Molecular Wheels

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$[Mn^{III}(salen)]_6[Fe^{III}(bpmb)(CN)_2]_6 \cdot 7H_2O$: A Cyanide-Bridged Nanosized Molecular Wheel[**]

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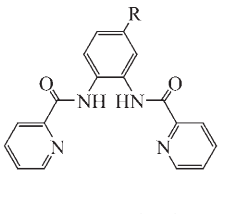
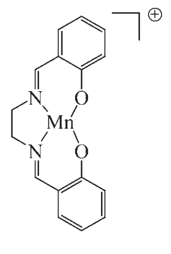
In the past decade, the design and synthesis of metallamacrocycles has attracted extensive interest in several research fields, including materials chemistry,[1] magnetochemistry,[2] supramolecular chemistry,[3] and molecular nanotechnology.[4] Many structurally appealing metallamacrocycles[1–8] have been synthesized and some unique physical properties have been observed to date. However, most of them are homometallic $[M–O]_n$,[2,3,5] $[M–N–O]_n$,[1,6] or $[M–N–N]_n$[7] cyclic clusters, which are easier to construct than heterometallic cycles. More significantly, as far as magnetic properties are concerned, homometallic compounds are usually antiferromagnetic and therefore in a low-spin ground state, which is unfavorable for single-molecule magnets (SMMs) because the observation of such phenomena requires a high-spin ground state and significant uniaxial magnetic anisotropy.[2,5,7]

As one of the more well-known linkers, the CN^- group has been used extensively to assemble heterometallic compounds because the topological structures and the nature of the magnetic interactions between different metal ions can be readily controlled and anticipated. Therefore, we have endeavored to synthesize large, cyanide-bridged, heterometallic cycles that might exhibit high-spin ground states and even single-molecule magnet behavior. Cyanide-bridged metallamacrocycles are still scarce, and only a few tetranuclear cyclic squares[9] have been synthesized by rational design.

Recently, we have shown that the use of the rigid building block *trans*-$[Fe^{III}(bpb)(CN)_2]^-$ (H_2bpb = 1,2-bis(pyridine-2-carboxamido)benzene) is a suitable strategy for the construction of low-dimensional heterometallic species.[10] In this study, we prepared a new cyanide-containing analog $[Fe^{III}(bpmb)(CN)_2]^-$ (H_2bpmb = 1,2-bis(pyridine-2-carboxamido)-4-methylbenzene).[11] We inferred that the reaction of $[Fe(bpb)(CN)_2]^-$ or $[Fe(bpmb)(CN)_2]^-$ with $[Mn(salen)]^+$ ($salen^{2-}$ = *N*,*N'*-ethylenebis(salicylideneaminato) dianion) might lead to a one-dimensional, polynuclear or metallacyclic compound. Indeed, we have successfully obtained a unique cyanide-bridged, dodecanuclear, nanosized molecular wheel $[\{Mn(salen)\}_6\{Fe(bpmb)(CN)_2\}_6] \cdot 7H_2O$ (**1**) with a repeating $[\text{-Fe-CN-Mn-NC-}]_6$ unit. Herein we report the synthesis of this novel metallamacrocycle together with the new one-dimensional chain complex $[\{Mn^{III}(salen)\}\{Fe^{III}(bpb)(CN)_2\}]_\infty$ (**2**). To the best of our knowledge, complex **1** is the largest cyanide-bridged heterometallic metallamacrocycle to date.



R = CH_3, H_2bpmb
R = H, H_2bpb



$[Mn(salen)]^+$

Compounds **1** and **2** were synthesized by the slow evaporation of a solution of equimolar amounts of $[Mn(salen)]ClO_4$ and $K[Fe(bpmb)(CN)_2]$ or $K[Fe(bpb)(CN)_2]$ in $MeOH/MeCN/H_2O$ (6:3:1) at room temperature. An X-ray single-crystal structural analysis[12] showed that complex **1** is comprised of six Mn^{III} and six Fe^{III} ions alternately bridged by cyanide ligands to give a centrosymmetrical, elliptical, dodecanuclear molecular wheel (Figure 1), while complex **2** has a neutral infinite chain structure in which alternating $[Fe(bpb)(CN)_2]^-$ and $[Mn(salen)]^+$ fragments are linked by the cyanide ligands in $[Fe(bpb)(CN)_2]^-$ (Figure 2).

All bond distances and bond angles in complexes **1** and **2** are in the normal range. The Fe–C bond lengths (1.941(6)–1.984(6) Å for **1** and 1.956(4)–1.990(4) Å for **2**) are in good agreement with those observed previously in related compounds.[10,11] The $Mn–N_{cyanide}$ bonds range from 2.258(5) to 2.354(4) Å for **1** and from 2.301(3) to 2.439(3) Å for **2**. The $Fe–C{\equiv}N$ bond angles in the two complexes are approximately linear (173.5(4)–178.2(5)°), except for $N2{\equiv}C2–Fe1$ in complex **1** (168.5(5)°). However, the $Mn–N{\equiv}C$ bond angles (140.8(4)–163.3(5)° for **1** and 151.8(3)–158.6(3)° for **2**) deviate significantly from strict linearity. The shortest intermolecular metal–metal separations are 6.808 and 5.387 Å for **1** and **2**, respectively. In addition, the cell packing diagram (Figure 3) of complex **1** along the *a* axis shows a highly ordered pattern.

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[**] This work was supported by the National Natural Science Foundation of China (project nos. 20201008 and 50272034) and the Fok Ying Tong Education Foundation. H_2bpmb = 1,2-bis(pyridine-2-carboxamido)-4-methylbenzene; $salen^{2-}$ = *N*,*N'*-ethylenebis(salicylideneaminato) dianion.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

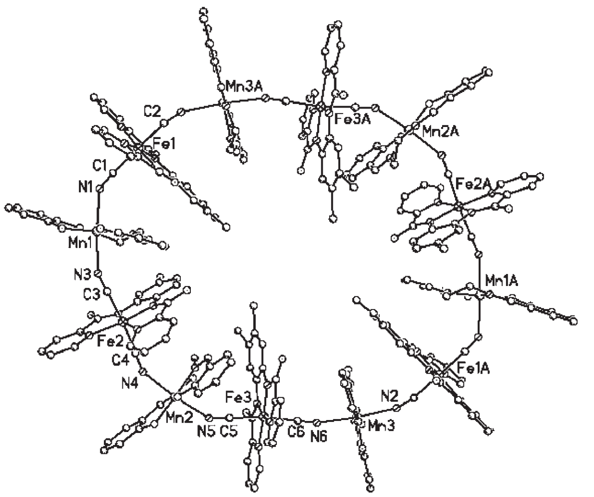

Figure 1. Structure of $[\{Mn(salen)\}_6\{Fe(bpmb)(CN)_2\}_6]\cdot7\,H_2O$ (**1**). All solvent molecules and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1–N1 2.354(4), Mn1–N3 2.322(4), Mn2–N4 2.290(5), Mn2–N5 2.258(5), Mn3–N2 2.327(5), Mn3–N6 2.309(5); Mn1–N1–C1 140.8(4), Mn1–N3–C3 151.7(4), Mn2–N4–C4 147.6(4), Mn2–N5–C5 147.8(4), Mn3–N6–C6 163.3(5), Mn3–N2–C2 158.0(4). Separations between opposite metal atoms [Å]: Fe1···Fe1a 21.152, Fe2···Fe2a 19.804, Fe3···Fe3a 17.728, Mn1···Mn1a 21.778, Mn2···Mn2a 19.776, Mn3···Mn3a 19.349.

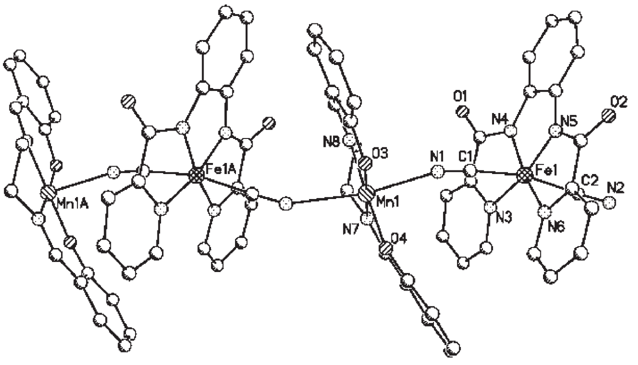

Figure 2. Structural unit of $[\{Mn(salen)\}\{Fe(bpb)(CN)_2\}]_\infty$ (**2**). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1–N1 2.301(3), Mn1–N2 2.439(3); Mn1–N1–C1 158.6(3), Mn1–N2–C2 151.8(3). The neighboring Fe···Mn distance is 5.280 Å.

It is worth noting that the largest intramolecular metal–metal distance is 2.178 nm, which corresponds to the major axis of the ellipse; the minor axis of the ellipse corresponds to a metal–metal separation of 1.773 nm, which indicates that complex **1** is a nanosized molecular wheel.

Similar to the wheel compounds previously reported,[1–8] the mechanism for the formation of wheel or chain structures is very subtle, and we have not yet been able to isolate the wheel compound containing $[Fe(bpb)(CN)_2]^-$ or the 1D compound with $[Fe(bpmb)(CN)_2]^-$. This indicates that only these two compounds are formed under the present synthetic conditions, as further proven by the powder XRD patterns (see Supporting Information). Steric effects are likely to be responsible for formation of the molecular wheel structure, although other factors (e.g. solvents) probably contribute. In this context, the study of the wheel-formation process and mechanism is worthwhile.

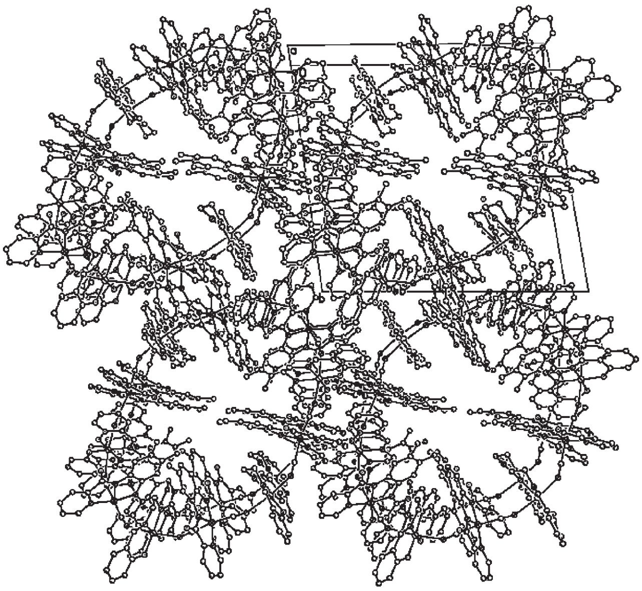

Figure 3. Cell packing diagram of complex **1** along the *a* axis showing the ordered architectural pattern.

The magnetic susceptibilities of complexes **1** and **2** were measured in the range 5–300 K in an external magnetic field of 1000 Oe. As shown in Figure 4, the room temperature $\chi_m T$ value for **1** is 20.3 emu K mol^{-1}, which is close to the spin-only value of 20.25 emu K mol^{-1} for six high-spin Mn^{III} ($S=2$) and six low-spin Fe^{III} ($S=1/2$) ions assuming that $g=2.00$. When the temperature is decreased, the $\chi_m T$ value of complex **1** gradually increases and reaches 29.64 emu K mol^{-1} at 5 K. The reciprocal magnetic susceptibilities in the 5–300 K range obey the Curie–Weiss law, with a Curie constant, C, of 20.06 emu K mol^{-1} and a Weiss constant, θ, of +3.5 K. The behavior of $\chi_m T$ and the positive Weiss constant confirm the presence of overall ferromagnetic interactions in complex **1**.

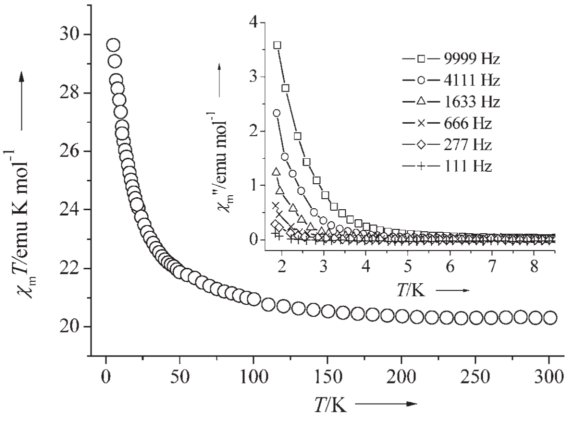

Figure 4. Temperature dependence of $\chi_m T$ for **1** at a field of 1000 Oe. Inset: the out-of-phase (χ_m'') signals in the ac susceptibility for **1**.

The field dependence of the magnetization for **1** at 2 K shows that the experimental values below 8 kOe are higher than the Brillouin curve corresponding to six noninteracting S_{Mn} and six S_{Fe} spins, thus confirming the overall ferromagnetic $\mathrm{Mn^{III}}$–$\mathrm{Fe^{III}}$ coupling (see Supporting Information). The high-field magnetization values are lower than calculated, which may be due to the zero-field splitting effect of $\mathrm{Mn^{III}}$.

For complex **2**, the room temperature $\chi_m T$ value is 3.45 emu K mol^{-1}, which is close to the spin-only value of 3.375 emu K mol^{-1} for one $\mathrm{Mn^{III}}$ ($S = 2$) and one $\mathrm{Fe^{III}}$ ($S = 1/2$) ion. As the temperature decreases, $\chi_m T$ remains nearly constant until about 50 K, and then decreases rapidly to 1.50 emu K mol^{-1} at 5 K (Figure 5). The Curie–Weiss law gives a Curie constant of 3.52 emu K mol^{-1} and a Weiss constant of -3.2 K. The field dependence of the magnetization for **2** shows that the experimental values are significantly lower than the Brillouin curve corresponding to one noninteracting S_{Mn} and one S_{Fe} spin, as displayed in the inset of Figure 5. This suggests an overall antiferromagnetic $\mathrm{Mn^{III}}$–$\mathrm{Fe^{III}}$ interaction in **2**. Similar to other cyanide-bridged high-spin $\mathrm{Mn^{III}}$ (d^4, $(t_{2g})^3(e_g)^1$) and low-spin $\mathrm{Fe^{III}}$ (d^5, $(t_{2g})^5$) systems, both ferromagnetic and antiferromagnetic contributions coexist. The overall magnetic interaction is determined by the coordination environment and configurations of the $\mathrm{Mn^{III}}$ and $\mathrm{Fe^{III}}$ ions to some extent. Therefore, the inversion of the magnetic coupling for **1** and **2** may be attributed to the different average Mn−N≡C angles of 151.4(5)° for **1** and 155.2(3)° for **2**, and the different linking of the $[\mathrm{Mn(salen)}]^+$ unit to the $[\mathrm{Fe(bpmb)(CN)_2}]^-$ or $[\mathrm{Fe(bpb)(CN)_2}]^-$ building blocks, which can alter the overlap between the magnetic orbitals.[13]

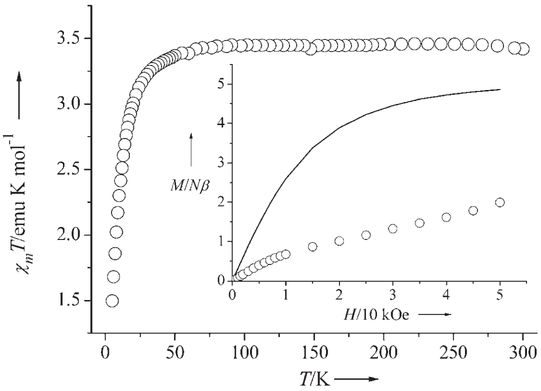

Figure 5. Temperature dependence of $\chi_m T$ for **2** at a field of 1000 Oe. Inset is the field dependence of the magnetization at 2.0 K. The line represents the Brillouin function that corresponds to noninteracting $S = S_{\mathrm{Mn}} + S_{\mathrm{Fe}}$ with $g = 2.0$.

As the largest cyanide-bridged, heterometallic, macrocyclic complex with ferromagnetic exchange between anisotropic $\mathrm{Mn^{III}}$ ions and low-spin $\mathrm{Fe^{III}}$ ions, **1** might represent a new type of SMM. One of the most important characteristics of an SMM is the observation of a frequency-dependent, out-of-phase (χ_m'') ac susceptibility signal. Thus, ac magnetic susceptibility measurements were performed in a 3 Oe ac field oscillating at 111–9999 Hz with a zero dc field (inset of Figure 4). Indeed, there is an obvious frequency-dependent χ_m'' signal below 4 K, along with a clear frequency-dependent decrease in the $\chi_m'T$ signals (see Supporting Information). These results are very similar to those observed for the recently published complexes $[\{\mathrm{Mn^{II}(tmphen)}\}_3\{\mathrm{Mn^{III}(CN)_6}\}_2]$[14a] (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline), $[\mathrm{(Tp)_8(H_2O)_6Cu^{II}{}_6Fe^{III}{}_8(CN)_{24}}]^{4+}$ ($\mathrm{Tp^-}$ = hydrotris(pyrazolyl)borate),[14b] $[\mathrm{Mn^{II}{}_4Mn^{III}{}_{22}(pdol)_{12}(\mu_3\text{-}CH_3O)_{12}(\mu_3\text{-}O)_{10}(\mu_4\text{-}O)_6(N_3)_6}]$ ($\mathrm{pdol^{2-}}$ = dipridylketonediolate ion),[14c] and $[\mathrm{Dy_6Mn_6(H_2shi)_4(Hshi)_2(shi)_{10}(CH_3OH)_{10}(H_2O)_2}]\cdot 9\,\mathrm{CH_3OH}\cdot 8\,\mathrm{H_2O}$[14d] ($\mathrm{H_3shi}$ = salicylhydroxamic acid), all of which have been considered as SMMs. Unfortunately, there is no maximum for the χ_m'' signals down to 2 K, and the observation of hysteretic behavior at 2 K was not possible. Thus, measurements are underway at lower temperatures to check hysteresis and to confirm whether the frequency dependence is in accord with Arrhenius-type behavior.

In summary, we have successfully synthesized a unique nanosized, dodecanuclear, molecular wheel that is the largest cyanide-bridged, heterometallic, supramolecular macrocycle known to date. Magnetic measurements indicate that **1** exhibits an interesting frequency-dependent ac magnetic susceptibility. The present study demonstrates that this synthetic route may be a promising approach to cyanide-bridged heterometallic macrocycles that may potentially exhibit SMM behavior. We are currently investigating other $\mathrm{Mn^{III}}$–Schiff base building blocks and various pyridine carboxamine ligands similar to $\mathrm{H_2bpb}$ and $\mathrm{H_2bpmb}$. Moreover, we will try to introduce other metal ions such as anistropic $\mathrm{Ru^{III}}$ and $\mathrm{Mn^{III}}$ into the system in place of the low-spin $\mathrm{Fe^{III}}$ ion, which may improve the magnetic properties.

Experimental Section

Complexes **1** and **2** were synthesized by the reaction of $[\mathrm{Mn(salen)}]\mathrm{ClO_4}$ (42.0 mg, 0.1 mmol) and $\mathrm{K[Fe(bpmb)(CN)_2]}$[11] (48.0 mg, 0.1 mmol) or $\mathrm{K[Fe(bpb)(CN)_2]}$[11] (46.5 mg, 0.1 mmol) in MeOH/MeCN/$\mathrm{H_2O}$ (10 mL, volume ratio 6:3:1) at room temperature. Uniform, well-shaped, red-brown single crystals were collected after about three days. Both **1** and **2** were isolated in high yield (ca. 60 %). $\mathrm{C_{220}H_{176}Fe_6Mn_6N_{48}O_{31}}$ (**1**) calcd: C 56.79, H 3.81, N 14.45; found: C 56.38, H 3.60, N 14.25. IR: $\tilde{\nu} = 2122$ (m, C≡N), 1622 cm^{-1} (vs, C=O). $\mathrm{C_{36}H_{26}FeMnN_8O_4}$ (**2**) calcd: C 58.01, H 3.52, N 15.03; found: C 57.65, H 3.57, N 15.07. IR: $\tilde{\nu} = 2134$(m, C≡N), 2109 (m, C≡N), 1619 cm^{-1} (vs, C=O).

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[12] Crystal data for **1**: $C_{220}H_{176}Fe_6Mn_6N_{48}O_{31}$, $M_w = 4652.83$, $T = 293$ K, triclinic, space group $P\bar{1}$, $a = 13.678(4)$, $b = 20.845(8)$, $c = 20.892(9)$ Å, $\alpha = 81.38(2)$, $\beta = 86.10(2)$, $\gamma = 76.84(2)°$, $U = 5731(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.348$ g cm^{-3}, $\mu = 0.762$ mm^{-1}, λ(Mo K$_\alpha$) = 0.71073 Å, 19761 unique reflections, 9621 observed reflections ($I > 2\sigma(I)$). $R1 = 0.0601$, $wR2 = 0.1571$ (all data), GOF = 0.998 based on 1403 parameters. **2**: $C_{36}H_{26}FeMnN_8O_4$, $M_w = 745.44$, $T = 293$ K, monoclinic, space group $P2_1/c$, $a = 9.2153(15)$, $b = 16.654(2)$, $c = 20.342(3)$ Å, $\beta = 93.664(15)°$, $U = 3115.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.589$ g cm^{-3}, $\mu = 0.928$ mm^{-1}, λ(Mo K$_\alpha$) = 0.71073 Å, 5473 unique reflections, 4125 observed reflections ($I > 2\sigma(I)$). $R1 = 0.0476$, $wR2 = 0.1604$ (all data), GOF = 1.067 based on 451 parameters. CCDC-279245 and -279246 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.

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