Cluster Compounds

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Covalently Linked Dimers of Clusters: Loop- and Dumbbell-Shaped Mn_{24} and Mn_{26} Single-Molecule Magnets**

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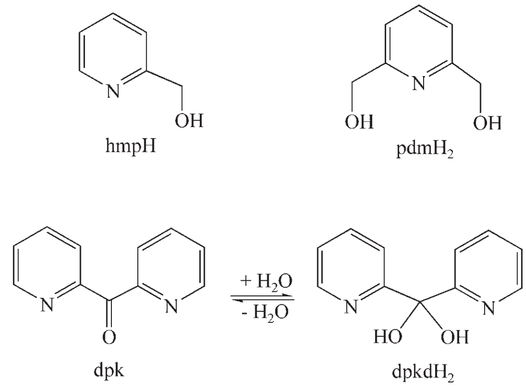
Molecular clusters of paramagnetic 3d transition metals continue to be a major research area because of their fascinating physical properties and their complex structures. In particular, they often have high-spin ground states and easy-axis-type magnetic anisotropy, giving a significant energy barrier to reversal of the magnetization vector. Thus, at sufficiently low temperatures they function as nanoscale magnetic particles.[1] Such single-molecule magnets (SMMs) also straddle the classical/quantum interface by displaying not just classical magnetization hysteresis but also quantum tunneling of magnetization (QTM)[2] and quantum phase interference.[3] SMMs represent a molecular, or "bottom-up", route to nanoscale magnetic materials,[4] with potential applications in information storage and spintronics at the molecular level[5a] and use as quantum bits (qubits) in quantum computation.[5b] The upper limit to the barrier (U) is given by $S^2|D|$ or $(S^2-1/4)|D|$ for integer and half-integer spins (S), respectively; in practice, QTM through upper regions of the barrier makes the true or effective barrier (U_{eff}) less than U.

Manganese carboxylate chemistry has been the main source of new SMMs,[1,6] and we are therefore developing new synthetic methods to Mn clusters of various types. The N_3^- ion bridging in the 1,1-fashion (end-on) is a strong ferromagnetic mediator for a wide range of M-N-M angles, and thus it opens an attractive route to new high-spin Mn clusters and SMMs.[7] In past work, we have shown that azide and the bidentate N,O chelate hmp^- (the anion of 2-(hydroxymethyl)pyridine) or the tridentate N,O,O chelates $pdmH^-/pdm^{2-}$ (the anions of 2,6-pyridinedimethanol) yield $[Mn_{10}O_4(N_3)_4(hmp)_{12}]^{2+}$ with $S=22$[8] and $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]^{2+}$ with $S=51/2$,[9] respectively. Both clusters are high-spin molecules, but with small U_{eff} values, and include coordinated azide groups as ancillary ligands.

In the present work, we have explored reactions of Mn precursors with azide and the potentially tetradentate N,N,O,O *gem*-diolate of di-2-pyridylketone, $(py)_2C(O)_2^{2-}$ ($dpkd^{2-}$), formed in situ from dpk, which has previously been a useful route to non-azido metal clusters.[10] We considered $dpkd^{2-}$ particularly attractive because it can be



seen as the fusion of two hmp^- chelates. Previous reports of Mn^{III}-containing products from reactions with $dpkdH_2$ were $[Mn_{14}O_4(O_2CMe)_{20}(dpkdH^-)_4]$ $(Mn^{II}_{10}Mn^{III}_4)$[11a] and $[Mn_{26}O_{16}(OMe)_{12}(dpkd)_{12}(X)_6]$ (X^- = terminal groups; $Mn^{II}_4Mn^{III}_{22}$).[11b] We report herein the results of our study, which has produced new high-nuclearity, mixed-valence Mn_{24} and Mn_{26} molecules with both $dpkd^{2-}$ and N_3^- ligands and unusual, covalently-linked, dimer-of-clusters topologies. In addition, we show that the products are SMMs, one of them with a large relaxation barrier for a $Mn^{II/III}$ species.

The reactions of Mn reagents, NaN_3, and dpk have been investigated with a variety of carboxylate sources and under a variety of conditions. The reaction of $Mn(ClO_4)_2\cdot 6H_2O$, NaO_2CCMe_3, dpk, NEt_3, and NaN_3 in a 1:2:1:1:1 molar ratio in MeCN/DMF (4:1, v/v) gave a dark brown solution from which was subsequently isolated **1** in 60% yield. The analogous reaction with $MeCO_2^-$ instead of $Me_3CCO_2^-$ gave **2** in 65% yield.

$[Mn_{24}O_{10}(N_3)_8(O_2CCMe_3)_{16}(dpkd)_{12}(dmf)_4]$ **1**

$[Mn_{26}O_8(OH)_4(N_3)_{12}(O_2CMe)_6(dpkd)_{14}(dmf)_4]$ **2**

The structure of **1**[12] consists of a mixed-valent $(Mn^{II}_4Mn^{III}_{20})$ centrosymmetric Mn_{24} loop (Figure 1) with a saddle-shaped or closed sinusoidal conformation.[13] It can also be described as two Mn_{12} "molecular chains" linked by two $\eta^1:\eta^1:\eta^1:\eta^1:\mu$ $dpkd^{2-}$ groups across the Mn1···Mn12 separations. Each Mn_{12} unit consists of two central $[Mn^{III}_4(\mu_3\text{-}O)_2]^{8+}$ butterfly subunits linked by a $\mu\text{-}O^{2-}$ and two $\eta^1:\eta^2:\eta^2:\eta^1:\mu_3$ and one $\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$ $dpkd^{2-}$ groups.[13] Each

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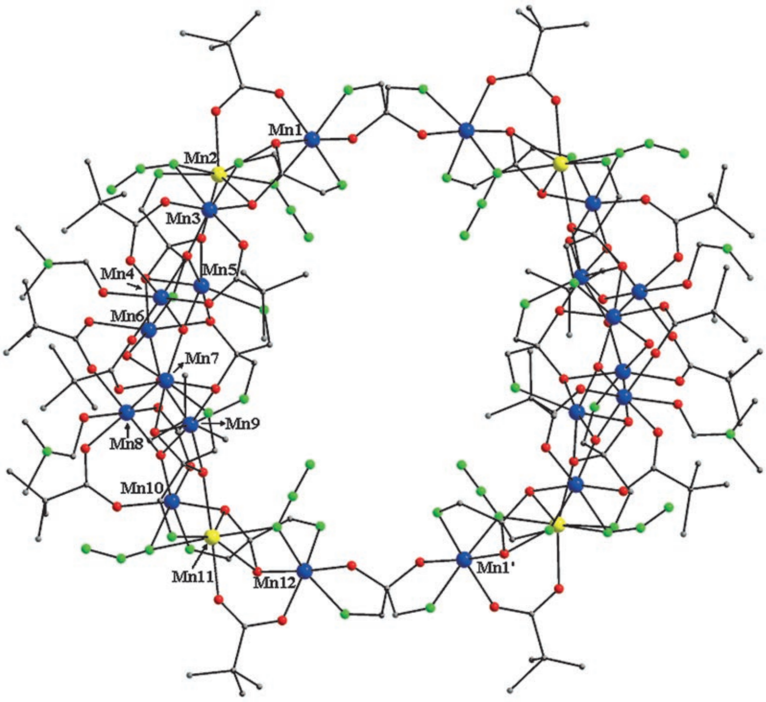

Figure 1. The loop-like structure of two covalently-linked Mn_{12} units in complex **1**. Only the *ipso* carbon atoms of the dpkd^{2-} phenyl groups are shown. H atoms have been omitted for clarity. Color code: Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray.

flexibility of the dpkd^{2-} group.[13] Complex **2** thus contains an overall $[Mn_{26}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}N_3)_4(\mu_3\text{-}OR)_4(\mu\text{-}OR)_{20}]^{18+}$ core, with peripheral ligation provided by six $\eta^1:\eta^1:\mu$ $MeCO_2^-$, eight N_3^-, and four DMF terminal ligands. Charge considerations, the metric parameters, and BVS calculations confirm the $Mn^{II}{}_{12}Mn^{III}{}_{14}$ mixed-valent description for **2**, with Mn(3,4,9,10,11,13) being the Mn^{II} atoms;[14] octahedrally coordinated Mn^{III} atoms Mn(1,5,6,7,8,12) exhibit JT axial elongations. Mn2 and Mn3 are five-coordinate with intermediate geometry for the former and distorted square pyramidal geometry for the latter (τ = 0.39 and 0.16, where τ is 0 and 1 for ideal sp and tbp geometries,[15] respectively). Three of the Mn^{II} atoms, Mn(9,11,13), are six-coordinate with distorted octahedral geometries, and the remaining two, Mn(4,10), are seven-coordinate with distorted pentagonal bipyramidal geometries. The protonation level of O^{2-}, OH^-, and OR^- groups was confirmed by BVS calculations.[14] Complexes **1** and **2** join only a handful of previously known clusters with 24 or more manganese centers,[6g,9,16] none of which have similar structures.

Mn_4 subunit is additionally bridged to two external Mn atoms, Mn(1,2) and Mn(11,12), by the O atoms of μ_4-dpkd^{2-} groups.[13] The eight μ-N_3^- ions each bridge a $Mn^{II}\cdots Mn^{III}$ pair in an $\eta^1:\eta^1$ (end-on) fashion. Peripheral ligation about the core is by sixteen $\eta^1:\eta^1:\mu$ $Me_3CCO_2^-$ and four terminal DMF groups. All Mn atoms are near-octahedrally coordinated, except seven-coordinate Mn2 and Mn11, which have distorted pentagonal bipyramidal geometry. The Mn^{II}/Mn^{III} oxidation states were established from the metric parameters, bond-valence sum (BVS) calculations,[14] and the presence of Jahn–Teller (JT) distortions at octahedrally coordinated Mn^{3+} centers; the latter are axial elongations of the two Mn–O(R) and Mn–N bonds in *trans* arrangement (average 2.117–2.394 Å). Overall, the complex comprises a dimer of two Mn_{12} near-semicircular units linked covalently but through a long, four-bond connection between the Mn1···Mn12 pairs.

The structure of complex **2**[12] ($Mn^{II}{}_{12}Mn^{III}{}_{14}$) also comprises two identical, covalently-linked units, in this case two symmetry-related Mn_{13} clusters linked by two $\eta^1:\eta^1$ (end-on) N_3^- ions to give a dumbbell structure (Figure 2, top). Each Mn_{13} unit consists of a $Mn^{II}{}_4Mn^{III}{}_4$ rod-like subunit (atoms Mn3–Mn10) attached on either side to a $[Mn^{III}{}_2(\mu\text{-}OR)_2]$ (Mn1 and Mn2) and a $[Mn^{II}Mn^{III}(\mu\text{-}OR)_2]$ (Mn11, Mn12) dinuclear unit (Figure 2, bottom). The latter are additionally bridged to another, central Mn^{II} (Mn13), and these are end-on bridged by the central N_3^- groups connecting the two halves of the molecule. Each Mn_{13} unit is bridged by a combination of two μ_4-O^{2-} (O10, O15), two μ_3-O^{2-} (O7, O16), two μ_3-OH^- (O14, O17), an $\eta^1:\eta^1$ (end-on) N_3^-, and six dpkd^{2-} ligands. The latter are of four types: $\eta^1:\eta^2:\eta^3:\eta^1:\mu_5$, $\eta^1:\eta^1:\eta^3:\eta^1:\mu_4$, and $\eta^1:\eta^2:\eta^1:\eta^1:\mu_3$ and $\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$, emphasizing the bridging

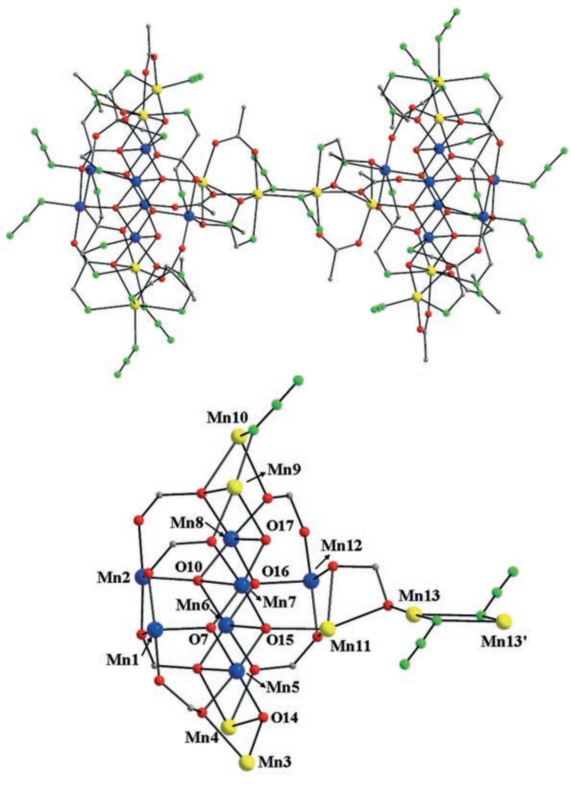

Figure 2. The dumbbell-shaped structure (top) and the Mn_{13} repeating unit (bottom) of complex **2**. Only the *ipso* carbon atoms of the dpkd^{2-} phenyl groups are shown. H atoms have been omitted for clarity. Color code: Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray.

Solid-state DC (direct current) magnetic susceptibility (χ_M) data were collected on **1** and **2**·DMF in a 1 kG (0.1 T) field in the 5–300 K range. The data are plotted as $\chi_M T$ versus T in Figure 3, and both **1** and **2**·DMF clearly have relatively large ground-state spin values. $\chi_M T$ for **1** decreases from 53.50 $cm^3 K mol^{-1}$ at 300 K to 45.60 $cm^3 K mol^{-1}$ at 80.0 K, and

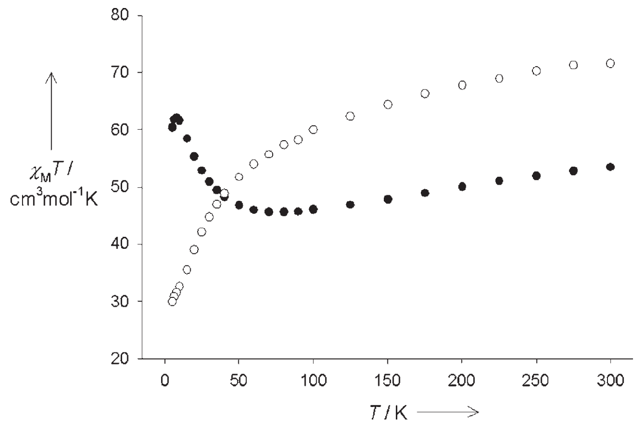

Figure 3. $\chi_M T$ versus T plots for complexes **1** (●) and **2**·DMF (○) in a 1 kG field.

then increases to 62.14 $cm^3 K mol^{-1}$ at 8.0 K, before dropping to 60.39 $cm^3 K mol^{-1}$ at 5.0 K; the latter decrease at the lowest temperatures is assigned to Zeeman effects, zero-field splitting and/or weak intermolecular interactions. The shape of the curve suggests that both ferro- and antiferromagnetic exchange interactions are likely present within **1**. For **2**·DMF, $\chi_M T$ steadily decreases from 71.64 $cm^3 K mol^{-1}$ at 300 K to 30.03 $cm^3 K mol^{-1}$ at 5.0 K, indicating the presence of dominant antiferromagnetic interactions within the molecule.

Attempted fits of magnetization data collected at various fields and at low temperature (< 10 K), and assuming that only the ground state is populated, were poor, suggesting population of low-lying excited states, as expected for such high-nuclearity complexes. As described elsewhere,[8,9,16,17] an alternative determination of S can be reached from AC (alternating current) susceptibility measurements in the 1.8–15 K range with a 3.5 G AC field oscillating at 5–1500 Hz; this precludes complications from a DC field and/or low-lying excited states. For **1**, the in-phase (χ_M') AC signal, shown as $\chi_M' T$ in Figure S6,[13] is strongly temperature-dependent in the 4–15 K region, confirming the conclusion from the DC studies of many very low-lying excited states. Extrapolating the plot above 4 K down to 0 K gives a value of about 52 $cm^3 K mol^{-1}$, suggesting an $S \approx 7$ ground state. In the corresponding plot for **2**·DMF (Figure 4), $\chi_M' T$ decreases only slightly with decreasing temperature in the 4–15 K region, indicating little population of excited states in this temperature range. Extrapolation of the data above 15 K down to 4 K gives about 30 $cm^3 K mol^{-1}$, indicating an $S = 8$ ground state with $g < 2$. At lower temperatures, both **1** and **2**·DMF display a frequency-dependent decrease in $\chi_M' T$ and concomitant appearance of out-of-phase χ_M'' signals; those for **1** are centered below the operating limit of our magnetometer (1.8 K), but those for **2**·DMF are entirely visible, a very rare

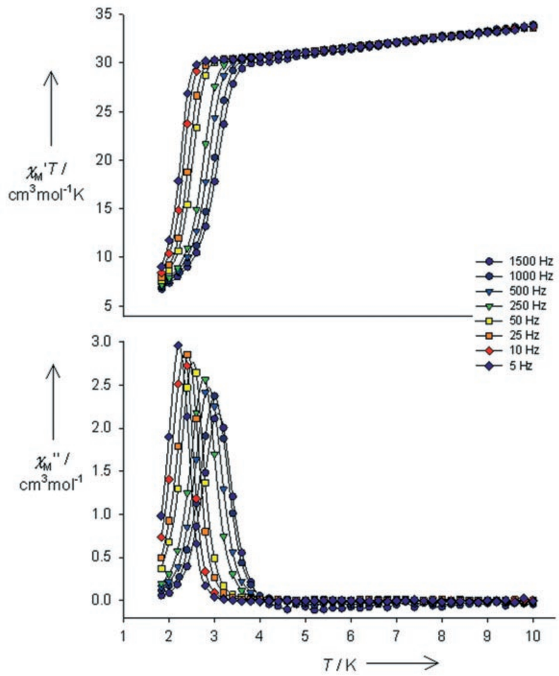

Figure 4. Plot of the in-phase (χ_M'; as $\chi_M' T$) and out-of-phase (χ_M'') AC susceptibility signals of complex **2**·2 DMF, measured in a 3.5 G field oscillating at the indicated frequencies.

situation for a high-nuclearity $Mn^{II/III}$ cluster[18] and indicative of a significant barrier to magnetization relaxation. Indeed, an Arrhenius plot constructed from the AC χ_M'' vs T data of Figure 4 gave $U_{eff} = 46$ K and $\tau_0 = 3.4 \times 10^{-11}$ s, where τ_0 is the pre-exponential factor. The U_{eff} value of 46 K is the highest yet observed for a $Mn^{II/III}$ mixed-valent complex,[18] although still significantly smaller than for the Mn^{III}_6 (86 K)[19] and $Mn^{III/IV}_{12}$ (74 K)[6f] complexes.

The χ_M'' signals for **1** and **2**·DMF were suggestive of SMMs, and confirmation was sought by magnetization versus DC field scans on single crystals of solvated **1** and **2** using an array of micro-SQUIDs.[20] These scans showed magnetization hysteresis loops below 0.8 K for **1** and 1.0 K for **2**, confirming both complexes to be SMMs. The loops exhibit coercivities that increase with decreasing temperature (Figure 5) and increasing field sweep rate,[13] as expected for SMMs, but do not show the steps characteristic of QTM, except for the one at zero field for **2**·18 MeCN·2 DMF; this is the usual case[21] for large SMMs because they are more susceptible to step-broadening effects from low-lying excited states, intermolecular interactions, and distributions of local environments owing to ligand and solvent disorder.[9,16,17] No sign of an exchange-bias was observed in the loops, suggesting that **1** and **2** behave magnetically as single SMMs rather than as weakly-coupled $[Mn_{12}]_2$ and $[Mn_{13}]_2$ dimers, respectively; a true exchange-bias has been previously observed in the hydrogen-bonded $[Mn_4]_2$ and $[Fe_9]_2$ dimers.[22]

In conclusion, azide and $dpkd^{2-}$ groups together have provided two new structural types that can be described as covalently-linked dimers rather than the more common hydrogen-bond-linked dimers. Both complexes are new SMMs, with **2** possessing the largest barrier to date for a

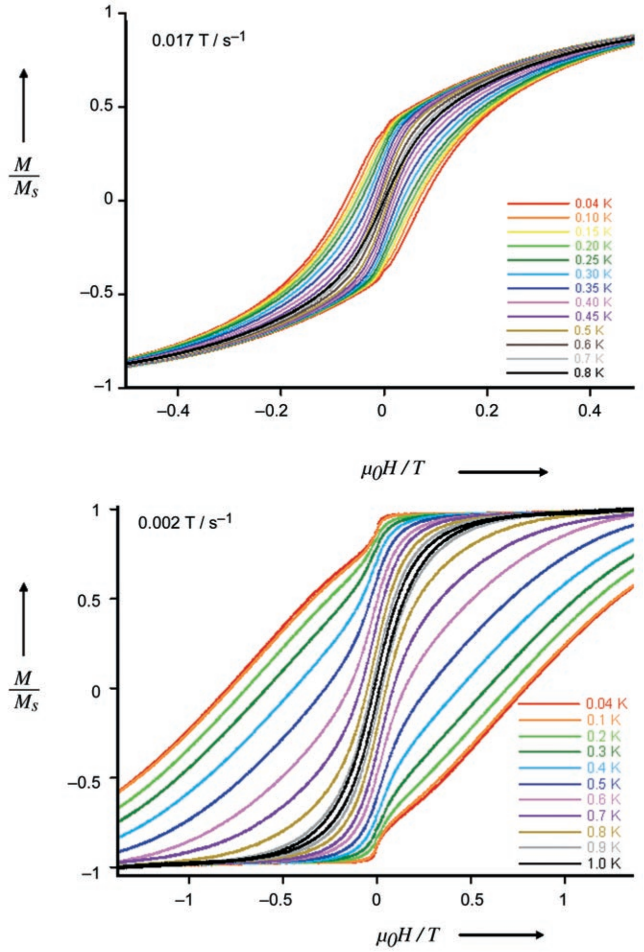

Figure 5. Magnetization (M) versus applied DC field (H) hysteresis loops for single crystals of solvated **1** (top) and **2** (bottom) at the indicated temperatures. The magnetization is normalized to its saturation value M_s.

$Mn^{II/III}$ complex; the many low-lying excited states typical of $Mn^{II/III}$ SMMs normally preclude significant U_{eff} values compared with Mn^{III} and $Mn^{III/IV}$ SMMs. However, the present results show that some high-nuclearity $Mn^{II/III}$ species can indeed exhibit significant U_{eff} barriers, as well as interesting new structural motifs. Finally, we emphasize that although **1** and **2** can be described structurally as dimers, they behave magnetically as single SMM units. This is logical since there is no reason to assume or expect in such mixed-valent $Mn^{II/III}$ complexes that the exchange interactions at the linkages connecting the two halves of the molecules will be the weakest.[16c]

Experimental Section

1: Solid $Mn(ClO_4)_2{\cdot}6H_2O$ (0.18 g, 1.0 mmol), $NaO_2CCMe_3{\cdot}H_2O$ (0.25 g, 2.0 mmol), and NaN_3 (0.07 g, 1.0 mmol) were added to a stirred, pale yellow solution of dpk (0.18 g, 1.0 mmol) and NEt_3 (0.14 mL, 1.0 mmol) in MeCN/DMF (25 mL, 4:1 v/v). The resulting orange mixture was stirred for 24 h, during which time all the solids dissolved and the color of the solution changed to dark brown. The solution was filtered, and C_6H_{12} (50 mL) diffused into the filtrate. After several days, X-ray quality dark-brown needle-shaped crystals of $\mathbf{1}{\cdot}7C_6H_{12}{\cdot}2DMF{\cdot}12MeCN{\cdot}16H_2O$ were collected by filtration, washed with MeCN (2×5 mL) and Et_2O (4×5 mL), and dried under vacuum. The yield was 60% (0.45 g). C,H,N analysis (%) calcd for $C_{224}H_{268}Mn_{24}N_{52}O_{70}$ (**1**): C 43.91, H 4.41, N 11.89; found: C 43.62, H 4.66, N 11.77. IR (KBr): $\tilde{\nu}=3335$ (mb), 2959 (m), 2945 (w), 2066 (vs), 1663 (vs), 1603 (w), 1549 (vs), 1481 (m), 1415 (s), 1337 (m), 1302 (w), 1229 (m), 1156 (w), 1101 (m), 1031 (m), 997 (m), 955 (m), 891 (w), 786 (m), 768 (m), 691 (m), 658 (s), 617 (s), 531 (w), 414 cm^{-1} (w).

2: This complex was prepared in the same manner as complex **1** but using $NaO_2CMe{\cdot}3H_2O$ (0.27 g, 2.0 mmol) in place of $NaO_2CCMe_3{\cdot}H_2O$. Dark-brown plate-shaped crystals of $\mathbf{2}{\cdot}18MeCN{\cdot}2DMF$ were collected by filtration, washed with MeCN (2×5 mL) and Et_2O (4×5 mL), and dried under vacuum. The yield was 65% (1.25 g). C,H,N analysis (%) calcd for $C_{181}H_{169}Mn_{26}N_{69}O_{57}$ ($\mathbf{2}{\cdot}DMF$): C 38.47, H 3.01, N 17.10; found: C 38.61, H 3.17, N 17.28. IR (KBr): $\tilde{\nu}=3367$ (mb), 2928 (w), 2056 (vs), 1659 (vs), 1596 (w), 1563 (vs), 1470 (m), 1433 (s), 1387 (w), 1338 (m), 1292 (m), 1254 (w), 1216 (m), 1145 (m), 1102 (m), 1075 (s), 1014 (s), 961 (m), 900 (w), 819 (m), 779 (m), 760 (m), 688 (m), 663 (m), 616 (mb), 512 (w), 412 cm^{-1} (w).

Safety note: Perchlorate and azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

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[12] a) Crystal structure data for **1**·7 C_6H_{12}·2 DMF·12 MeCN·16 H_2O: $C_{290}H_{412}Mn_{24}N_{64}O_{86}$, $M_r = 7489.40$, monoclinic, space group $C2/c$, $a = 24.523(2)$, $b = 43.749(4)$, $c = 36.827(3)$ Å, $\beta = 96.133(2)°$, $V = 39283(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.266$ g cm^{-3}, $T = 173(2)$ K, 108502 reflections collected, 39634 unique ($R_{int} = 0.0862$), $R1 = 0.0585$ and $wR2 = 0.1480$, using 11373 reflections with $I > 2\sigma(I)$. The asymmetric unit contains half a Mn_{24} cluster (located on a twofold rotation axis) and a large solvent area. The latter was estimated by using results from Difference Fourier maps and the estimated solvent area with the count of its electron total. The best estimate of the solvent in the asymmetric unit are 3.5 cyclohexane (C_6H_{12}), 1 DMF, 6 MeCN, and 8 H_2O molecules. The solvent molecules were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The methyl groups of six pivalic acid ligands are disordered and each was refined in two parts. One of the azide ligands had its terminal N atom disordered and was also refined in two parts. Crystal structure data for **2**·18 MeCN·2 DMF: $C_{220}H_{232}Mn_{26}N_{88}O_{58}$, $M_r = 6465.38$, triclinic, space group $P\bar{1}$, $a = 16.2744(16)$ Å, $b = 17.5914(17)$ Å, $c = 26.754(3)$ Å, $\alpha = 99.326(2)$, $\beta = 93.402(2)$, $\gamma = 115.505(2)°$, $V = 6749.6(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.591$ g cm^{-3}, $T = 173(2)$ K, 43920 reflections collected, 30257 unique ($R_{int} = 0.0475$), $R1 = 0.0669$ and $wR2 = 0.1585$, using 18138 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of a half Mn_{26} cluster, 9 MeCN molecules and a disordered DMF molecule; b) CCDC-679548, and -679549 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.

[13] See the Supporting Information.

[14] a) Bond-valence sum (BVS) calculations for the Mn ions of **1** gave values of 1.81 for Mn^{2+} ions and 2.86–3.11 for Mn^{3+} ions, whereas for **2** the BVS values range from 1.94–2.04 for Mn^{2+} ions and 2.85–3.06 for Mn^{3+} ions. BVS calculations for selected oxygen atoms in both **1** and **2** gave values of 1.78–1.87 for O^{2-}, 1.06–1.11 for OH^-, and 1.91–2.05 for RO^-; b) W. Liu, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 4102–4105; c) I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247.

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