (°): Fe(1)-C(67) 1.928(5), Fe(1)-C(68) 1.945(5), Fe(1)-C(69) 1.945(5), Fe(1)···Mn(2) 4.9983(7), Mn(2)-N(7) 2.116(3), N(7)-C(67) 1.160(5), N(8)-C(68) 1.161(5), N(9)-C(69) 1.163(5); C(67)-Fe(1)-C(67)<sup>#</sup> 180.00 (1), C(67)-Fe(1)-Mn(2) 165.97(13), Symmetry code #: 1-x, 1-y, 1-z.

charged, a countercation [Mn(TPP)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> locates near the trimer at perpendicular direction. The angle of TPP rings of the anionic trimer cluster and the TPP ring of [Mn(TPP)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> is 80.42(3)° from their best fitted planes. The coordination mode of cyanide to Mn(III) highly deviates from a linearity, ∠(C(67)-N(7)-Mn(2)) = 148.4(4)°. The bond distances between Mn(2) and N(7) is 2.116(3) Å. This bending can be attributed to the *sp*<sup>2</sup> type bonding character of the cyanides proposed by a previous report.<sup>8</sup> We believe this highly distorted structure and the size of Mn(TPP)<sup>+</sup> unit hinder the formation of a 1D chain structure.<sup>5</sup> However, the bond angle Fe(1)-C(67)-N(7), 177.6(4)°, is close to the linear value. Two acetone and eight water molecules were found in the crystal structure as solvates. They exhibited very complicated hydrogen bonds.

In addition to the ferricyanide system, we could obtain the tetracyano palladate(II) system and found that it formed a

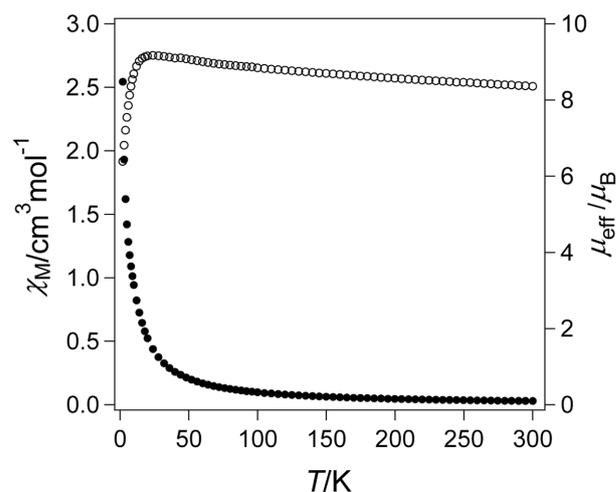
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**Figure 2.** Crystal structure of **2** (30% probability). Selected bond lengths (Å) and angles (°): Pd(1)-C(45) 2.007(5), Pd(1)-C(46) 2.000(6), Mn(1)-N(5) 2.225(5), Mn(1)-O(1) 2.298(3), N(5)-C(45) 1.153(5), N(6)-C(46) 1.150(5), C(46)-Pd(1)-C(46)<sup>#</sup> 180.00(1), C(45)-Pd(1)-C(46) 91.99(19), N(1)-Mn(1)-N(5) 89.45(14), N(3)-Mn(1)-N(5) 95.40(14), N(4)-Mn(1)-N(5) 88.04(14), N(1)-Mn(1)-O(1) 87.49(13), Symmetry code #: -x, -y, -z.

similar discrete neutral heterotrimetallic compound instead of polymeric structures. The crystal structure of **2** is depicted in Figure 2. The Mn(TPP)<sup>+</sup> moieties of the trimers show highly distorted saddle-type structures in both **1** and **2**. The r.m.s. deviation of the TPP ring of anionic moiety of **1** [ $\{\text{Mn}(\text{TPP})\}_2\{\text{Fe}(\text{CN})_6\}^-$ ] is 0.2372 Å. The distance of Mn(2) to the best plane is 0.2080(9) Å. On the other hand, the r.m.s. deviation of the TPP ring of  $[\text{Mn}(\text{TPP})(\text{H}_2\text{O})_2]^+$  moiety is only 0.0401 Å. For **2**, the r.m.s. deviation of the TPP ring is 0.1892 Å.

In order to evaluate the magnetic property of **1**, thermal magnetic susceptibilities of **1** were measured on a SQUID magnetometer in the temperature range 2–300 K. A plot of  $\chi_M$  vs.  $T$  for **1** ( $H = 500$  Oe) is shown in Figure 3, where  $\chi_M$  is the molar magnetic susceptibility of the single crystals of the ion pair. **1** shows a ferromagnetic interaction above 24 K (9.17  $\mu_B$  at 24 K) and drops of magnetic momentum below 24 K. The drops seem to be caused by zero-field splitting of Mn<sup>III</sup> ions.<sup>5</sup> However, intermolecular antiferromagnetic interactions should not be ruled out. The room temperature value, 8.36  $\mu_B$  (8.74  $\text{cm}^3 \text{K mol}^{-1}$ ), is slightly smaller than the expected uncoupled value of  $\{\text{HS Mn}^{\text{III}} + \text{LS Fe}^{\text{III}} + \text{HS Mn}^{\text{III}}\}$  trinuclear cluster unit and a HS Mn<sup>III</sup> cationic unit, 8.66  $\mu_B$  (9.38  $\text{cm}^3 \text{K mol}^{-1}$ ). Such a smaller value is often observed on Mn<sup>III</sup> compounds which have small  $g$  values ( $< 2.00$ ). In fact, the ferromagnetic interaction between HS Mn<sup>III</sup> ( $S = 2$ ) and LS Fe<sup>III</sup> ( $S = 1/2$ ) through cyanide-bridge was previously observed by Miyasaka *et al.* and Choi *et al.*<sup>7</sup> The magnetic susceptibility above 40 K of **1** follows Curie-Weiss law ( $\chi_M = C/(T-\theta)$ ) with a positive Weiss constant,  $\theta$ ,



**Figure 3.** Temperature dependence of the magnetic susceptibility of **1**,  $\chi_M$  (●) and  $\mu_{\text{eff}}$  (○).

of 12.01 K and  $C$  is 8.53  $\text{cm}^3 \text{K mol}^{-1}$ . The positive Weiss constant indicates the ferromagnetic interaction between Mn<sup>III</sup> and Fe<sup>III</sup> centers.

In conclusion, we have prepared new metalloporphyrins bearing a metallocyanide bridging ligand and studied the thermal magnetic property of the Mn<sup>III</sup>-NC-Fe<sup>III</sup>-CN-Mn<sup>III</sup> system which shows a ferromagnetic behavior above 24 K.

## References

- (a) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283. (b) Kahn, O. *Nature* **1999**, *399*, 22. (c) Ovcharenko, V. I.; Sagdeev, R. Z. *Russ. Chem. Rev.* **1999**, *68*, 345.
- Gadet, V.; Mallah, T.; Castro, I.; Verdaguer, M.; Veillet, P. *J. Am. Chem. Soc.* **1992**, *114*, 9213.
- Rittenberg, D. K.; Sugiura, K.-i.; Arif, A. M.; Sakata, Y.; Incarvito, C. D.; Rheingold, A. L.; Miller, J. S. *Chem. Eur. J.* **2000**, *6*, 1811.
- Ohba, M.; Ōkawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313.
- Synthesis of **1**: A solution of Mn(TPP)ClO<sub>4</sub> (38 mg, 0.05 mmol) in 10 mL acetone was mixed with an aqueous methanol solution (10 mL) of K<sub>3</sub>[Fe(CN)<sub>6</sub>] (16.5 mg, 0.05 mmol) and the reaction mixture was subsequently heated at 60 °C under N<sub>2</sub> atmosphere for 1 h (dark condition). The resulting solution was filtered on a frit and stored at -20 °C for several days. Dark green platelets were obtained which were X-ray quality crystals (16 mg). Calc. for C<sub>144</sub>H<sub>116</sub>FeMn<sub>3</sub>N<sub>18</sub>O<sub>12</sub> (**1**) C, 68.87; N, 10.04; H, 4.66. Found: C, 68.57; N, 10.46; H, 4.35%. IR (KBr, cm<sup>-1</sup>):  $\nu(\text{CN})$ , 2105. M.p. > 260 °C (decomposed). CCDC 239764.
- Synthesis of **2**: A solution of Mn(TPP)ClO<sub>4</sub> (38 mg, 0.05 mmol) in 20 mL acetone was mixed with an aqueous methanol solution (30 mL, 1/2 vol%) of K<sub>2</sub>[Pd(CN)<sub>4</sub>] (17 mg, 0.05 mmol) and the reaction mixture was subsequently heated at 60 °C under N<sub>2</sub> atmosphere for 1 h (dark condition). Upon cooling of the reaction solution, small needles were grown immediately. The resulting solution was filtered on a frit and stored at -20 °C for 1 h. Calc. for C<sub>98</sub>H<sub>76</sub>Mn<sub>2</sub>N<sub>12</sub>O<sub>6</sub>Pd (**2**) C, 67.88; N, 9.69; H, 4.42. Found: C, 68.04; N, 10.18; H, 4.17%. IR (KBr, cm<sup>-1</sup>):  $\nu(\text{CN})$ , 2136. CCDC 239765.
- (a) Miyasaka, H.; Matsumoto, N.; Ōkawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. (b) Choi, H. J.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2004**, *43*, 1606.
- Lim, B. S.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 4898.