Supramolecular Chemistry

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Influencing the Symmetry of High-Nuclearity and High-Spin Manganese Oxo Clusters: Supramolecular Approaches to Manganese-Based Keplerates and Chiral Solids**

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Over the last decades there has been continuous interest in the synthesis and characterization of coordination clusters and cages, which are intriguing sub-classes of supramolecular compounds.[1] The electronic and magnetic properties in such nanoscopic systems are often highly related to the symmetry, topology, and connectivity of their metal centers.[2] Supramolecular chemistry approaches to influence the symmetry and nuclearity may provide a tool to generate multifunctional materials with tunable and desired attributes.[3] Mixed-valent, polynuclear Mn coordination compounds are excellent systems to investigate these structure–property relationships.[4] Very recently symmetric Mn coordination clusters were reported to show enhanced magnetocaloric effects (MCE),[5] allowing the compounds to be envisioned as technologically important low-temperature magnetic coolers.[6] Less-symmetrical polynuclear manganese species with high magnetic anisotropy often give rise to single-molecule magnet (SMM) properties and quantum behavior which might be applicable in next-generation information storage devices.[7] Moreover, chiral manganese coordination clusters can promote magnetochiral dichroism or induce ferroelectric and piezoelectric properties making this class of compounds highly desired candidates for modern multifunctional materials.[8]

In the course of our research into hybrid polyoxovanadates,[9] we recently found that chloride ions can be applied as templates to direct the assembly of tetranuclear $\{V_4\}$ secondary building units (SBUs) resulting in a series of high-nuclearity vanadium cages with controllable topologies.[10] A remarkable vanadium-based Keplerate was obtained in which an Archimedean $\{V_{24}\}$ cage encapsulates a Platonic $\{Cl_6\}$ template. To generalize this supramolecular approach we decided to apply this concept to the Mn system and explore the formation of coordination clusters by comproportionation reactions in phosphonate-stabilized reaction systems. Herein we report the syntheses, structures, and properties of three related and rather unique mixed-valent Mn coordination clusters (**I**–**III**):

$[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_8(\mu_4\text{-}Cl)_6(\textit{tert}\text{-butyl-}PO_3)_8][Mn^{II}(CH_3CN)_6]Cl_2\cdot 6\,CH_3CN\cdot 5.25\,H_2O$ **I**

$(C_5H_7N_2)_3[Mn^{II}_3Mn^{III}_{10}(\mu_4\text{-}O)_6(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_4\text{-}Cl)_4(Cl)(\textit{tert}\text{-butyl-}PO_3H)(\textit{tert}\text{-butyl-}PO_3)_9]\cdot 3\,CH_3CN\cdot 2\,H_2O$ **II**

$(C_5H_7N_2)_2[Mn^{II}_3Mn^{III}_{11}(\mu_4\text{-}O)_6(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)(\mu_4\text{-}Cl)_4(\textit{tert}\text{-butyl-}PO_3H)(\textit{tert}\text{-butyl-}PO_3)_{10}(2\text{-aminopyridine})]\cdot(C_5H_6N_2)\cdot 3\,CH_3CN\cdot 2\,H_2O$ **III**

We observe a distinct structure-directing effect of Cl^- ions that stabilize tetranuclear, square $\{Mn_4\}$ subunits. The symmetry of the species can be influenced through variation of the molar ratios between Cl^- and *tert*-butylphosphonate ligands, resulting in the assembly of the highly symmetric Mn-based Keplerate **I**, non-centrosymmetric and chiral oxo-clusters **II** and **III**, respectively. The complexes are stable in solution and have high-spin ground states as a result of intramolecular ferromagnetic interactions.

The reaction of $MnCl_2\cdot 4\,H_2O$, $KMnO_4$ and *tert*-butyl-PO_3H_2 in a molar ratio of 10:1:5 in the presence of Et_3N and CH_3CN led to formation of red crystals of **I**. Single-crystal X-ray diffraction reveals that this compound crystallizes in the cubic space group $Pm\bar{3}a$ (no. 223) and its structure contains two co-crystallized species, the $\{Mn^{II}Mn^{III}_{12}\}$ coordination cluster $[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_8(\mu_4\text{-}Cl)_6(\textit{tert}\text{-butyl-}PO_3)_8]$ (**1**) and the isolated, octahedral complex $[Mn^{II}(CH_3CN)_6]^{2+}$.[11] The $\{Mn^{II}Mn^{III}_{12}\}$ aggregate is shown in Figure 1 and its packing arrangement in the crystal structure is shown in Figure 2. A Mn^{II} atom is located in the center of the cluster core; it adopts a cubic coordination environment and is coordinated by eight $\mu_4\text{-}O^{2-}$ oxo ligands. These oxo ligands link the central Mn^{II} atom to 12 Mn^{III} atoms to give the $\{Mn^{II}Mn^{III}_{12}\}$ structure. This binding mode results in a cuboctahedral arrangement of the 12 Mn^{III} centers. Each of the six square faces of the polyhedron is capped by a $\mu_4\text{-}Cl^-$ ligand. The eight triangular faces are capped by eight fully deprotonated *tert*-butylphosphonate ligands each bridging three Mn^{III} atoms in a $\eta^1{:}\eta^1{:}\eta^1{:}\mu_3$ binding mode. The oxidation states were assigned

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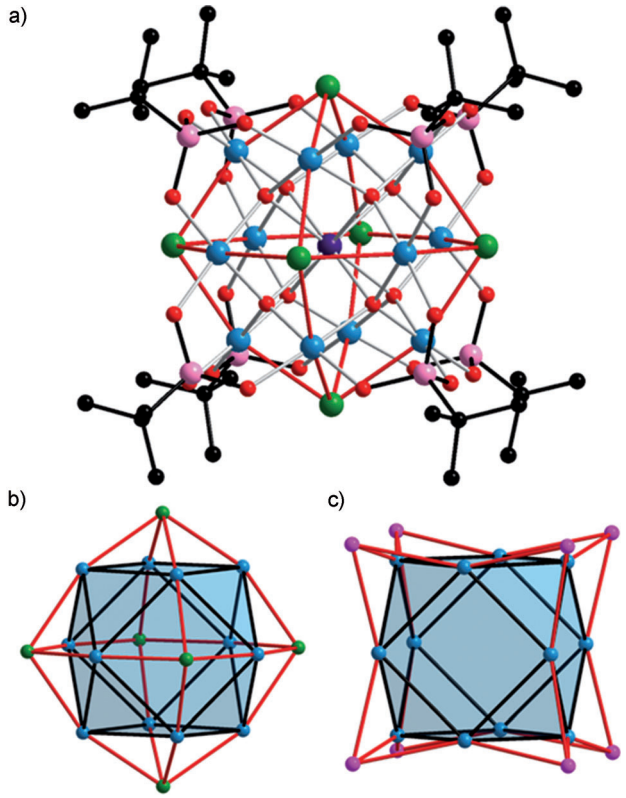

Figure 1. a) Crystal structure of cluster **1**. Polyhedral representation of the $\{Mn_{12}\}$ cuboctahedron in **1**, with b) six square faces each capped by a Cl atom, and c) eight triangular faces each capped by a phosphonate group (only P atoms are shown for clarity). Mn^{II} violet, Mn^{III} light blue, P pink, Cl green, C black.

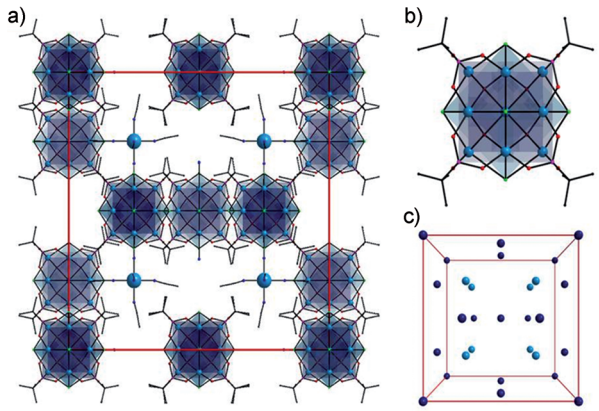

Figure 2. a) Packing structure of **I** with view in the direction of the crystallographic *c*-axis. b) **1** shown in polyhedral representation of endohedral $\{Mn_{12}\}\subset\{P_8\},\{Cl_6\}$ arrangement. c) Simplified arrangement of **1** (dark blue spheres) and $[Mn^{II}(CH_3CN)_6]^{2+}$ complexes (light blue spheres) in the unit cell of **I** (only centroid atoms represented).

by bond valence sum analyses (BVSA) and consideration of the observed coordination environments. All Mn^{III} atoms adopt tetragonal distorted octahedral coordination environments whereby the elongation of the axial Cl-Mn-Cl bonds is in agreement with the Jahn–Teller theorem.

The highly symmetrical cuboctahedral $\{4^6,3^8\}$ tiling motif in **1** is characteristic for an Archimedean solid and can mathematically be realized by truncating the eight corners of a cube or the six corners of an octahedron with the resulting vertices located at the midpoints of the edges of either.[12] Based on this, the polyhedron can be classified either as a rectified cube or octahedron. In the present case the squares are stabilized by six Cl^- ligands which adopt an octahedral arrangement and the triangular faces are stabilized by eight organophosphonate ligands whose P atoms adopt a cubic arrangement (Figure 1 b,c). That the Cl^- ions are on the outside of the cluster core of **1** is in contrast to other polyoxovanadate systems in which the Cl^- ions reside inside hollow cage structures.

It is of note that **I** can be recognized as first Mn-based Keplerate—an oxo-cluster that consists of endohedral encapsulating arrangements of both, Platonic ($\{Cl_6\}$ octahedron and $\{P_8\}$ cube) and Archimedean bodies ($\{Mn_{12}\}$ cuboctahedron).[2d,13] Since being introduced by Müller around 10 years ago, Keplerates have received significant attention owing to their fascinating structures and associated physical attributes.[14] In particular, studies on magnetic "quantum" Keplerates have provided a deeper understanding of basic aspects of magnetic frustration, correlating intrinsic spins with the topology and symmetry of a cluster.[14a]

From the coordination geometry of the Cl^- ligands and the topology of **1** we can conclude that the halides employed have a significant influence on the symmetry and the structure of the Mn cluster. This observation is comparable to the template effect in the previously studied polyoxovanadate systems.[10] Thus the structure of **1** prompted us to investigate the possibility of influencing the symmetry by varying the halide concentration in the reaction mixture. Upon lowering the Cl^- concentration (molar ratios between Cl^- and *tert*-butyl-PO_3 4:1 and 2:1), we obtained two structurally related Mn coordination complexes, **II** and **III**, with lower symmetry. Their core structures **2** and **3**

$[Mn^{II}_3Mn^{III}_{10}(\mu_4\text{-}O)_6(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_4\text{-}Cl)_4(Cl)$-
$(tert\text{-butyl-}PO_3H)(tert\text{-butyl-}PO_3)_9]^{3-}$ **2**

$[Mn^{II}_3Mn^{III}_{11}(\mu_4\text{-}O)_6(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)(\mu_4\text{-}Cl)_4$-
$(tert\text{-butyl-}PO_3H)(tert\text{-butyl-}PO_3)_{10}(2\text{-aminopyridine})]^{2-}$ **3**

are similar to that of **1** and are stabilized by eight organophosphonate ligands that adopt a cubic arrangement (Figure 3). However in these cases, only four μ_4-Cl^- ligands cap the square tetranuclear Mn^{III} units. As a consequence of this, one Mn^{III} vertex of the original cuboctahedron has been removed. The central Mn^{II} atom is connected to the 11 Mn^{III} centers by six μ_4-O^{2-} and one μ_3-O^{2-} oxo and one μ_3-OH hydroxo ligands. For **2**, two additional phosphonate ligands attach one additional Mn^{II} center to the cluster core structure. In the case of **3**, three additional phosphonates attach a dinuclear $\{Mn^{II}\text{-OH-}Mn^{III}\}$ subunit to the core structure. Octa-coordinated Mn^{II} centers similar to those present in **1–3** are relatively rare but have been observed in large coordination clusters.[15] In a $\{Mn^{II}_9Mn^{III}_{12}\}$ structure, 8 μ_4-O^{2-} ligands connect 12 Mn^{III} centers to a central Mn^{II} atom to form an

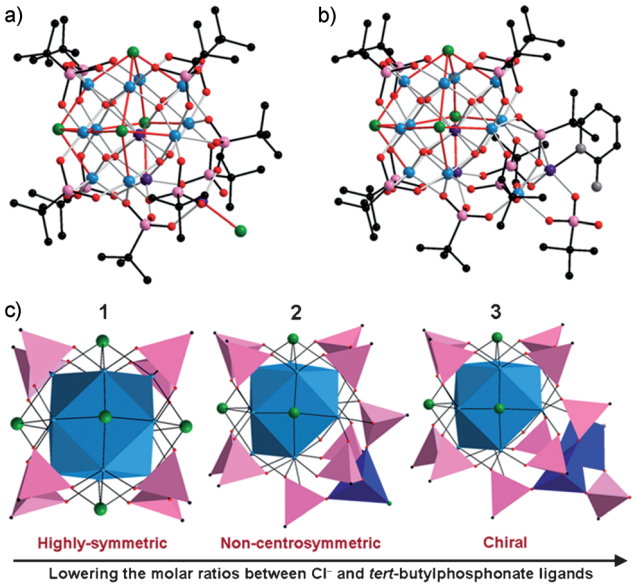

Figure 3. Structures of a) **2** and b) **3**. c) Symmetry reduction for **1**–**3** shown in polyhedral representation. Mn^{II} violet, Mn^{III} light blue, P pink, Cl green, C black. The additionally attached outer Mn^{II} atom in **2** and dinuclear {Mn^{II}-OH-Mn^{III}} subunit in **3** are highlighted in dark blue.

icosahedral Platonic arrangement that differs significantly from the Archimedean arrangement in **1**.[15a] The less symmetrically coordinated, central Mn^{II} atoms in **2** and **3** can be related to octa-coordinate Mn^{II} centers in other reported coordination clusters. However, in contrast to the compounds described herein, in the earlier systems the Mn^{II} centers often act as binodal linkers to produce dumbbell-type complexes.[15d,e]

Our studies demonstrate that the halide concentration provides us with a tool to influence the symmetry of the coordination clusters. The symmetry of **1** is characterized by the Schoenflies Symbol O_h[3]. In **2** the O_h symmetry of the oxo cluster is lowered and only the C_{2h} symmetry elements that involve the additional Mn^{II} center which is outside the core structure are maintained (Figure 3c). For **3**, the attachment of an unsymmetrical dinuclear moiety gives rise to supramolecular chirality and only C_2 symmetry elements are retained.

Despite an ever-increasing interest in manganese coordination complexes, their solution behavior is often poorly understood. We used electrospray-ionization mass spectrometry (ESI-MS) to investigate the solution stability of the new compounds. As shown in Figure 4a, the signal centered at m/z 1079.0 can be attributed to a species of $\{\mathbf{1}+H_2O\}^{2-}$; signals centered at m/z 1101.1 and 1155.1 correspond to species of $\{\mathbf{2}-Cl_5\}^{2-}$ and $\{\mathbf{2}-Cl_2+H\}^{2-}$, respectively; the signal centered at m/z 1222.0 can be assigned to $\{\mathbf{3}-Cl_3-H-(2\text{-aminopyridine})\}^{2-}$. These studies confirm the high solution stability of the cluster cores of **1**–**3**. The MS spectrum of **1** confirms that the six chloride ions remain coordinated even in the solution state. More interestingly, the chirality of **3** can also be confirmed and maintained when selected crystals are dissolved in methanol and investigated by circular dichroism (CD) spectroscopy (Figure 4b). Both the solution stability and the chirality persist over a time period of two weeks and longer.

The magnetic properties of these compounds were studied on powdered microcrystalline samples (Figure 4c,d, and Supporting Information, S16–S18). The room temperature χT products are 62.7, 52.9, and 55.5 $cm^3\,K\,mol^{-1}$ for **I**, **II**, and **III**, respectively. When the temperature is lowered, the χT products increase reaching 172.4 $cm^3\,K\,mol^{-1}$ at 22 K for **I**, 151.6 $cm^3\,K\,mol^{-1}$ at 19 K for **II**, and 183.0 $cm^3\,K\,mol^{-1}$ at 4 K for **III**. These temperature dependencies clearly indicate the

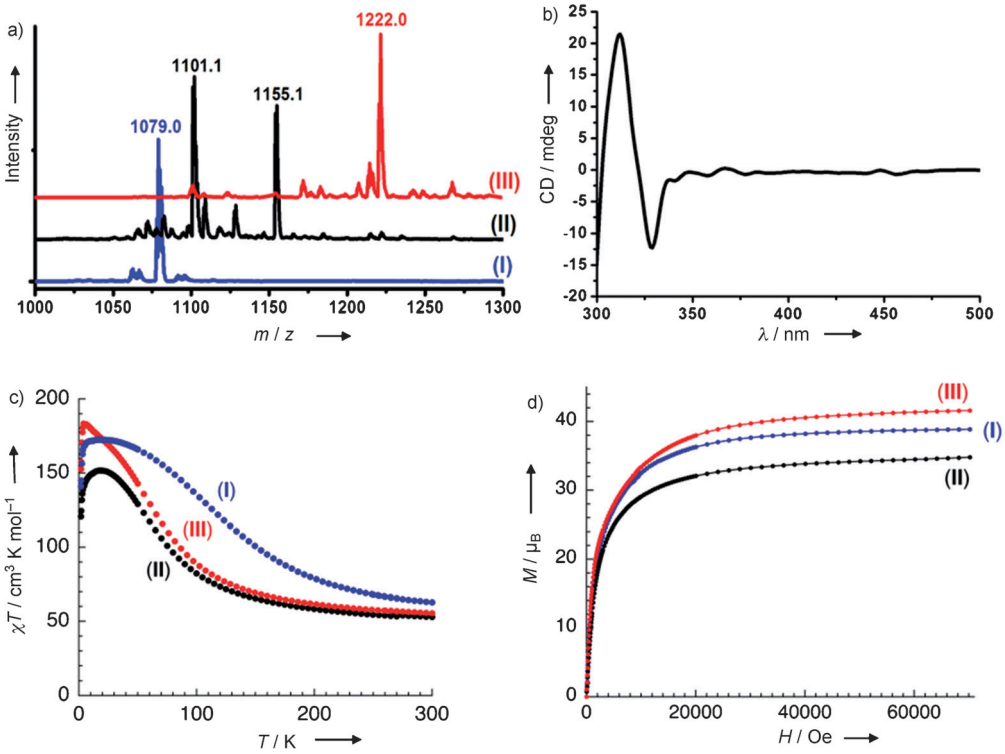

Figure 4. a) Negative-mode ESI-MS spectra of **I** (blue), **II** (black), and **III** (red) in acetonitrile solution. b) CD spectrum of a methanol solution of **III**. c) Temperature dependence of the χT product of **I** (blue), **II** (black), and **III** (red) at 1000 Oe (with χ being the molar magnetic susceptibility equal to M/H per complex). d) Field dependence of the magnetization M of **I** (blue), **II** (black), and **III** (red) at 2 K.

presence of strong intracomplex ferromagnetic interactions between the Mn spin centers. Note that such strong ferromagnetic exchange interactions are rare in mixed-valent Mn coordination clusters with nuclearity greater than four.[4b–d,5,7b,c,16] The magnitudes of the ferromagnetic interactions can be quantified by Weiss constants obtained from the fit of the magnetic susceptibility data to the Curie–Weiss law above 150, 80, and 90 K leading to $C = 45.5\ cm^3\,K\,mol^{-1}$ and $\theta = +83$ K for **I**, $C = 45.1\ cm^3\,K\,mol^{-1}$ and $\theta = +45$ K for **II** and $C = 47.1\ cm^3\,K\,mol^{-1}$ and $\theta = +47$ K for **III**. These Curie constants are in excellent agreement with the expected values of 44.75, 43.125, and 46.125 $cm^3\,K\,mol^{-1}$ (for $g = 2$).

The field dependence of the magnetization was measured in the temperature range of 1.8–15 K (Supporting Information, Figure S16–S18). At 2 K (Figure 4d), the magnetization almost saturates below 7 T reaching values of 38.8 μ_B for **I**, 34.8 μ_B for **II**, and 41.5 μ_B for **III**. These results further underline that the complex topologies stabilize high-spin ground states. In the case of **I**, the magnetization at saturation (ca. 39 μ_B) and the χT value at around 20 K ($172.4\ cm^3\,K\,mol^{-1}$) are in good agreement with a spin ground state $S_T = 35/2$, based on the presence of the isolated $S = 5/2$ $[Mn^{II}(CH_3CN)_6]^{2+}$ units in **I**. The magnetic data confirms that **II** and **III** stabilize spin ground states $\geq 35/2$.

High-spin and highly symmetric coordination clusters are interesting candidates for magnetic refrigeration due to enhanced magnetocaloric effects (MCE) reaching $-\Delta S_m$ values of over $40\ J\,Kg^{-1}\,K^{-1}$.[5a,6e,17] Our supramolecular approach that allows us to generate highly symmetric Mn oxo clusters and to influence the symmetry of closely related core structures provides us with means to explore a structure–property relationship with respect MCE phenomenon. For **I**–**III**, the lack of an out-of-phase (χ'') signal in ac susceptibility studies, the M vs H data and corresponding M vs H/T plots (Figure 4d and Supporting Information S16–18) are in agreement with a weak magnetic anisotropy as expected from the core structures. For $\Delta H = 7$ T, **I** exhibits a moderate magnetocaloric effect with $-\Delta S_m$ reaching $12.0\ J\,Kg^{-1}\,K^{-1}$ at 3.5 K. Lower $-\Delta S_m$ values are observed for **II** and **III** with maximum values of 7.5 and $8.7\ J\,Kg^{-1}\,K^{-1}$ at 2.5 and 5.5 K respectively.

In summary, we have developed a rational and highly applicable supramolecular approach to construct a family of mixed-valent Mn coordination clusters with different symmetries. A $\{Cl_6\}$ octahedral arrangement stabilizes six square, corner-sharing $\{Mn_4\}$ units that self-organize in the presence of phosphonates to produce a $\{Mn_{12}\}$ cuboctahedron. The approach results in the first structurally characterized Mn-based Keplerate which has one of the highest symmetries of the high-nuclearity Mn coordination clusters reported to date. Non-centrosymmetric $\{Mn^{II}{}_3Mn^{III}{}_{10}\}$ and chiral $\{Mn^{II}{}_3Mn^{III}{}_{11}\}$ cluster cores can be obtained by lowering the Cl^- ion concentrations. ESI-MS clearly confirms that these coordination clusters are stable in solution for a long time. Studies of the magnetic properties confirm strong ferromagnetic interactions between the Mn spin centers stabilizing large spin ground states. Our studies suggest that the applied synthetic approach can be generalized to other transition-metal or mixed-metal coordination clusters providing a way to tune the physicochemical properties of these metallo-supramolcular systems.

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[11] Crystal data for **I**: cubic, $Pm\bar{3}n$, $C_{224}H_{450}Cl_{32}Mn_{56}N_{48}O_{137}P_{32}$, $a = b = c = 28.423(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 22962(4)$ Å^3, $Z = 2$, $T = 200(2)$ K, $M = 11210.46$, $\rho = 1.601$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $R_1 = 0.0618$ for 202 parameters and 2741 unique reflections with ($I > 2\sigma(I)$) and $\omega R_2 = 0.1987$ for all 5047 reflections with GOF = 1.065; Crystal data for **II**: monoclinic, $P2_1/c$, $C_{61}H_{126}Cl_5Mn_{13}N_9O_{40}P_{10}$, $a = 15.631(3)$, $b = 27.563(5)$, $c = 27.949(6)$ Å, $\beta = 97.34(3)°$, $V = 11943(4)$ Å^3, $Z = 4$, $T = 200(2)$ K, $M = 2826.90$, $\rho = 1.567$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $R_1 = 0.0724$ for 1218 parameters and 13777 unique reflections with ($I > 2\sigma(I)$) and $\omega R_2 = 0.1855$ for all 21023 reflections with GOF = 1.019; Crystal data for **III**: monoclinic, $P2_1$, $C_{70}H_{141}Cl_4Mn_{14}N_{11}O_{44}P_{11}$, $a = 16.047(3)$, $b = 24.775(5)$, $c = 16.994(3)$ Å, $\beta = 103.82(3)°$, $V = 6561(2)$ Å^3, $Z = 2$, $T = 200(2)$ K, $M = 3092.59$, $\rho = 1.559$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $R_1 = 0.0603$ for 1347 parameters and 14127 unique reflections with ($I > 2\sigma(I)$) and $\omega R_2 = 0.1471$ for all 18290 reflections with GOF = 0.985. Details of data collection and refinement for the compounds are given in the Supporting Information. Crystallographic data, CCDC 832684 (**I**), 832685 (**II**), 832686 (**III**), 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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