Single-Chain Magnets

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Stringing Oxo-Centered Trinuclear [Mn^{III}_3O] Units into Single-Chain Magnets with Formate or Azide Linkers**

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Dedicated to Professor Heiko Lueken on the occasion of his 65th birthday

The study of molecular nanomagnets is currently one of the key topics in the field of molecular magnetism.[1] Among these compounds, single-molecule magnets (SMMs)[2,3] and single-chain magnets (SCMs)[4,5] have received a great deal of attention owing to their unique magnetic properties, such as slow relaxation and large hysteresis of magnetization, and their potential application in information storage and quantum computation at a molecular level. SCMs are expected to exhibit slow relaxation at higher temperatures than SMMs. The design of SCMs requires large uniaxial anisotropy, strong intrachain magnetic interactions between the high-spin magnetic units, and good isolation of the chains. Uniaxial anisotropy is a critical prerequisite and the most widely used anisotropic sources are Mn^{III}, $Fe^{II/III}$, Co^{II}, and lanthanide ions. The interaction between the spin carriers within the chain can be either ferro- (FM) or antiferromagnetic (AF).[6,7]

A step-by-step synthetic strategy has been introduced whereby SMM building blocks can be linked by covalent bonds in a rational manner to control the dimensions of the structure and magnitude of the inter-SMM magnetic interaction. This procedure has allowed the formation of 1D–3D frameworks that exhibit properties ranging from classical to quantum magnetism.[8]

Compounds that show SCM behavior have been designed based on trinuclear or tetranuclear SMMs. These compounds have an improved blocking temperature (T_B) and much higher energy barrier than the original SMM building blocks.[6a,g,7g] Oximato ligands have been used to create polynuclear compounds that show SMM behavior.[9,10] The presence of competing antiferromagnetic interactions in these compounds, which often contain a trinuclear [Mn^{III}_3O]$^{n+}$ unit, usually results in a net magnetic moment.

Recently we have begun to explore the use of bulky ligands based on 3,5-di-*tert*-butylsalicylaldoxime (*t*Bu-saoH_2) to produce an isolated trinuclear compound [Mn_3O(*t*Bu-sao)$_3$Cl(CH_3OH)$_5$]·H_2O (**1**) in which the elongation axes of all three Mn^{III} ions are almost parallel. Linkage of these predesigned trinuclear units through bridges along the easy axis of the magnetization, which corresponds to the chain direction, could produce an anisotropy-enhanced SCM. Herein we report the synthesis of two chain compounds by this strategy using formato ($HCOO^-$) and azido (N_3^-) anions, respectively, as bridges. These compounds show interesting SCM behavior at low temperature.

An X-ray structure analysis[11] showed that **1** consists of discrete neutral trinuclear [Mn_3O(*t*Bu-sao)$_3$Cl(CH_3OH)$_5$] species (Figure 1a). The three octahedrally coordinate Mn^{III} ions form a triangle by sharing a μ_3-oxo center, with Mn–O_{center} bonds of 1.876–1.895 Å and Mn···Mn distances of 3.247–3.268 Å. Each Mn···Mn edge of the triangle is bridged by an oxime (NO) group of one *t*Bu-sao ligand. The peripheral *t*Bu-sao ligand binds to Mn^{III} through its other oxygen atom, and this O atom, the μ_3-oxo center, and the NO bridge occupy the equatorial positions of Mn^{III}, with Mn–O/N distances of 1.837–2.006 Å. One apical position of one Mn^{III} ion is occupied by one Cl^- ion, while the remaining apical sites of the Mn ions are occupied by methanol molecules. The Mn–O_{apical} distances are 2.214–2.624 Å and the unique Mn–Cl distance is 2.597 Å, which means that the three Mn^{III} ions display a Jahn–Teller (JT) elongation, as expected for the high-spin $3d^4$ ion Mn^{III}. The JT axes of all three Mn^{III} ions are nearly parallel to each other and are roughly perpendicular to the [Mn^{III}_3O] plane. The molecule has a bent pan-like shape. The Mn_3 cores are well separated in the lattice because of the bulky *t*Bu-sao ligands, and the shortest intermolecular Mn···Mn distance is 7.5 Å (see the Supporting Information).

Replacement of the apical Cl^- ion by formate ($HCOO^-$) gives the chain-like complex [Mn_3O(*t*Bu-sao)$_3$(HCOO)(CH_3OH)$_4$]·CH_3OH·0.5H_2O (**2**; Figure 1b). The [Mn^{III}_3O] units in this complex are bridged by single *anti-anti* formate anions that link the two apical sites of adjacent [Mn^{III}_3O] units. Each {Mn^{III}_3O} unit in the chain has two different Mn^{III} ions coordinated through a formato bridge, while the third one is free. The molecular geometry of the {Mn^{III}_3O} unit is similar to that observed in **1**, with Mn–$O_{formato}$ distances of 2.280 and 2.286 Å, respectively. The Mn···Mn separation through the formato bridge is 6.471 Å and the dihedral angle between the adjacent {Mn^{III}_3} planes is 39°, probably arising

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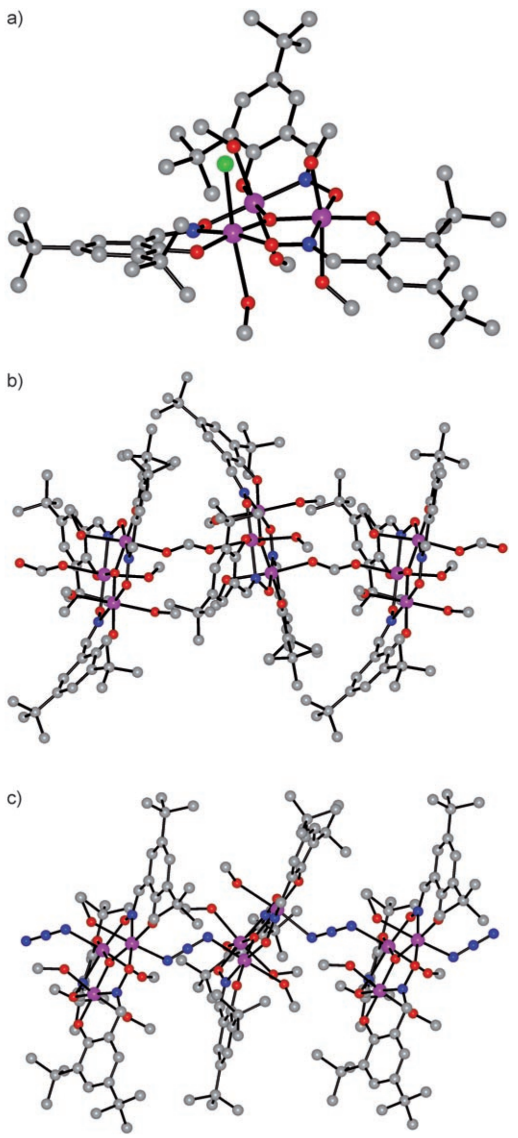

Figure 1. a) The molecular structure of **1**. b) The chain of $\{Mn^{III}{}_3O\}$ units bridged by $HCOO^-$ ions in compound **2** and c) by N_3^- ions in compound **3** (C gray, O red, N blue, Cl green, Mn purple).

from the bent coordination character of the *anti-anti* formato bridges and the stacking of the alkyl groups between the chains. The JT axes of the Mn^{III} ions in the different units are therefore not closely parallel to each other along the chain direction. The chains run parallel to the *b* direction in the lattice and the shortest interchain Mn···Mn distance is 11.5 Å, which suggests that the chains are well isolated from each other by the bulk alkyl groups of the ligands (see the Supporting Information).

The azide ion (N_3^-), which has a similar coordination ability to formate, was also used to string the trinuclear units together to give a similar chain-like compound $[Mn_3O(t\text{Bu-sao})_3N_3(CH_3OH)_4]\cdot 0.5\,CH_3OH$ (**3**). The $\{Mn^{III}{}_3O\}$ units in this compound are linked by an end-to-end (EE) azide instead of an *anti-anti* formate anion (Figure 1 c), with similar molecular geometries for the $\{Mn^{III}{}_3O\}$ unit to those in **1** and **2**. The Mn–N_{azido} distances are 2.262 and 2.264 Å, respectively. The azide-bridged Mn···Mn distance is 5.964 Å, which is significantly shorter than the formate-bridged distance in **2**, and the adjacent $\{Mn^{III}{}_3\}$ planes are nearly parallel to each other (dihedral angle: 8.5°). This feature should be a result of the linear coordination orientation of the EE azide, which is different to the bent one of *anti-anti* formate. All the Mn^{III} ions therefore have their JT axes aligned nearly parallel. The well-separated chains are arranged in a parallel manner along the *c* direction with a shortest interchain Mn···Mn distance of 10.2 Å (see the Supporting Information).

The magnetic properties of **1**–**3** were studied with a Quantum Design MPMS XL-5 SQUID magnetometer. The temperature-dependent $\chi_M T$ value per Mn_3 unit for **1** decreases from $8.56\,cm^3\,mol^{-1}\,K$ at 300 K, which is close to the expected value of $9.0\,cm^3\,mol^{-1}\,K$ for three isolated Mn^{III} ions, to $2.49\,cm^3\,mol^{-1}\,K$ at 2 K (see the Supporting Information), which corresponds to an antiferromagnetic interaction within an $\{Mn^{III}{}_3O\}$ triangle with an uncompensated ground state. The data above 10 K were well fitted to the Curie–Weiss law, with $C = 9.04\,cm^3\,mol^{-1}\,K$ and $\theta = -15.3\,K$. The data above 5 K, analyzed by the isosceles triangle (J_1, J_2) model ($H = -2J_1(\Sigma S_1S_2 + \Sigma S_1S_3) - 2J_2\Sigma S_2S_3$, with $S_1 = S_2 = S_3 = 2$), gave $J_1 = -0.56\,cm^{-1}$, $J_2 = -1.97\,cm^{-1}$, and $g = 1.99$, with $R = 1.7\times10^{-5}$ ($R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{obs}]^2$). These results indicate that an AF coupling is present in the oximato-bridged $\{Mn^{III}{}_3O\}$ units, although this interaction is rather weak.[10a] The ac susceptibility data at zero dc field show a weak signal but clear frequency dependence, and a plot of the ac susceptibility values as a function of ac frequency (ν) at 1.8 K shows an uncompleted semicircle (see the Supporting Information).

Oxo-centered triangular $[M_3O(O_2CR)_6L_3]^{n+}$ ($n = 0, 1$) cationic complexes have been studied for a long time and have been widely used to construct magnetic materials.[12] However, AF exchange often leads to a non-magnetic or a low-spin ground state without SMM behavior, with the only exception being a ferromagnetic SMM.[13] The probable reason for this is the inconsistent easy axis of magnetization in the trinuclear unit. Magnetic anisotropy is one of the important factors that must be considered when constructing SMMs.[14] Complex **1** has a triangular $\{M_3O\}$ structure where the JT axes of all Mn^{III} ions are almost parallel. This complex exhibits an ac frequency dependence of its SMM-like magnetism; ultralow-temperature studies are expected to provide further support for this.

The temperature-dependent dc susceptibility of **2** shows a similar behavior to that of **1** (see the Supporting Information). The data above 10 K follow Curie–Weiss behavior, with $C = 9.42\,cm^3\,mol^{-1}\,K$ and $\theta = -11.3\,K$. Considering the structural similarities between these two complexes, the $\chi_M T$ data could be well fitted by the same triangle model used for **1** with the addition of an interunit interaction by the mean-field approximation (zJ'), which results in $J_1 = -0.38\,cm^{-1}$, $J_2 = -1.37\,cm^{-1}$, $zJ' = -0.059\,cm^{-1}$, and $g = 2.03$, with $R = 3.7\times10^{-5}$. The zJ' approximation should include the intrachain (J_3) interaction between adjacent $\{Mn^{III}{}_3\}$ units and interchain (J_4) interactions, although J_4 is likely to be very small because of the large interchain separation. The couplings within the triangle are similar to those in **1**, while the intrachain coupling, which occurs mainly through the formato bridge, is weak. Consequently, the temperature of the irreversibility in the field-cooled (FC) and zero-field-cooled (ZFC) plots is as low as 1.9 K (see the Supporting Information). The field-dependent magnetization at 1.8 K (see the Supporting Information) displays a small hysteresis with a coercive field of 50 Oe.

The ac susceptibility data collected in the frequency range 0.1–1500 Hz show a strong frequency-dependence below 4.5 K (Figure 2). This behavior precludes the possibility of three-dimensional long-range ordering and indicates the slow relaxation of the magnetization, as observed for SMMs or SCMs. Considering the one-dimensional character of **2**, the present magnetization dynamics indicate the occurrence of SCM-like behavior. Moreover, the shift of the peak temperature (T_p) of χ' can be quantified as $\varphi = (\Delta T_p/T)/\Delta(\log f) = 0.16$, which is larger than that of a typical spin glass (where φ is generally about 0.01).[15] The peak temperatures of χ'' can be fitted by the Arrhenius law (see the Supporting Information), which gives $\tau_0 = 4.4 \times 10^{-11}$ s and $\Delta_\tau/k_B = 47.9$ K, thereby confirming the superparamagnetic behavior. The Cole–Cole diagram (see the Supporting Information) exhibits a quasi-semicircle shape.

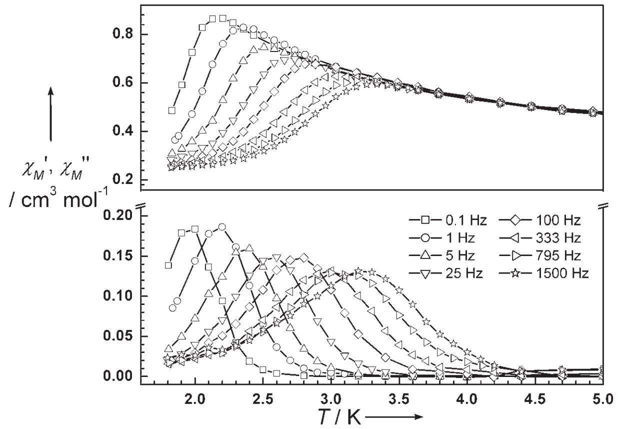

Figure 2. Temperature-dependence of the real (χ' upper panel) and imaginary components (χ'' lower panel) of the ac susceptibility for **2** in zero dc field with an ac field of 3 Oe.

During the preparation of this manuscript a new 1D chain was reported with *anti-anti* acetato-bridged {$Mn^{III}{}_3O$} units. This chain displays the coexistence of SCM behavior and dielectric relaxation,[7k] although the relaxation temperature and the energy barrier are not particularly high. In our case the *anti-anti* formato bridge induces the anisotropy of all the Mn^{III} ions in the same orientation in chain compound **2**. Despite the fact that the inter-trinuclear interaction is about three times larger than that in a similar chain compound[7k] there is no distinct increase of T_B or the energy barrier because of the nonparallel {$Mn^{III}{}_3$} planes and of the weak nature of the coupling.

The introduction of an azido bridge, which is a stronger magnetic coupler, in **3** results in a quite different magnetic behavior to the formate-bridged chain **2** and its acetate-bridged analogue.[7k] The $\chi_M T$ value of 8.55 cm^{3}mol^{-1}K at 300 K per {Mn_3} unit decreases gradually upon lowering the temperature and reaches a minimum at 42 K (4.89 cm^{3}mol^{-1}K). It then increases abruptly below 20 K to a maximum of 53.6 cm^{3}mol^{-1}K at 9 K, thereby suggesting a ferrimagnetic-like or canted antiferromagnetic-like character (Figure 3). The susceptibility data above 50 K obey the Curie–Weiss law, with $C = 10.29$ cm^{3}mol^{-1}K and $\theta = -60.9$ K. Analysis of the $\chi_M T$ data above 20 K using the same model as for **2** gave $J_1 = -5.04$ cm^{-1}, $J_2 = -9.51$ cm^{-1}, $zJ' = 3.94$ cm^{-1}, and $g = 2.07$, with $R = 7.8 \times 10^{-5}$. The couplings between the metal ions in the {$Mn^{III}{}_3O$} unit (J_1 and J_2) are similar to those of related materials.[9] The positive sign of zJ' indicates that coupling through the EE azide could be ferromagnetic, which is in contrast to the mainly AF interactions shown by other EE azide-bridged Mn^{III} compounds.[16] Treatment of the trinuclear {$Mn^{III}{}_3O$} moiety as the repeat unit in a uniform chain model gave similar results, which is consistent with a ferromagnetic-like behavior at low temperature in the dc measurement.

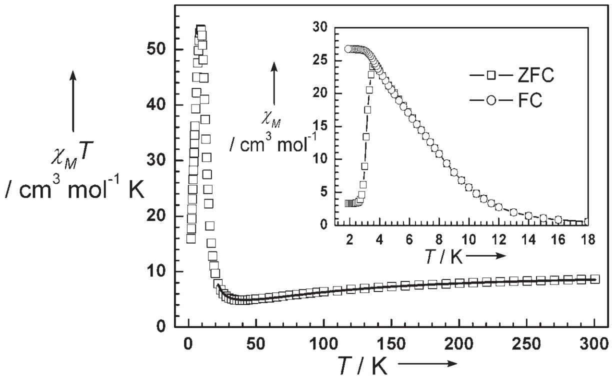

Figure 3. Plots of $\chi_M T$ and $1/\chi_M$ versus T for **3** in an applied field of 1 kOe from 2 to 300 K; the solid lines represent the best theoretical fit of the data (see text). Inset: Field-cooled (FC) and zero-field-cooled (ZFC) magnetization for **3** at an applied field of 5 Oe.

Irreversibility was observed in the ZFC and FC magnetization below 3.7 K (Figure 3, inset), thereby indicating the presence of a slowing down of the magnetization relaxation. Furthermore, the field dependence of the magnetization of **3** was measured in the temperature range 1.8–3.5 K (Figure 4), where slow relaxation of the magnetization gives a coercive field of about 14.5 kOe at 1.8 K. This value decreases dramatically with increasing temperature, a behavior which is reminiscent of various other one-dimensional Mn^{III} chain compounds.[7h,17] This behavior might be due to the presence of a frozen magnetized state without regard to the three-dimensional ordering.

The ac susceptibility data for **3** in the temperature range 1.8–12 K show a strong frequency-dependence in both the real (χ') and imaginary (χ'') parts (Figure 5). This behavior precludes the presence of three-dimensional long-range ordering and indicates slow relaxation of the magnetization,

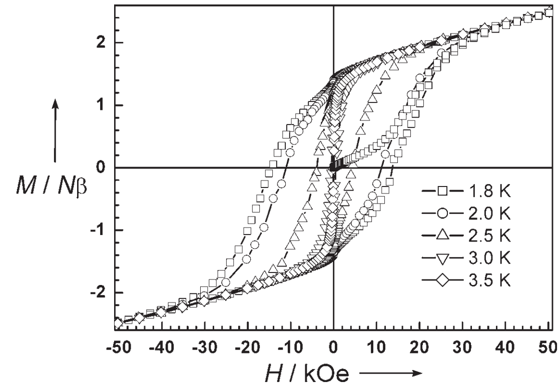

Figure 4. Magnetization versus field hysteresis loops measured for **3** at different temperatures.

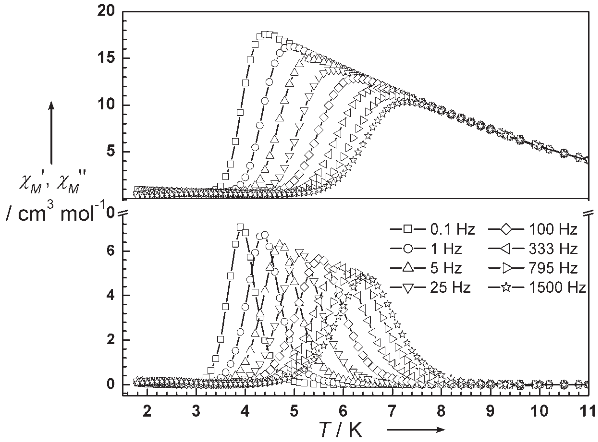

Figure 5. Temperature- and frequency-dependence of the real (χ', upper panel) and imaginary (χ'' lower panel) parts of the ac susceptibility for **3**.

as observed for SCMs, owing to the chain arrangement in **3** and its one-dimensional magnetism, which is similar to that in **2.** The φ value is 0.16 according to the shift of the peak temperature (T_p) of χ'. The frequency-dependence of the peak temperatures of χ'' can be fitted well to the Arrhenius law (see the Supporting Information), with physically reasonable values of $\tau_0 = 3.7 \times 10^{-11}$ s and $\Delta_\tau/k_B = 96.6$ K.

Additional ac susceptibility measurements as a function of ac frequency were performed at fixed temperature of 5 K (see the Supporting Information). These data were fitted by a generalized Debye model[18] with an α parameter of 0.17, which indicated a narrow distribution of relaxation times. As expected from this chain model, a plot of $\ln(\chi_M'T)$ against T^{-1} decreases almost linearly between 20 and 13 K with an energy gap, Δ_ξ/k_B, of 48.5 K, thus confirming the 1D nature of **3** (see the Supporting Information). The low-temperature deviation (below 10 K) from the linear regime is consistent with a geometrical limitation of the correlation length owing to the presence of defects.[19]

One essential requirement for an SCM is the existence of uniaxial anisotropy in the unit ultimately intended to be an Ising chain.[8] The JT axes of all three Mn^{III} ions in the {Mn$^{III}_3$O} unit of **1** are parallel and this complex therefore shows SMM-like behavior, which makes it a good building block to be strung into a 1D assembly through the apical positions with an appropriate linker, such as formato or azido, to enhance the uniaxial anisotropy. Azide usually mediates a much stronger coupling between metal ions than formate.[20] A comparison of the magnetic coupling in compounds **2** and **3** shows that the two kinds of bridges not only mediate the different interactions but also influence the intra-trinuclear coupling. The shortest inter-trinuclear distance between the Mn^{III} ions in compounds **1**–**3** also decreases from 7.531 Å in **1** to 6.471 Å in **2** and 5.964 Å in **3**. This change results in stronger coupling between the {Mn$^{III}_3$O} units and more evident SCM-type behavior, which suggests that a consistent anisotropy and large magnetic interactions are critical parameters for the formation of SCMs with higher blocking temperatures. Trinuclear compound **1**, which has a consistent anisotropy, could be a good candidate for use as a magnetic building block for constructing a new family of SCMs.

Experimental Section

All starting materials were purchased as reagent grade and were used without further purification.

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

1: A mixture of $MnCl_2 \cdot 4H_2O$ (0.06 g, 0.3 mmol) and *t*Bu-saoH$_2$ (0.075 g, 0.3 mmol) in methanol (10 mL) was stirred for 5 min and NaOH (0.02 g, 0.5 mmol) was added. The solution turned dark brown. It was then stirred for one hour and filtered. The filtrate was allowed to stand for several days to give complex **1** as dark brown crystals (70 % yield). Elemental analysis (%) calcd for $C_{50}H_{85}ClMn_3N_3O_{13}$: C 52.84, H 7.54, N 3.70; found: C 53.01, H 7.42, N 3.79. IR (pure sample): $\tilde{\nu} = 3356$(w), 2958(s), 2907(m), 2870(m), 1603(w), 1582(w), 1548(m), 1536(m), 1463(w), 1430(s), 1392(w), 1363(w), 1296(m), 1275(m), 1254(m), 1233(w), 1201(w), 1176(m), 1042(s), 845(m), 735 cm^{-1} (m).

2: A methanol solution (10 mL) of $Mn(HCOO)_2 \cdot 2H_2O$ (0.06 g, 0.3 mmol), *t*Bu-saoH$_2$ (0.075 g, 0.3 mmol), and NaOH (0.004 g, 0.1 mmol) was stirred for one hour. The brown-green precipitate formed was removed by filtration and the filtrate was left undisturbed. Slow evaporation of the solvents gave large crystals of **2** (yield: 30 %). Elemental analysis (%) calcd for $C_{52}H_{89}Mn_3N_3O_{15.5}$: C 53.42, H 7.67, N 3.59; found: C 53.82, H 7.49, N 3.34. IR (pure sample): $\tilde{\nu} = 3298$(w), 2957(s), 2907(m), 2870(m), 1603(m), 1572(s), 1549(m), 1536(m), 1463(w), 1429(s), 1392(w), 1362(m), 1296(m),1275(m), 1253(s), 1201(m), 1176(m), 1135(w), 1039(s), 846(m), 735 cm^{-1} (m).

3: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.08 g, 0.3 mmol) and *t*Bu-saoH$_2$ (0.075 g, 0.3 mmol) were dissolved in methanol (10 mL) whilst stirring for 5 min. NaN_3 (0.035 g, 0.5 mmol) was then added and the solution turned dark brown. After stirring for an hour the solution was filtered and the filtrate was left undisturbed to give dark brown crystals of **3** (yield: 50 %). Elemental analysis (%) calcd for $C_{49.5}H_{81}Mn_3N_6O_{11.5}$: C 53.61, H 7.36, N 7.58; found: C 53.42, H 7.26, N 7.41. IR (pure sample): $\tilde{\nu} = 3398$(w), 2958(s), 2907(m), 2870(m), 2075(s), 1603(w), 1535(m), 1429(s), 1275(m), 1253(s), 1176(m), 1040(s), 845(m), 735 cm^{-1} (m).

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[11] Crystal structure data for **1**: $C_{50}H_{85}ClMn_3N_3O_{13}$, $M_r = 1136.48$, monoclinic, space group $P2_1/c$, $a = 14.8075(3)$, $b = 28.5208(6)$, $c = 15.6968(4)$ Å, $\beta = 111.0574(7)°$, $V = 6186.4(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.220\ \mathrm{g\,cm^{-3}}$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.701\ \mathrm{mm^{-1}}$, $F(000) = 2408$, GOF = 0.889, $T = 273$ K, final $R1 = 0.0621$ and $wR2 = 0.1226$ for $I > 2\sigma(I)$. **2**: $C_{49.5}H_{81}Mn_3N_6O_{11.5}$, $M_r = 1109.02$, monoclinic, space group $P2_1/c$, $a = 15.6891(4)$, $b = 28.7759(6)$, $c = 14.5171(3)$ Å, $\beta = 110.4250(10)°$, $V = 6142.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.199\ \mathrm{g\,cm^{-3}}$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.662\ \mathrm{mm^{-1}}$, $F(000) = 2348$, GOF = 0.921, $T = 273$ K, final $R1 = 0.0609$ and $wR2 = 0.1464$ for $I > 2\sigma(I)$. **3**: $C_{52}H_{89}Mn_3N_3O_{15.5}$, $M_r = 1169.08$, monoclinic, space group $P2_1/c$, $a = 14.0749(2)$, $b = 15.0723(2)$, $c = 31.7811(5)$ Å, $\beta = 97.3385(4)°$, $V = 6686.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.161\ \mathrm{g\,cm^{-3}}$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.615\ \mathrm{mm^{-1}}$, $F(000) = 2484$, GOF = 0.990, $T = 180$ K, final $R1 = 0.0625$ and $wR2 = 0.1774$ for $I > 2\sigma(I)$. The data were collected on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the Sortav program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms with the SHELX-97 program. CCDC-646481 to CCDC-646483 (**1**–**3**) 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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