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mer-[Fe(pcq)(CN)$_3$]$^-$: A Novel Cyanide-Containing Building Block and Its Application to Assembling Cyanide-Bridged Trinuclear $Fe^{III}{}_2Mn^{II}$ Complexes [pcq$^-$ = 8-(Pyridine-2-carboxamido)quinoline Anion]

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A new cyanide-containing building block K[Fe(pcq)(CN)$_3$] [**1**; pcq$^-$ = 8-(pyridine-2-carboxamido)quinoline anion] containing a low-spin Fe^{III} center with three cyanide groups in a meridional arrangement has been successfully designed and synthesized. Three cyanide-bridged trinuclear $Fe^{III}{}_2Mn^{II}$ complexes, [Fe(pcq)(CN)$_3$]$_2$[Mn(CH$_3$OH)$_2$(H$_2$O)$_2$]·2H$_2$O (**2**), [Fe(pcq)(CN)$_3$]$_2$[Mn(bipy)$_2$]·CH$_3$OH·2H$_2$O (**3**), and [Fe(pcq)(CN)$_3$]$_2$[Mn(phen)$_2$]·CH$_3$OH·2H$_2$O (**4**), have been synthesized and structurally characterized. The magnetic susceptibilities of the three heterometallic complexes have been investigated.

The synthesis and magnetism of metal−cyanide clusters have currently attracted extensive interest in order to fully understand the magnetostructural correlations in these species.[1]

Recently, the employment of versatile cyanide-containing building blocks $[M(L)_x(CN)_y]^{q-}$ (M = Fe^{III}, Cr^{III}, Ru^{III}, Re^{II}, and Co^{II}; L = blocking ligands)[1−16] in place of the commonly used cyanometalates $[M^{III}(CN)]_6{}^{3-}$ (M = Fe, Cr, Mn)[17] and $[M^{V}(CN)]_8{}^{3-}$ (M = W, Mo)[18] seems to be an interesting strategy for assembling heterometallic polynuclear complexes because $[M(L)_x(CN)_y]^{q-}$ can readily control nuclearity,

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(1) (a) Toma, L.; Lescouëzec, R.; Vaissermann, J.; Delgado, F. S.; Ruiz-Pérez, C.; Carrasco, R.; Cano, J.; Lloret, F.; Julve, M. *Chem.*—*Eur. J.* **2004**, *10*, 6130. (b) Zhang, Y.-Z.; Gao, S.; Wang, Z.-M.; Su, G, Sun, H.-L.; Pan, F. *Inorg. Chem*. **2005**, *44*, 4534. (c) Ni, Z.-H.; Kou, H.-Z.; Zheng, L.; Wang, R.-J.; Cui, A.-L.; Sato, O. *Inorg. Chem*. **2005**, *44*, 2050.

(2) (a) Beltran, L. M. C.; Long, J. R. *Acc. Chem. Res*. **2005**, *38*, 325. (b) Rebilly, J.-N.; Catala, L.; Rivière, E.; Guillot, R.; Wernsdorfer, W.; Mallah, T. *Inorg. Chem*. **2005**, *44*, 8194.

(3) (a) Lescouëzec, R.; Vaissermann, J.; Toma, L. M.; Carrasco, R.; Lloret, F.; Julve, M. *Inorg. Chem*. **2004**, *43*, 2234. (b) Lescouëzec, R.; Vaissermann, J.; Lloret, F.; Julve, M.; Verdaguer, M. *Inorg. Chem*. **2002**, *41*, 5943. (c) Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M. *Inorg. Chem*. **2002**, *41*, 818.

(4) (a) Schelter, E. J. Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc*. **2004**, *126*, 15004. (b) Karadas, F.; Schelter, E. J.; Prosvirin, A. V.; Bacsa, J.; Dunbar, K. R. *Chem. Commun*. **2005**, 1414.

(5) (a) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000. (b) Schilt, A. A. *Inorg. Chem.* **1964**, *3*, 1323.

(6) (a) Yeung, W.-F.; Man, W.-L.; Wong, W.-T.; Lau, T.-C.; Gao, S. *Angew. Chem., Int. Ed*. **2001**, *40*, 3031. (b) Yoon, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem*. **2005**, *44*, 7714. (c) Yeung, W.-F.; Lau, P.-H.; Lau, T.-C.; Wei, H.-Y.; Sun, H.-L.; Gao, S.; Chen, Z.-D.; Wong, W.-T. *Inorg. Chem.* **2005**, *44*, 6579.

(7) (a) Oshio, H.; Tamada, O.; Onodera, H.; Ito, T.; Ikoma, T.; Tero-Kubota, S. *Inorg. Chem.* **1999**, *38*, 5686. (b) Oshio, H.; Onodera, H.; Ito, T. *Chem.*—*Eur. J.* **2003**, *9*, 3946.

(8) (a) Kim, J.; Han, S.; Cho, I.-K.; Choi, K. Y.; Heu, M.; Yoon, S.; Suh, B. J. *Polyhedron* **2001**, *23*, 1333. (b) Wang, S.; Zuo, J.-L.; Zhou, H.-C.; Song, Y.; Gao, S.; You, X.-Z. *Eur. J. Inorg. Chem.* **2004**, 3681.

(9) (a) Ray, M.; Mukherjee, R.; Richardson, J.; Buchanan, F. R. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2451. (b) Ni, Z.-H.; Kou, H.-Z.; Zheng, L.; Zhao, Y.-H.; Zhang, L.-F.; Wang, R.-J.; Cui, A.-L.; Sato, O. *Inorg. Chem*. **2005**, *44*, 4728.

(10) (a) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656. (b) Wang, S.; Zuo, J.-L.; Zhou, H.-C.; Choi, H. J.; Ke, Y.; Long, J. R.; You, X.-Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 5940. (c) Li, D.; Parkin, S.; Wang, G.; Yee, G. T.; Prosvirin, A. V.; Holmes, S. M. *Inorg. Chem.* **2005**, *44*, 4903.

(11) (a) Lescouëzec, R.; Vaissermann, J.; Ruiz-Pérez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdaguer, M.; Dromzee, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed*. **2003**, *42*, 1483. (b) Toma, L. M.; Lescouezec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M. *Chem. Commun*. **2003**, 1850. (c) Wang, S.; Zuo, J.-L.; Gao, S.; Song, Y.; Zhou, H.-C.; Zhang, Y.-Z.; You, X.-Z. *J. Am. Chem. Soc.* **2004**, *126*, 8900.

(12) Zhang, Y.-Z.; Gao, S.; Sun, H.-L.; Su, G.; Wang, Z.-M.; Zhang, S. W. *Chem. Commun*. **2004**, 1906.

(13) Goto, M.; Koga, N.; Ohse, Y.; Kudoh, Y.; Kukihara, M.; Okuno, Y.; Kurosaki, H. *Inorg. Chem.* **2004**, *43*, 5120.

(14) (a) Hayami, S.; Gu, Z.-Z.; Einaga, Y.; Kobayasi, Y.; Ishikawa, Y.; Yamada, Y.; Fujishima, A.; Sato, O. *Inorg. Chem.* **2001**, *40*, 3240. (b) Matsuda, M.; Yamaura, J.-I.; Tajima, H.; Inabe, T. *Chem. Lett.* **2005**, *34*, 1524.

(15) Rotthaus, O.; Le Roy, S.; Tomas, A.; Barkigia, K. M.; Artaud, I. *Inorg. Chim. Acta* **2004**, *357*, 2211.

(16) Dutta, S. K.; Beckmann, U.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 3355.

(17) Ōkawa, H.; Ohba, M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1191.

(18) Sieklucka, B.; Podgajny, R.; Korzeniak, T.; Przychodzeń, P.; Kania, R. *C. R. Chim.* **2002**, *5*, 639.

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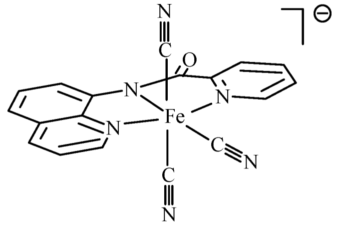
Chart 1. Structure of $[Fe(pcq)(CN)_3]^-$ in **1**



topology, and dimensionality. More importantly, some of resulting cyanide-bridged polynuclear complexes exhibit interesting single-molecule magnets.[4a,14] Apparently, this strategy opens a broad world for cyanide-bridged complexes because a larger number of $[M(L)_x(CN)_y]^{q-}$ building blocks can be designed by changing the ligand L. Nevertheless, until now only several such stable building blocks[1c,2−12] have been exploited to assemble magnetic complexes, and it remains a challenge to design and synthesize such building blocks.

Apparently, the stability is a key factor for the synthesis and application of $[M(L)_x(CN)_y]^{q-}$, which is determined by the blocking ligand L. Realizing that Julve's group and our group have respectively exploited the stable building blocks $[Fe(bpca)(CN)_3]^-$ and $[Fe(bpb)(CN)_2]^-$ [$bpca^-$ = bis(2-pyridylcarbonyl)amidate anion; bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate] containing large in-plane pyridine imide and pyridinecarboxamide ligands $bpca^-$ and bpb^{2-}, we introduced an asymmetric ligand 8-(pyridine-2-carboxamido)quinoline (Hpcq) containing a carboxamide group as well as a pyridine ring. A stable building block $K[Fe(pcq)(CN)_3]$ (**1**) with three cyanide groups in a meridional arrangement and the in-plane ligand pcq^- in the equatorial plane has been successfully synthesized, as shown in Chart 1. The reaction of **1** with $Mn(ClO_4)_2{\cdot}6H_2O$, $Mn(bipy)_2Cl_2$, and $Mn(phen)_2Cl_2$ led to three cyanide-bridged $Fe^{III}{}_2Mn^{II}$ clusters, **2**−**4** (Figure 1).

X-ray crystallography[19] shows that the crystal structures of **2**−**4** consist of one $[Mn(CH_3OH)_2(H_2O)_2]^{2+}$, $[Mn(bipy)_2]^{2+}$, or $[Mn(phen_2)]^{2+}$ and two $[Fe(pcq)(CN)_3]^-$ units, where each $[Fe(pcq)(CN)_3]^-$ unit acts as a monodentate ligand through one of its three cyanide groups cis toward the Mn^{II} ion, which are different from the one-dimensional ladder complex $\{[Mn(H_2O)_3][Fe(bpca)(CN)_3]\}[Fe(bpca)(CN)_3]$.[3a]

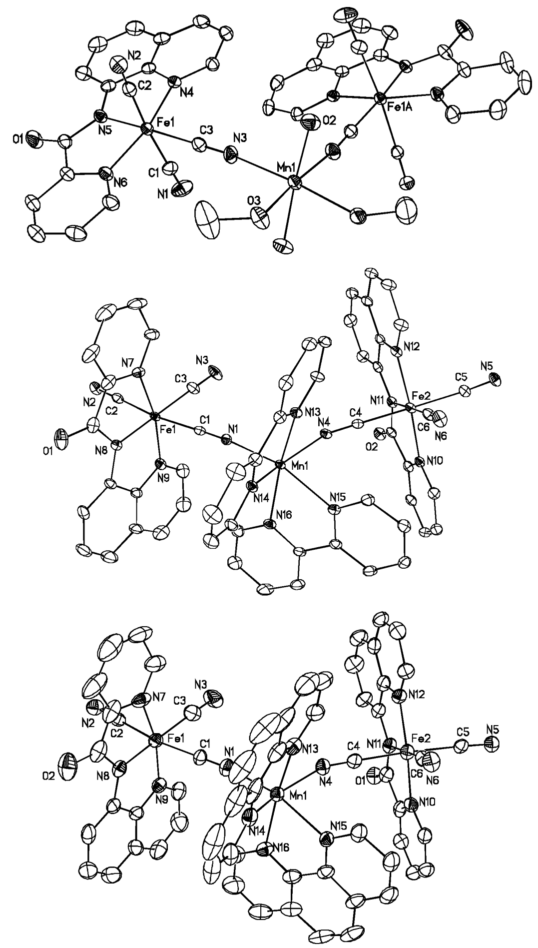


Figure 1. ORTEP plot of **2** (top), **3** (middle), and **4** (bottom) drawn at 30% probability thermal ellipsoid (hydrogen atoms and the solvate molecules are omitted for clarity).

The iron(III) ions in complexes **2**−**4** are coordinated by three pcq^- nitrogen atoms and three cyanide carbon atoms in a slightly distorted octahedral geometry. The iron(III) ions and the three chelating nitrogen atoms from the pcq^- ligand are practically planar. The Fe−C bond lengths range from 1.944(7) to 1.989(4) Å in the three complexes, which are in good agreement with those in the $[Fe^{III}(bpca)(CN)_3]^-$ and $[Fe^{III}(bpb)(CN)_2]^-$ compounds.[1c,3a,16] The $Fe-N_{amide}$ bond distances [1.869(5)−1.881(3) Å] are significantly shorter than those of $Fe-N_{pyridine}$ [1.953(3)−1.969(3) Å], indicating that the deprotonated amide group is a very strong σ donor. The $Fe-C\equiv N$ linkages are almost linear [175.3(6)−179.7(4)°].

The manganese atom in **2** is hexacoordinated with two water oxygen atoms at trans positions, two methanol oxygen atoms, and two cyanide nitrogen atoms, yielding MnN_2O_4 octahedral surroundings. The manganese atoms in **3** and **4** are coordinated by six nitrogen atoms, leading to MnN_6 octahedral surroundings. The average $Mn-N_{cyano}$ bond distances are 2.195(3) Å for **2**, 2.194(3) Å for **3**, and 2.174(5) Å for **4**. The $Mn-N\equiv C$ bond angle is 171.1(3)° for Mn1−N3−C3 in **2**, whereas the $Mn-N\equiv C$ bond angles in **3** and **4** are different: Mn1−N1−C1 = 172.5(3)° and Mn1−N4−C4 = 154.1(3)° for **3**; Mn1−N1−C1 = 173.0(5)° and Mn1−N4−C4 = 149.6(5)° for **4**. The intramolecular Fe- - -Mn separations through bridging cyanides are 5.279 Å for

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(19) Crystal data: **2** ($Fe_2MnC_{38}H_{36}N_{12}O_8$), M_w = 955.43, T = 293 K, monoclinic, space group $C2/c$, a = 21.125(16) Å, b = 14.483(10) Å, c = 15.061(12) Å, β = 113.302(3)°, U = 4232(5) Å^3, Z = 4, ρ_{calcd} = 1.499 g cm^{-3}, μ = 1.035 mm^{-1}, λ(Mo Kα) = 0.710 70 Å, 16 791 measured reflections, 4815 unique reflections, 3685 observed reflections [$I > 2\sigma(I)$]. R1 = 0.0510, wR2 = 0.1225 (all data), GOF = 1.108 based on 288 parameters. **3** ($Fe_2MnC_{57}H_{44}N_{16}O_5$), M_w = 1199.72, T = 293 K, monoclinic, space group $P2_1/a$, a = 17.477(3) Å, b = 16.156(3) Å, c = 18.996(4) Å, β = 101.6990(10)°, U = 5252.5(16) Å^3, Z = 4, ρ_{calcd} = 1.517 g cm^{-3}, μ = 0.850 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, 37 468 measured reflections, 10 113 unique reflections, 8582 observed reflections [$I > 2\sigma(I)$]. R1 = 0.0700, wR2 = 0.1877 (all data), GOF = 1.052 based on 739 parameters. **4** ($Fe_2MnC_{61}H_{44}N_{16}O_5$), M_w = 1247.76, T = 293 K, monoclinic, space group $P2_1/c$, a = 19.388(4) Å, b = 16.273(3) Å, c = 17.849(4) Å, β = 104.58(3)°, U = 5450.1(19) Å^3, Z = 4, ρ_{calcd} = 1.521 g cm^{-3}, μ = 0.822 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, 9533 measured reflections, 9533 unique reflections, 6397 observed reflections [$I > 2\sigma(I)$]. R1 = 0.0870, wR2 = 0.2337 (all data), GOF = 1.011 based on 766 parameters.

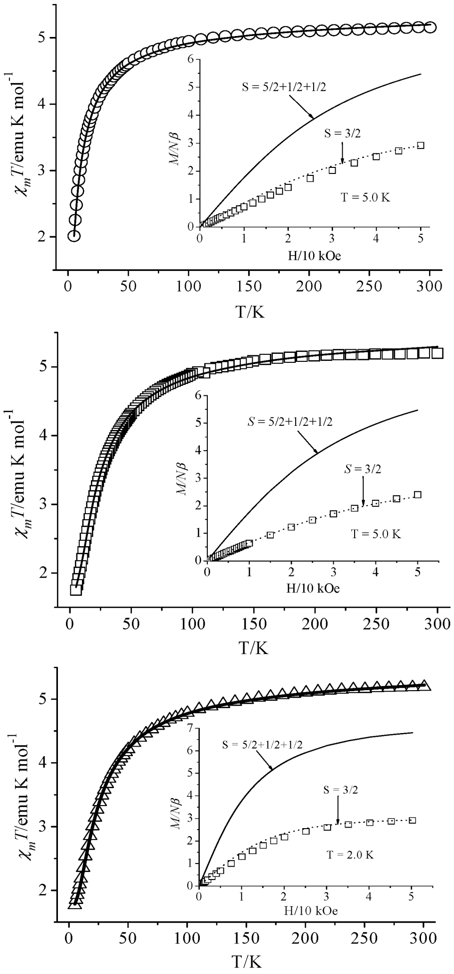

Figure 2. Temperature dependences of $\chi_m T$ for **2** (upper), **3** (middle), and **4** (below). The solid lines represent the best fit in the temperature range 5−300 K based on the parameters discussed in the text. Inset: Field dependences of magnetization. The lines represent the Brillouin functions that correspond to noninteracting $S = S_{Mn} + 2S_{Fe}$ (solid) and $S = {}^{3}/_{2}$ (dotted) with $g = 2.0$.

2, 5.294 Å (Mn1- - -Fe1) and 5.182 Å (Mn1- - -Fe2) for **3**, and 5.254 Å (Mn1- - -Fe1) and 5.101 Å (Mn1- - -Fe2) for **4**. The shortest intermolecular metal−metal separations are 6.932 Å for **2**, 7.783 Å for **3**, and 7.828 Å for **4**, respectively.

The temperature dependences of magnetic susceptibilities are measured in the temperature range 2−300 K for **1** (see S7 in the Supporting Information) and 5−300 K for **2**−**4** (Figure 2) in the applied field of 2000 Oe. The $\chi_m T$ value for **1** at room temperature (0.618 emu K mol^{-1}) together with the field dependence of magnetization at 2 K demonstrates the low-spin character of iron(III) in **1**, which is in good agreement with those reported for other low-spin cyano-containing mononuclear iron(III) species.[3] The orbital contribution to the magnetization should be responsible for the high room-temperature $\chi_m T$ value. The room-temperature $\chi_m T$ values of **2**−**4** are in a narrow range of 5.25−5.31 emu K mol^{-1}. Upon a lowering of the temperature, $\chi_m T$ decreases gradually until about 75 K for **2** and 100 K for **3** and **4** and then sharply decreases. This is characteristic of antiferromagnetic coupling in the three cyanide-bridged trimeric Fe$^{III}_2$-Mn^{II} clusters, which is also proven by the Brillouin curves (inset of Figure 2).

On the basis of the trimeric model, the magnetic susceptibilities of complexes **2**−**4** can be fitted accordingly by the following expression derived from the isotropic exchange spin Hamiltonian $H = -2JS_{Mn}(S_{Fe1} + S_{Fe2})$ for **2**−**4**. The best-fit parameters in the whole temperature range 5−300 K obtained are $J = -1.11(6)$ cm^{-1}, $g = 2.05(1)$, $zJ' = -0.39(2)$ cm^{-1}, and $R = \sum(\chi_{obsd}T - \chi_{cald}T)^2/\sum(\chi_{obsd}T)^2 = 2.94 \times 10^{-5}$ for complex **2**, $J = -3.73(3)$ cm^{-1}, $zJ' = -0.17(1)$ cm^{-1}, $g = 2.06(1)$, and $R = 3.23 \times 10^{-5}$ for complex **3**, and $J = -4.03(3)$ cm^{-1}, $zJ' = -0.15(1)$ cm^{-1}, $g = 2.05(1)$, and $R = 1.88 \times 10^{-5}$ for complex **4**, where zJ' accounts for the contributions except intramolecular magnetic coupling. Meanwhile, considering the difference in the bond angles of Mn−N≡C in **3** and **4**, we have tried to fit the magnetic susceptibilities of the two complexes using the CLUMAG program[20] on the basis of the Hamiltonian $H = -2J_1S_{Mn}S_{Fe1} - 2J_2S_{Mn}S_{Fe2}$. The fits above 20 K are satisfactory, giving the best-fit parameters $J_1 = -3.25(1)$ cm^{-1}, $J_2 = -5.10(1)$ cm^{-1}, $g = 2.07(1)$, and $R = 4.2 \times 10^{-4}$ for **3** and $J_1 = -3.10(1)$ cm^{-1}, $J_2 = -5.50(1)$ cm^{-1}, $g = 2.06$-(1), and $R = 2.4 \times 10^{-5}$ for **4** (see S8 in the Supporting Information). The averages of J_1 and J_2 are much close to the former J values.

The J values in **2**−**4** are comparable with each other and with those in the cyanide-bridged Fe^{III}Mn^{II} clusters.[3c,8,9b] The structural differences (coordination surroundings around the Mn^{II} ion, the bond bending of Mn−N≡C−Fe linkages, etc.) can answer for the slight variation of J in these complexes, which also can explain why the J values are almost the same for **3** and **4** with very similar molecular structure. The larger absolute J values in **3** and **4** probably correspond to the linear Mn−N≡C bond and the shorter Mn−N bond lengths that commonly enhance the antiferromagnetic coupling between Fe^{III} and Mn^{II} ions.

In summary, we have successfully designed and synthesized a novel asymmetric meridional tricyanide-containing building block **1** and obtained a new series of cyanide-bridged Fe$^{III}_2$Mn^{II} trinuclear complexes based on **1**. The present study further suggests that the pyridinecarboxamide ligand is suitable for the preparation of stable $[M(L)_x(CN)_y]^{q-}$ building blocks, which also opens a wider perspective for assembling novel magnetic heterometallic complexes.

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Supporting Information Available: X-ray crystallographic file (CIF), syntheses of **1**−**4**, cell packing diagrams of **2**−**4**, and magnetic data of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231. The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator formalism.