Molecular Wheels

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Reversible Size Modification of Iron and Gallium Molecular Wheels: A Ga_{10} "Gallic Wheel" and Large Ga_{18} and Fe_{18} Wheels**

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Complexes of high nuclearity, symmetry, and architectural beauty have long fascinated chemists, owing both to their aesthetically pleasing nature and to their often interesting properties. A particularly intriguing type within this class is the single-strand molecular wheel, whose prototype [{Fe-$(OMe)_2(O_2CCH_2Cl)$}$_{10}$] was dubbed the "ferric wheel"[1] and was also later reported with other carboxylates.[2] Many other Fe_x wheels have since been reported and now comprise the largest family of known molecular wheels.[3] There are, however, other examples composed of Co,[4] Cr,[2c,5] Cu,[6] Dy,[7] Mo,[8] Mn,[9] Ni[10] and V metal centers.[11]

Molecular wheels almost always contain an even number of metal ions, with nuclearities including 6,[3a,c] 8,[2e,3h,11a] 10,[2c,7] 12,[3g,6b,9d,10c] 16,[9c] 18,[12] 24,[10b] and 84;[9b] there are only a very few odd-membered wheels.[11b,13] Most even-membered wheels are antiferromagnetic with $S=0$ ground states,[2a,6b,14] and represent ideal model systems for the study of one-dimensional magnetism, magnetic anisotropy,[15] and quantum effects such as coherent tunneling of the Néel vector.[16] However, there are also many wheels with large S values, such as Ni_{12},[10c] Mn_{12},[9d] and Mn_{16} species,[9c] that are also single-molecule magnets (SMMs). Antiferromagnetic odd-membered wheels represent a simple system for studying spin frustration.[17] Multiple-strand, torus-shaped wheels are also known, such as Mn_{84},[9b] Mo_{154},[8] and Mo_{176} species.[8]

We have recently become interested in developing new synthetic routes to molecular wheels, but also in developing some level of control of the metal nuclearity (that is, the wheel size) for a given ligand type. Almost all wheel compounds were originally prepared serendipitously, but methods of deliberately altering the wheel size after the initial synthesis are very few and all based on a template approach. Saalfrank et al. elegantly showed that the size of certain Fe_x wheels could be controlled by the central Group 1 metal ion template around which the wheel forms, thus giving $\{Fe_6M\}$ for $M=Li^+$ or Na^+, but $\{Fe_8M\}$ for $M=Cs^+$.[18] Similarly, Winpenny, Timco, and co-workers found that the organic amine template controls the nuclearity of the M_x ($x=$ 8–10) homo- or heterometallic wheels.[19] Because almost all

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single-strand wheels are of nuclearity 12 or less and because a template approach is much less feasible for larger wheels (since it requires a correspondingly larger template), we have sought alternative means of modifying the wheel size. We report herein a) the first gallium(III) molecular wheels and b) a nontemplate route for reversibly interconverting the Ga and Fe wheel size between M_{10} and M_{18}. Result (b) arises from use of 1,3-propanediolate, a ligand type with little previous employment in metal chemistry.[20]

We suspected the Ga^{III} analogue of the "ferric wheel" should be accessible, and sought it from the reaction of $Ga(NO_3)_3$ with NaO_2CMe in a 1:1 ratio in MeOH. Diffusion of Et_2O into the resulting solution yielded colorless crystals of $[\{Ga(OMe)_2(O_2CMe)\}_{10}]\cdot x\,MeOH$ (**1**$\cdot x\,$MeOH) in 26% yield. The crystal structure of **1** (Figure 1)[21a] confirms the desired

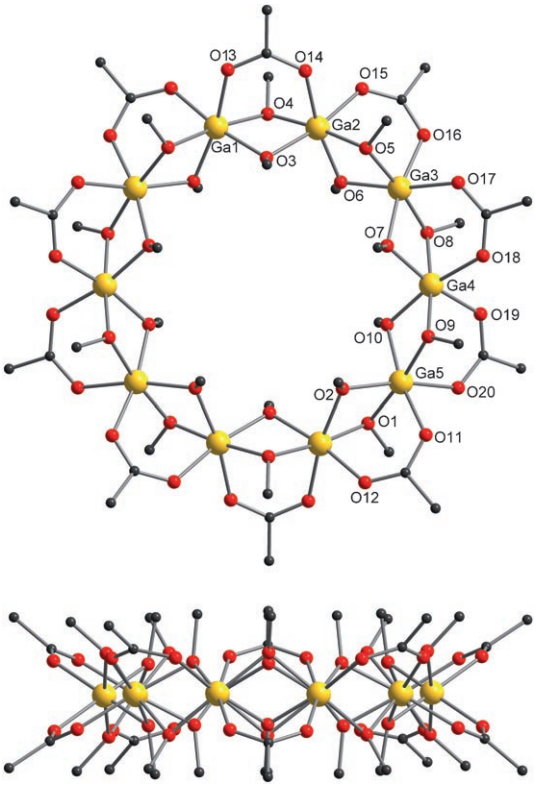

Figure 1. Top: Molecular structure of **1**. Bottom: Side view of **1** emphasizing the wheel planarity and O/Ga/O layered structure (Ga yellow, O red, C gray). Hydrogen atoms have been omitted for clarity.

"gallic wheel", which consists of ten Ga^{III} ions of near-octahedral geometry with each Ga_2 pair bridged by one $MeCO_2^-$ ligand and two MeO^- groups, thus isostructural with the "ferric wheels". The side view in Figure 1 shows the planar Ga_{10} unit sandwiched between two layers of O atoms.

We then undertook the challenge of altering the wheel size in a nontemplate manner. Figure 1 shows that the methoxide locations would allow a bulkier alkoxide ligand to be accommodated without requiring wheel expansion. We thus reasoned instead that if adjacent MeO^- groups were linked within a diolate group, this might affect the ring curvature and yield a bigger wheel. A smaller wheel seemed unlikely in view of the resulting steric congestion in the central hole. Of course, the extra restrictions imposed by the diolate group could instead lead to a nonwheel product, as nothing is guaranteed in synthetic chemistry. Nevertheless, we chose 1,3-propanediol (pdH_2) as the diol, and carried out the 1:1 reaction of $Ga(NO_3)_3$ with NaO_2CMe in pdH_2/MeCN, followed by diffusion of Et_2O into the resulting solution. Colorless crystals slowly grew to give the wheel complex $[Ga_{18}(pd)_{12}(pdH)_{12}(O_2CMe)_6(NO_3)_6](NO_3)_6\cdot x\,MeCN$ (**2**$\cdot x\,$MeCN) in 35% yield. The centrosymmetric cation of **2** (Figure 2)[21b] comprises 18 Ga^{III} ions linked through acetate, pd^{2-}, and pdH^- bridges to form a puckered wheel, which can be conveniently described as a hexagon of $\{Ga_3(pd)_2(NO_3)\}$ units (Ga9-Ga1-Ga2, Ga3-Ga4-Ga5, etc.) linked at each vertex by an acetate group and two pdH^- groups (Figure 2, bottom); the latter groups each bridge separate Ga_3 units with their deprotonated O atom and bind terminally with their protonated OH group. The central Ga ion (Ga1, Ga4, Ga7) of each

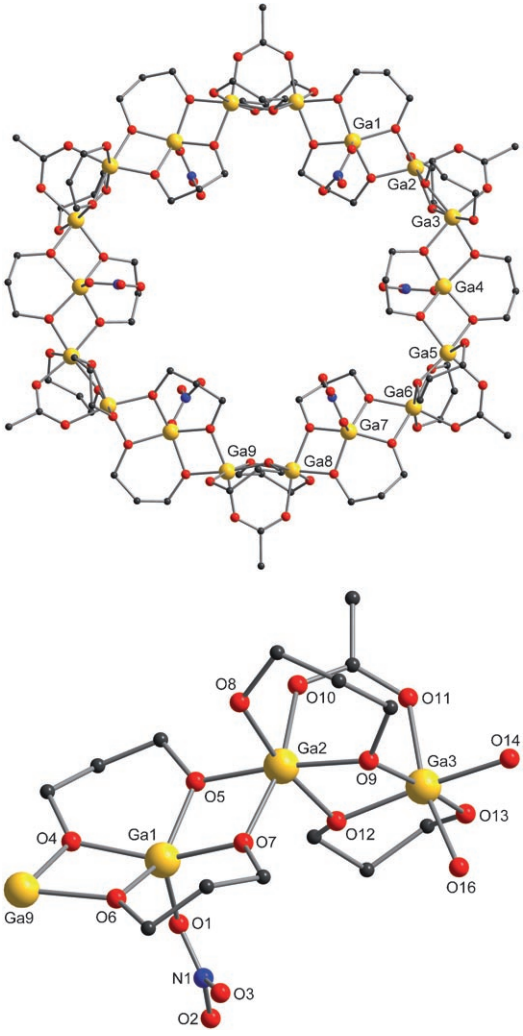

Figure 2. Top: Molecular structure of the cation of **2**. Bottom: Enlarged view of a trinuclear $\{Ga_3(pd)_2(NO_3)\}$ unit (Ga9/Ga1/Ga2) and the means of attachment to Ga3 of an adjacent unit(Ga yellow, O red, N blue, C gray). Hydrogen atoms have been omitted for clarity.

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near-linear Ga_3 unit (Ga-Ga-Ga 146.81–153.39°) exhibits square-pyramidal geometry, whereas the others have octahedral geometry. The pd^{2-} groups within each Ga_3 unit doubly bridge with each O atom, as seen previously in a Ga-Fe-Ga complex.[19b] Thus, although each pd^{2-} group did not merely replace two MeO^- groups of $[\{Ga(OMe)_2(O_2CMe)\}_{10}]$ (**1**) to give a larger $[\{Ga(pd)(O_2CMe)\}_x]$ wheel ($x > 10$), its restrictive diolate nature nevertheless did as we had hoped, but in a different way, and gave a large $[Ga_x(pd)_{2x/3}(pdH)_{2x/3}(O_2CMe)_{x/3}(NO_3)_{x/3}]_x^{6+}$ ($x = 18$) wheel.

Since pdH_2 gave a Ga_{18} wheel instead of Ga_{10}, we investigated whether it would similarly give an Fe_{18} wheel rather than Fe_{10}. Various carboxylates were explored, and benzoate gave the most crystalline product. Thus, the 1:1 reaction of $Fe(NO_3)_3 \cdot 9H_2O$ with NaO_2CPh in pdH_2/MeCN and subsequent diffusion of Et_2O into the yellow solution yielded yellow crystals of $[Fe_{18}(pd)_{12}(pdH)_{12}(O_2CPh)_6(NO_3)_6](NO_3)_6 \cdot x\,MeCN$ (**3**·*x* MeCN) in 87% yield. The cation of **3**[21c] is isostructural with **2**, except for the carboxylate identity (Figure 3). The cation of **3** thus joins $[Fe_{18}(OH)_6(OMe)_{24}(xdk)_6(O_2CMe)_{12}]$[12] (xdk = *m*-xylenediamine bis(Kemp's triacid imide) dianion) as the largest Fe^{III} wheels to date.

Wheels **1**–**3** are shown as space-filling representations in Figure 4. The Ga_{10} wheel **1** has a diameter of 16.7 Å, with a central hole of diameter 8.1 Å. The Ga_{18} wheel **2** is larger, with a diameter of 23.7 Å and a central hole of diameter 10.4 Å. The Fe_{18} wheel **3** is larger than **2** owing to the different carboxylate groups and has a diameter of 29.9 Å, but the central hole is very similar to that of **2** with a diameter of 10.7 Å. In all three complexes, there is no residual electron density in the central hole, and the wheels stack to form tubular channels.

We conclude that the M_{10} versus M_{18} wheel size is a result of the differing nature of MeO^- versus diolate bridges. In support of this conclusion, we successfully converted the M_{18} wheels into M_{10} by dissolution of **3** in MeOH; yellow needles slowly formed that were identified by elemental analysis and X-ray crystallography as $[Fe_{10}(OMe)_{20}(O_2CPh)_{10}]$ (**4**) in

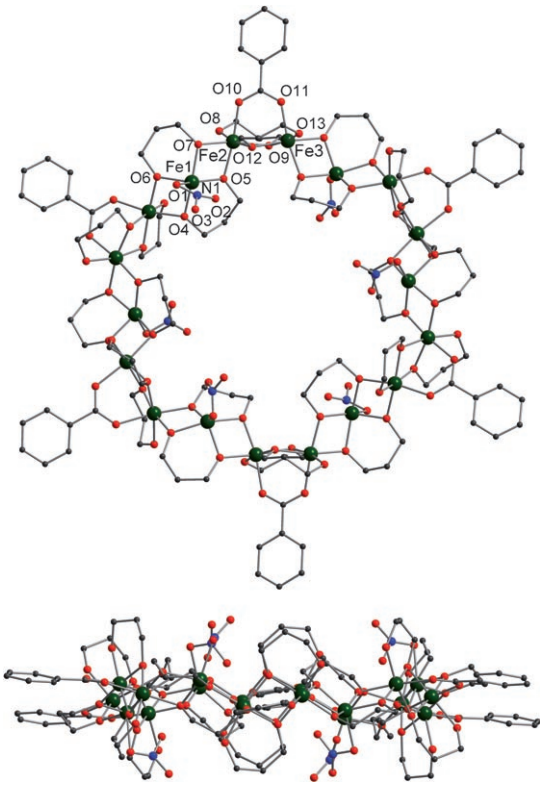

Figure 3. Top: Molecular structure of the cation of **3**. Bottom: Side view emphasizing the puckering (Fe green, O red, N blue, C gray). Hydrogen atoms have been omitted for clarity.

greater than 90% yield. Similar treatment of **2** gave white crystals of **1**. Thus, replacement of the pd^{2-} and pdH^- groups with MeO^- converts M_{18} wheels into M_{10}, consistent with this being the preferred size with methoxide. Similarly, dissolution of the Fe_{10} wheel in pdH_2/MeCN/$NaNO_3$ led to subsequent isolation of the corresponding Fe_{18} wheel in about 20% yield, but the product was contaminated with white solids. A cleaner conversion was achieved by addition of soluble $Fe(NO_3)_3$ to the Fe_{10} wheel in pdH_2/MeCN, which increased the yield of

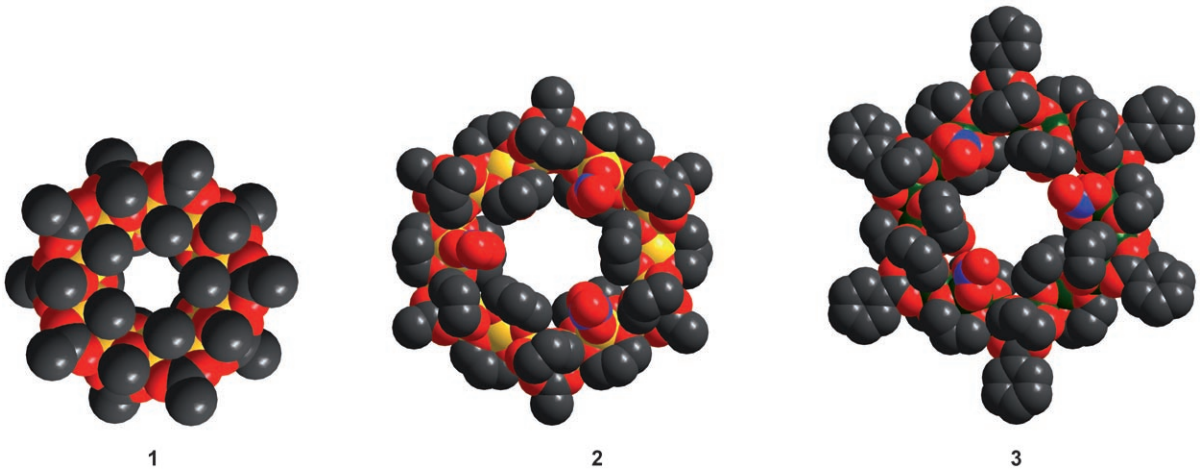

Figure 4. Comparison of the space-filling representations of compounds **1**, **2**, and **3** showing the differing interior cavity diameters (Ga yellow, O red, N blue, C gray, Fe green).

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the Fe_{18} wheel to 40%, presumably by helping sequester the carboxylate groups. The conclusion is again that the pd^{2-} group gives a larger wheel than methoxide.

Magnetic susceptibility (χ_M) measurements were performed on a vacuum-dried, polycrystalline sample of **3** in the 5.0–300 K range and in a 0.1 T magnetic field. The value of $\chi_M T$ decreases steadily with decreasing temperature from 29.22 $cm^3 mol^{-1} K$ at 300 K to 0.90 $cm^3 mol^{-1} K$ at 5.0 K (Figure 5). This trend indicates an $S = 0$ ground state, as expected for antiferromagnetic interactions between an even number of high-spin ($S = 5/2$) Fe^{III} ions.[2a,e,14]

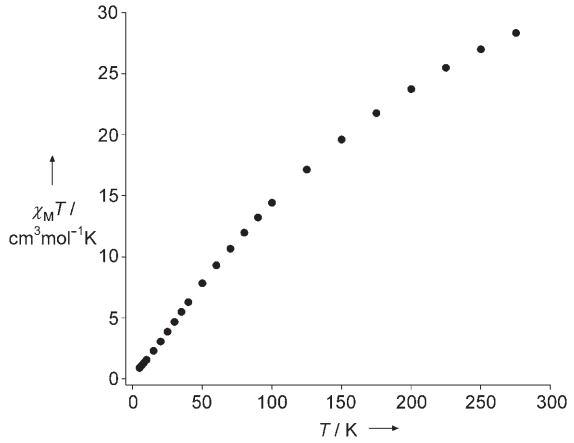

Figure 5. Plot of $\chi_M T$ versus T for complex **3**.

In conclusion, the first gallium wheels have been prepared, together with a nontemplate method for increasing the size of both Ga_{10} and Fe_{10} wheels. This procedure keeps the central cavity empty, imparting tubular channels to the crystal. The "gallic wheel" **1** is isostructural with the "ferric wheel",[1] and Ga_{18} and Fe_{18} are also isostructural, thus consistent with the similar chemistry of Fe^{III} and Ga^{III}. Moreover, M_{10} and M_{18} can be interconverted by alkoxide substitution. This work is currently being extended to other diols, such as 1,2-ethanediol and 1,4-butanediol.

Experimental Section

1: $Ga(NO_3)_3 \cdot x H_2O$ (0.051 g, 0.20 mmol) was added to a stirred solution of sodium acetate (0.016 g, 0.20 mmol) in MeOH (10 mL). The colorless solution was stirred for 10 min further and filtered, and the filtrate was layered with Et_2O. After one day, colorless crystals of $[Ga_{10}(OMe)_{20}(O_2CMe)_{10}] \cdot x$ MeOH were collected by filtration, washed with MeOH, and dried in vacuo. Yield: 26%. Elemental analysis (%) calcd for **1**: C 25.18, H 4.75; found: C 24.97, H 4.61. Selected IR data (KBr): $\tilde{\nu} = 3440$(w), 2940(m), 2833(s), 1633(m), 1551(s), 1452(s), 1384(s), 1052(m), 682(s), 621(s), 548(s), 507(s), 474(s), 425 cm^{-1} (s).

2: $Ga(NO_3)_3 \cdot x H_2O$ (0.051 g, 0.20 mmol) was added to a stirred solution of sodium acetate (0.016 g, 0.20 mmol) in pdH_2/MeCN (3 mL/20 mL). The solution was stirred for 10 min further and filtered, and the filtrate was layered with Et_2O. After one day, colorless crystals of $[Ga_{18}(O_2CMe)_6(pd)_{12}(pdH)_{12}(NO_3)_6](NO_3)_6 \cdot 12$ MeCN were collected by filtration, washed with MeCN, and dried in vacuo. Yield: 35%. The dried material is hygroscopic and was analyzed as $2 \cdot 6NO_3 \cdot 8H_2O$. Elemental analysis (%) calcd for $2 \cdot 6NO_3 \cdot 8H_2O$: C 23.53, H 4.47, N 3.92; found: C 23.37, H 4.27, N 3.75. Selected IR data (KBr): $\tilde{\nu} = 3391$(w), 2950(m), 2890(m), 1656(m), 1559(s), 1384(m), 1180(s), 1059(m), 979(s), 937(m), 825(s), 684(s), 527 cm^{-1} (w).

3: $Fe(NO_3)_3 \cdot 9H_2O$ (0.081 g, 0.20 mmol) was added to a stirred solution of sodium benzoate (0.029 g, 0.20 mmol) in pdH_2/MeCN (3 mL/20 mL). The yellow solution was stirred for 10 min further and filtered, and the filtrate was layered with Et_2O. After one day, yellow crystals of $[Fe_{18}(O_2CPh)_6(pd)_{12}(pdH)_{12}(NO_3)_6](NO_3)_6 \cdot 48$ MeCN had formed and were collected by filtration, washed with MeCN, and dried in vacuo. Yield: 87%. The dried material is hygroscopic and was analyzed as $3 \cdot 6NO_3 \cdot 10H_2O$. Elemental analysis (%) calcd for $3 \cdot 6NO_3 \cdot 10H_2O$: C 30.80, H 4.67, N 3.78; found: C 30.62, H 4.42, N 3.59. Selected IR data (KBr): $\tilde{\nu} = 3380$(w), 2944(m), 2864(m), 1647(m), 1592(s), 1527(s), 1493(s), 1404(s), 1384(s), 1352(s), 1177(s), 1122(s), 1050(s), 974(s), 936(m), 822(s), 722(s), 679(s), 538(m), 476 cm^{-1} (m).

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[21] a) Crystal structure data for **1**·*x*MeOH: $C_{40}H_{90}Ga_{10}O_{40}$ (without MeOH), $M_r = 1908.32$, monoclinic, space group $P2_1/n$, $a = 17.440(2)$, $b = 15.812(2)$, $c = 26.090(3)$ Å, $\beta = 99.000(3)°$, $V = 7106(16)$ Å^3, $T = 173$ K, $Z = 4$, $\rho_{calcd} = 1.784$ g cm^{-3}, 46564 reflections collected, 16196 unique ($R_{int} = 0.0929$), $R1 = 0.0435$, w$R2 = 0.1085$, using 16196 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of two half wheels and partial MeOH molecules above and below the plane of each. The latter represents a small fraction which could not be properly modeled or removed using the program SQUEEZE, a part of the PLATON package (PLATON: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 1–34) of crystallographic software, owing to the proximity to the wheel. b) Crystal structure data for **2**·*x*MeCN: $C_{114}H_{218}Ga_{18}N_{12}O_{96}$, $M_r = 4716.08$ (without MeCN), monoclinic, space group $P2_1/c$, $a = 17.8400(11)$, $b = 29.6264(19)$, $c = 18.4009(12)$ Å, $\beta = 103.615(2)°$, $V = 9452(1)$ Å^3, $T = 173$ K, $Z = 2$, $\rho_{calcd} = 1.657$ g cm^{-3}, 39439 reflections collected, 12350 unique ($R_{int} = 0.1205$), $R1 = 0.0529$, w$R2 = 0.1003$, using 12350 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of half of the Ga_{18} wheel, three nitrate anions, and approximately 6 MeCN molecules of crystallization. The latter were disordered and could not be modeled properly, thus the program SQUEEZE was used to calculate the area of solvent disorder and remove its contribution to the overall intensity data. The six pdH$^-$ hydroxyl protons of the asymmetric unit were located from a difference Fourier map and refined as riding on their parent O atoms. c) Crystal structure data for **3**·*x*MeCN: $C_{212}H_{342}Fe_{18}N_{60}O_{96}$, $M_r = 6272.76$ (without MeCN), rhombohedral, space group $R\bar{3}$, $a = 32.5526(19)$, $c = 20.503(2)$ Å, $\beta = 120°$, $V = 18816(3)$ Å^3, $T = 173$ K, $Z = 3$, $\rho_{calcd} = 1.661$ g cm^{-3}, 55780 reflections collected, 9578 unique ($R_{int} = 0.1061$), $R1 = 0.0469$, w$R2 = 0.1165$, using 9578 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of one-sixth of the Fe_{18} wheel (lying on S_6 symmetry axes), one nitrate anion and approximately 8 MeCN molecules of crystallization. The latter were disordered and could not be modeled properly, thus the program SQUEEZE was used to calculate the area of solvent disorder and remove its contribution to the overall intensity data. CCDC-609458–609460 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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