“Depolymerization” Approach in Mn Cluster Chemistry: Controlled Cleavage of a 1D Coordination Polymer Consisting of Mn₈ Units in Its Constituent, Discrete Mn₈ Complex

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The cleavage of a 1D coordination polymer (Mn²⁺₂Mn₃⁺₈)ₙ containing recognizable octanuclear units to obtain the discrete Mn²⁺₂Mn₃⁺₈ cluster is reported.

The preparation and study of molecular clusters of paramagnetic 3d metal ions continues to be a major research area for many groups around the world.¹⁻³ This is particularly true for Mn clusters containing at least some Mn³⁺ centers.⁴,⁵ Thus, there is a need for the development of new synthetic methods that can yield new 3d metal clusters.

One of the synthetic goals in polynuclear coordination chemistry with flexible organic ligands is to try to control the nature of the final product. In most cases, the precise nuclearity and structure of the reaction products cannot be predicted from the reagents and synthetic conditions employed, even though the reactions are certainly directed toward the formation of higher-nuclearity species.⁶ Elegant approaches toward the achievement of this synthetic goal include the coupling or linkage of smaller fragments for making larger assemblies⁷ and oligomerization of low-nuclearity clusters by desolvation,⁸ among others.⁹ Almost all such efforts involve a transition from lower- to higher-nuclearity complexes. An alternative, equally attractive approach would be the controlled cleavage of coordination polymers (Mₙ)ₙ containing recognizable high-nuclearity Mₙ units (“polymers of clusters”) to obtain the discrete Mₙ clusters. We have applied this approach once.¹⁰

However, we have been seeking other examples of such a “depolymerization” approach to contribute to its generalization. We herein report a second realization of this idea for M = Mn and x = 8. It should be mentioned that the opposite approach, i.e., the transformation of discrete Mₙ clusters into the corresponding (Mₙ)ₙ coordination polymers, is well-known in inorganic chemistry.¹¹a,b Also note that various discrete cluster forms were targeted in the past, when the polymeric forms had been identified, and obtained from simple starting materials by procedures containing some elements of synthetic control.¹¹c

The reaction of Mn₂(O₂CEt)₂(O₂CMe)₂(OMe)₃[ClO₄]₉ with 3:1 molar ratio in MeOH (see the Supporting Information) led to a red-brown solution, which upon storage at room temperature gave deep-red crystals of [Mn²⁺₂Mn₃⁺₈(O₂CMe)₂(HCO₂)]ₙ(ClO₄)ₙ·nMeOH·2nH₂O (see the Supporting Information) led to a red-brown solution, which upon storage at room temperature gave deep-red crystals of [Mn²⁺₂Mn₃⁺₈(O₂CMe)₂(HCO₂)]ₙ(ClO₄)ₙ·nMeOH·2nH₂O.
Figure 1. (Top) Metal-labeled representation of the cationic Mn$_8$ repeating unit of 1. The squared atoms belong to neighboring units. An extra HCO$_2^-$ has been drawn to emphasize the intercluster connections. (Bottom) Core of the Mn$_8$ cluster unit of 1. Color scheme: Mn$^{II}$, yellow; Mn$^{III}$, black; O, red; N, blue; C, gray.

(1·MeOH·2H$_2$O) in 80% yield (based on the ligand), where (py)$_2$CO$_2^-$ is the dianion of the gem-diol form [(py)$_2$-Cl(OH)$_2$] of (py)$_2$CO and (py)$_2$C(OMe)O$^-$ is the anion of the hemiketal form [(py)$_2$Cl(OMe)(OH)] of (py)$_2$CO. Di-2-pyridyl ketone is a currently popular ligand in transition-metal chemistry. Water and alcohols (ROH), among other nucleophiles, have been shown to add to the carboxyl group upon coordination of the carbonyl oxygen and/or the 2-pyridyl rings, forming the ligands (py)$_2$C(OH)$_2$ and (py)$_2$C(O)(OR)(OH), respectively (Figure S1 in the Supporting Information).

The crystal structure of 1·MeOH·2H$_2$O consists of positively charged, sinusoidal 1D chains (Figure S2 in the Supporting Information). CIO$_4^-$ ions (located in prism-shaped cavities among three adjacent chains), and solvate units. Each chain is assembled by the linking of octanuclear \{Mn$^{III}$_2Mn$^{III}$O$_2$(py)$_2$CO$_2$\}$_4$(py)$_2$C(OMe)O$_2$(O$_2$CEt)$_6$ cluster units (Figure 1, top) through anti-$\mu$-HCO$_2^-$ ligands formed by the oxidation of MeOH. The HCO$_2^-$ groups connect two Mn$^{III}$ atoms (Mn1 and Mn8) of adjacent cluster units. The (py)$_2$CO$_2^-$, (py)$_2$C(OMe)O$^-$, and EtCO$_2^-$ groups bind in $\eta^1$-$\eta^1$-$\eta^1$-$\eta^1$-$\eta^1$-$\eta^1$ modes, respectively (Chart 1), while the two o xo groups are $\mu_3$. The Mn$^{III}$_2Mn$^{III}$ repeating unit contains a central

\[ \text{[Mn}^{III}$_2$Mn$^{III}$(py)$_2$CO$_2$\}$_4$(py)$_2$C(OMe)O$_2$(O$_2$CEt)$_6]^{2+} \]

\[ \text{[Mn}^{III}$_2$Mn$^{III}$(py)$_2$CO$_2$\}$_4$(py)$_2$C(O)(OH)$_2$\] of (py)$_2$CO and (py)$_2$C(OMe)O$^-$ respectively (Figure S1 in the Supporting Information).

The molecule of 1·MeOH·2H$_2$O: C$_{94}$H$_{70}$Mn$_8$N$_{12}$O$_{35}$Cl, $M_w = 2353.71$, monoclinic, space group $P2_1$ with $a = 10.9527(17)$ Å, $b = 39.602(6)$ Å, $c = 13.043(1)$ Å, $\beta = 113.813(3)^\circ$, $V = 5175.8(14)$ Å$^3$, $T = 134.02(2)$ $K$, $Z = 2$. $R_1 = 0.0694$, $wR_2 = 0.1306$.

Crystall structure data for 2·MeOH·H$_2$O: C$_{94}$H$_{70}$Mn$_8$N$_{12}$O$_{35}$Cl, $M_w = 2287.31$, triclinic, space group $P$ with $a = 11.4032(2)$ Å, $b = 15.4674(4)$ Å, $c = 16.4846(3)$ Å, $\alpha = 74.020(2)^\circ$, $\beta = 88.595(2)^\circ$, $\gamma = 86.895(2)^\circ$, $V = 100(2)$ Å$^3$, $Z = 1$. $R_1 = 0.0694$, $wR_2 = 0.1306$. The contribution of the disordered solvent area to the structure factors was determined using the Platon Squeeze procedure.


(15) Crystal structure data for 1·MeOH·2H$_2$O: C$_{94}$H$_{70}$Mn$_8$N$_{12}$O$_{35}$Cl, $M_w = 2353.71$, monoclinic, space group $P2_1$ with $a = 10.9527(17)$ Å, $b = 39.602(6)$ Å, $c = 13.043(1)$ Å, $\beta = 113.813(3)^\circ$, $V = 5175.8(14)$ Å$^3$, $T = 150(2)$ K, $Z = 2$. $R_1 = 0.0694$, $wR_2 = 0.1306$.


Chart 1. Bridging and Terminal Modes Displayed by the Ligands Present in Complexes 1 and 2$^a$

$^a$Multiple $\eta$ values refer to the number of metal ions to which each ligand atom attaches.

$\text{[Mn}^{III}$_2$(\mu$_2$-O$_2$)$_2$\}$_4$]^{8+}$ subunit (atoms Mn3, Mn4, Mn5, Mn6, O64, and O65), which links to two [Mn$^{II}$_2Mn$^{III}$(\mu-OR)$_2$(\mu-OR')$_2$]$_{3+}$ subunits via the wingtip Mn$^{III}$ ions, each through one bridging O atom and one triatomic OCO bridge of two different (py)$_2$CO$_2^-$ ligands; the monatomic bridge is part of the triatomic OCO bridge, which connects the body Mn$^{III}$ atom of the butterfly subunit with the Mn$^{III}$ atom of one mixed-valence dinuclear subunit. Considering only the monatomic bridges, the core is $\text{[Mn}^{III}$_2$Mn$^{III}$_2$(\mu$_2$-O$_2$)$_2$(\mu-OR)$_2$(\mu-OR')$_2$]_{3+}$ (Figure 1, bottom), where $R'$ = (py)$_2$C(O)- and $R$ = (py)$_2$C(OMe)$. The Mn oxidation states were obtained from metric parameters, bond valence sum (BVS) calculations (Table S1 in the Supporting Information), and the clear Jahn–Teller axial elongation at the near-octahedral Mn$^{III}$ atoms, Mn2–Mn7. The Mn$^{II}$ atoms, Mn1 and Mn8, are six-coordinate with distorted octahedral geometries.

The presence of well-defined Mn$_8$ cluster units in 1 suggested that replacement of the bridging HCO$_2^-$ groups by terminal monodentate or bidentate ligands might cause polymer cleavage and formation of the constituent Mn$_8$ cluster. We tried many reactions of 1 with a great variety of neutral (in the presence of CIO$_4^-$ ions) or monoanionic monodentate and bidentate terminal ligands (e.g., SCN$, $$^-$, bpy, acac$, $ etc.), but we could not crystallize the obtained products. The “solution” came from the use of less “logical” ligands, namely, monocarboxylates (can act either as terminal or bridging groups) other than formates (in the majority of cases, HCO$_2^-$ ions act as bridging ligands$^{18}$). Treatment of a slurry of 1 in MeOH with an excess (3–4 equiv) of EtCO$_2$H led to a homogeneous deep-red solution, from which the desired discrete octanuclear cluster $\text{[Mn}^{III}$_2$Mn$^{III}$_2$(\mu$_2$-O$_2$)$_2$(\mu$_2$-O$_2$)$_2$$_3$]^{8+}$ (2) slowly crystallized in moderate yield (35%); the product analyzed satisfactorily as 2 (see the Supporting Information).

The molecular structure of 2 (Figure 2) is centro symmetric. Its structure is strikingly similar to that of the cluster unit that is present in 1, with the only difference being that the halves of formate ligands (summing to a full HCO$_2^-$ group per Mn$_8$ unit) in the latter have been replaced by two extra


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Figure 2. Metal and partly oxygen-labeled representation of 2. Primes are used for symmetry-related atoms. The color scheme is the same as that in Figure 1.

pseudochelating EtCO₂⁻ groups (Chart 1) in the former (M₄₋O₇ = 2.179 Å; Mn₄₋O₈ = 2.696 Å). A consequence of the pseudochelating (anisobidentate) nature of the additional EtCO₂⁻ groups is that the outer Mn⁺⁺ centers (Mn₄ and Mn⁴⁺) in 2 are becoming seven-coordinate. The core of 2 (Figure S3 in the Supporting Information) is identical with that of the Mn₈ unit in 1. Complex 2 joins a handful of Mn⁺²-Mn⁺³₆ clusters¹⁹ and is a member of a very small family of Mn clusters with forms of (py)₂CO as ligands.¹³a Interestingly, the process proved to be reversible: complex 2 reacts with 1 equiv of HCO₂H in the presence of ClO₄⁻ to give the 1D polymer 1D in low yield (20−25%).

The answer to the question of “why the carboxylate affects the product so much and makes depolymerization possible” is not easy. It seems the possible reason is the bulk of the formate because its ethyl group (Et) would bump into the carboxylate R group, i.e., that propionate cannot bind like e.g., MeCO₂⁻ and PhCO₂⁻ in low yield (20−25%).

Solid-state direct-current magnetic susceptibility (χM) data on dried 1 and 2 were collected in a 0.3 T field in the 2.0−300 K range and are plotted as χM vs T in Figure 3. The 300 K values are slightly (1) or significantly (2) lower than the spin-only (g = 2) value of 26.75 cm³ K mol⁻¹ expected for two Mn⁺⁺ and six Mn⁺⁺ noninteracting ions. The measurements show a continuous decrease to χM values of 4.51 (2) and 1.52 (1) cm³ K mol⁻¹ down to 2.0 K, indicating the presence of antiferromagnetic interactions. Preliminary analysis of the magnetic data²⁰ indicates that there is weak antiferromagnetic coupling between the central $S = 3$ butterfly $\{\text{Mn}^{III}_d(\mu_3-O)_{12}\}_{3}^{1+}$ and the two $S = 1/2$ $\{\text{Mn}^{III}_d(\mu-OR)\}_{3}^{1+}$ subunits (an $1/2 - 3 - 1/2$ antiferromagnetic scheme), leading to a ground state with $S = 2$ in 2 and very weakly antiferromagnetically coupled $S = 2$ Mn₈ units in 1.

In summary, this work represents a successful “test of feasibility” for our “depolymerization” approach that could also prove useful for the isolation in discrete form of the repeating cluster of other coordination polymers. We recognize that the formation of 2 from 1 relies on the EtCO₂⁻ ligand and its flexibility in participating in two different ligation modes (η¹-η¹′ μ and η²-η²′) in the same compound. The utility of this approach is shown by the fact that we have not yet prepared 2 from reaction systems that involve simple Mn starting materials.

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Supporting Information Available: Crystallographic data in CIF format, structural representations (Figures S1−S3), BVS calculations (Table S1), and synthetic procedures for 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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²⁰ Details will be reported in a forthcoming full paper.