Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 359–361 **359**
DOI: 10.1021/ic901974d

“Depolymerization” Approach in Mn Cluster Chemistry: Controlled Cleavage of a 1D Coordination Polymer Consisting of Mn_8 Units in Its Constituent, Discrete Mn_8 Complex

Constantinos C. Stoumpos,[†] Olivier Roubeau,[‡] Guillem Aromí,[§] Anastasios J. Tasiopoulos,[⊥] Vassilios Nastopoulos,[†] Albert Escuer,*[,§] and Spyros P. Perlepes*[,†]

[†]*Department of Chemistry, University of Patras, 265 04 Patras, Greece,* [‡]*Instituto de Ciencia de Materiales de Aragón, CSIC y Universidad de Zaragoza, Plaza San Francisco, Zaragoza 50009, Spain,* [§]*Departament de Quimica Inorganica, Universitat de Barcelona, Marti Franqués 1-11, Barcelona 08028, Spain, and* [⊥]*Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus*

Received October 6, 2009

The cleavage of a 1D coordination polymer $(Mn^{II}{}_2Mn^{III}{}_6)_n$ containing recognizable octanuclear units to obtain the discrete $Mn^{II}{}_2Mn^{III}{}_6$ 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 Mn^{III} 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 assemblies[7] 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 $(M_x)_n$ containing recognizable high-nuclearity M_x units (“polymers of clusters”) to obtain the discrete M_x 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 M_x clusters into the corresponding $(M_x)_n$ 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 $Mn(O_2CEt)_2 \cdot 0.35H_2O$,[12a] di-2-pyridyl ketone, and $[Mn_3O(O_2CEt)_6(py)_3](ClO_4)$[12b] in a 3:3:1 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 $[Mn^{II}{}_2Mn^{III}{}_6O_2\{(py)_2CO_2\}_4\{(py)_2C(OMe)O\}_2(O_2CEt)_6(HCO_2)]_n(ClO_4)_n \cdot nMeOH \cdot 2nH_2O$

---

*To whom correspondence should be addressed. E-mail: albert.escuer@qi.ub.es (A.E.), perlepes@patreas.upatras.gr (S.P.P.).

(1) Winpenny, R. E. P. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, The Netherlands, 2004; Vol. *7*, pp 125−175.

(2) For example, see:Theil, E. C.; Matzapetakis, M.; Liu, X. *J. Biol. Inorg. Chem.* **2006**, *11*, 803.

(3) (a) Aromí, G.; Brechin, E. K. *Struct. Bonding* (*Berlin*) **2006**, *122*, 1. (b) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.

(4) Hewitt, I. J.; Tang, J. K.; Maddhu, N. T.; Clérac, R.; Buth, G.; Anson, C. F.; Powell, A. K. *Chem. Commun.* **2006**, 2650.

(5) (a) Bagai, R.; Christou, G. *Chem. Soc. Rev.* **2009**, *38*, 1011. (b) Milios, C. J.; Inglis, R.; Vinslava, A.; Bagai, R.; Wernsdorfer, W.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 12505.

(6) Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2002**, 1.

(7) (a) Libby, E.; Folting, K.; Huffman, C. J.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2549. (b) Wang, S.; Tsai, L.-H.; Folting, K.; Martin, J. D.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1994**, 671.

(8) Brechin, E. K.; Harris, S. G.; Parsons, S.; Winpenny, R. E. P. *Chem. Commun.* **1996**, 1439.

(9) (a) Christou, G. *Polyhedron* **2005**, *24*, 2065. (b) Ako, A. M.; Mereacre, V.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2009**, 544.

(10) Lalioti, N.; Raptopoulou, C. P.; Terzis, A.; Aliev, A. E.; Gerothanassis, I. P.; Manessi-Zoupa, E.; Perlepes, S. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 3211.

(11) Examples in Mn chemistry:(a) Ma, C.-B.; Hu, M.-Q.; Chen, H.; Chen, C.-N.; Liu, Q.-T. *Eur. J. Inorg. Chem.* **2008**, 5274. (b) Roubeau, O.; Clérac, R. *Eur. J. Inorg. Chem.* **2008**, 4325. (c) Moushi, E. E.; Stamatatos, T. C.; Wernsdorfer, W.; Nastopoulos, V.; Christou, G.; Tasiopoulos, A. *Inorg. Chem.* **2009**, *48*, 5049.

(12) (a) Aromí, G.; Bhaduri, S.; Artús, P.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2002**, *21*, 1779. (b) Cañada-Vilalta, C.; Huffman, J. C.; Christou, G. *Polyhedron* **2001**, *20*, 1785.

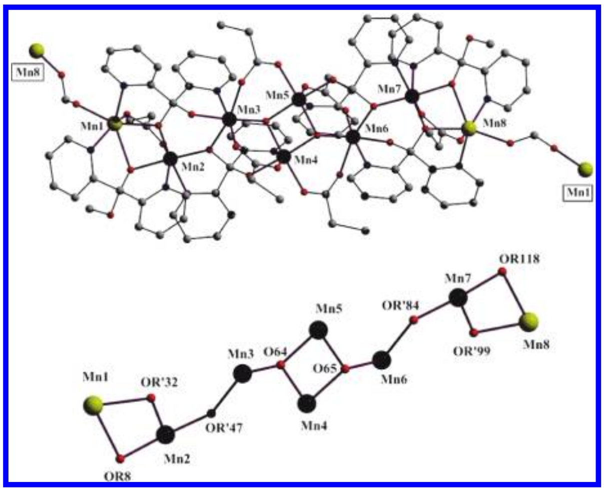
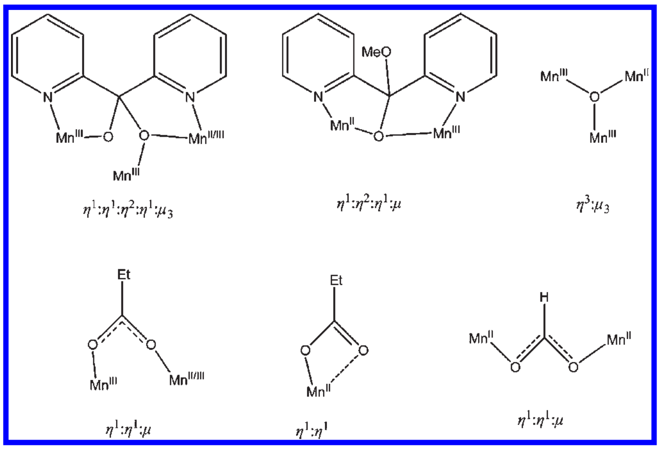


Figure 1. (Top) Metal-labeled representation of the cationic Mn_8 repeating unit of **1**. The squared atoms belong to neighboring units. An extra HCO_2^- has been drawn to emphasize the intercluster connections. (Bottom) Core of the Mn_8 cluster unit of **1**. Color scheme: Mn^{II}, yellow; Mn^{III}, black; O, red; N, blue; C, gray.

(**1**·MeOH·2H_2O) in 80% yield (based on the ligand), where $(py)_2CO_2^{2-}$ is the dianion of the *gem*-diol form $[(py)_2C(OH)_2]$ of $(py)_2CO$ and $(py)_2C(OMe)O^-$ is the anion of the hemiketal form $[(py)_2C(OMe)(OH)]$ of $(py)_2CO$. Di-2-pyridyl ketone is a currently popular ligand in transition-metal chemistry.[13] Water and alcohols (ROH), among other nucleophiles, have been shown to add to the carbonyl group *upon coordination* of the carbonyl oxygen and/or the 2-pyridyl rings, forming the ligands $(py)_2C(OH)_2$ and $(py)_2C(OR)(OH)$, respectively (Figure S1 in the Supporting Information).[14]

The crystal structure[15] of **1**·MeOH·2H_2O consists of positively charged, sinusoidal 1D chains (Figure S2 in the Supporting Information), ClO_4^- ions (located in prism-shaped cavities among three adjacent chains), and solvate molecules. Each chain is assembled by the linking of octanuclear $\{Mn^{II}_2Mn^{III}_6O_2\{(py)_2CO_2\}_4\{(py)_2C(OMe)O\}_2(O_2CEt)_6\}^{2+}$ cluster units (Figure 1, top) through *anti*,*anti*-HCO_2^- ligands formed by the oxidation of MeOH.[16] The HCO_2^- groups connect two Mn^{II} atoms (Mn1 and Mn8) of adjacent cluster units. The $(py)_2CO_2^{2-}$, $(py)_2C(OMe)O^-$, and $EtCO_2^-$ groups bind in $\eta^1:\eta^1:\eta^2:\eta^1:\mu_3$, $\eta^1:\eta^2:\eta^1:\mu$ and *syn*,*syn*-$\eta^1:\eta^1:\mu$ modes, respectively (Chart 1), while the two oxo groups are μ_3. The $Mn^{II}_2Mn^{III}_6$ repeating unit contains a central $\{Mn^{III}_4(\mu_3\text{-}O)_2\}^{8+}$ subunit (atoms Mn3, Mn4, Mn5, Mn6, O64, and O65), which links to two $\{Mn^{II}Mn^{III}(\mu\text{-}OR)(\mu\text{-}OR')\}^{3+}$ subunits via the wingtip Mn^{III} ions, each through one bridging O atom and one triatomic OCO bridge of two different $(py)_2CO_2^{2-}$ 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 $\{Mn^{II}_2Mn^{III}_6(\mu_3\text{-}O)_2(\mu\text{-}OR')_4(\mu\text{-}OR)_2\}^{8+}$ (Figure 1, bottom), where R′ = $(py)_2C(O)-$ and R = $(py)_2C(OMe)-$. The Mn oxidation states were obtained from metric parameters, bond valence sum (BVS) calculations (Table S1 in the Supporting Information),[17] 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.

Chart 1. Bridging and Terminal Modes Displayed by the Ligands Present in Complexes **1** and **2**[a]



[a] Multiple η values refer to the number of metal ions to which each ligand atom attaches.

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 ClO_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 (these 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 $EtCO_2H$ led to a homogeneous deep-red solution, from which the desired discrete octanuclear cluster $[Mn^{II}_2Mn^{III}_6O_2\{(py)_2CO_2\}_4\{(py)_2C(OMe)O\}_2(O_2CEt)_8]$ (**2**) slowly crystallized in moderate yield (35%); the product analyzed satisfactorily as **2** (see the Supporting Information).

The molecule of **2** (Figure 2) is centrosymmetric.[15] 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

---

[13] Recent examples in Mn chemistry:(a) Stoumpos, C. C.; Gass, I. A.; Milios, C. J.; Lalioti, N.; Terzis, A.; Aromí, G.; Teat, S. J.; Brechin, E. K.; Perlepes, S. P. *Dalton Trans.* **2009**, 307. (b) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Inorg. Chem.* **2009**, *48*, 807.

[14] Papaefstathiou, G. S.; Perlepes, S. P. *Comments Inorg. Chem.* **2002**, *23*, 249.

[15] Crystal structure data for **1**·MeOH.2H_2O: $C_{88}H_{93}Mn_8N_{12}O_{35}Cl$, M_w = 2353.71, monoclinic, space group $P2_1$ with a = 10.9527(17) Å, b = 39.602(6) Å, c = 13.043(2) Å, β = 113.813(3)°, V = 5175.8(14) Å^3, T = 150(2) K, Z = 2, R1 $[I > 2\sigma(I)]$ = 0.0694, wR2 (F^2, all data) = 0.1838. Crystal structure data for **2**: $C_{92}H_{94}Mn_8N_{12}O_{30}$, M_w = 2287.31, triclinic, space group $P\bar{1}$ with a = 11.4032(3) Å, b = 15.4674(4) Å, c = 16.4846(3) Å, α = 74.020(2)°, β = 88.595(2)°, γ = 86.895(2)°, V = 2790.92(11) Å^3, T = 100(2) K, Z = 1, R1 $[I > 2\sigma(I)]$ = 0.0529, wR2 (F^2, all data) = 0.1306. The contribution of the disordered solvent area to the structure factors was determined using the Platon/Squeeze procedure.

[16] Biswas, B.; Khanra, S.; Weyhermüller, T.; Chaudhuri, P. *Chem. Commun.* **2007**, 1059.

[17] Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *42*, 4102.

[18] Xu, X.-B.; Wang, B. W.; Pan, F.; Wang, Z.-M.; Gao, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 7388.

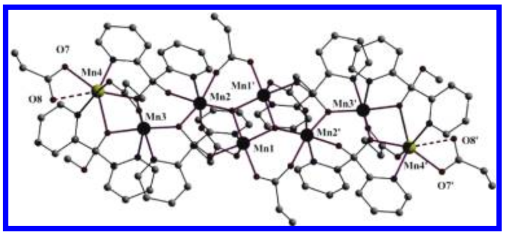


Figure 2. Metal and partly oxygen-labeled representation of **2**. Primes are used for symmetry-related atoms. The color scheme is the same as that in Figure 1.

pseudochelating $EtCO_2^-$ groups (Chart 1) in the former (Mn4−O7 = 2.179 Å; Mn4−O8 = 2.696 Å). A consequence of the pseudochelating (anisobidentate) nature of the additional $EtCO_2^-$ groups is that the outer Mn^{II} 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 Mn_8 unit in **1**. Complex **2** joins a handful of $Mn^{II}{}_2Mn^{III}{}_6$ clusters[19] 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 HCO_2H in the presence of ClO_4^- ions in MeOH to give the 1D polymer **1** 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 carboxylate R group, i.e., that propionate cannot bind like the formate because its ethyl group (Et) would bump into the adjacent ligands. In accordance with our opinion, "depolymerization" of **1** can be achieved by a variety of carboxylates, e.g., $MeCO_2^-$ and $PhCO_2^-$.[20]

Solid-state direct-current magnetic susceptibility (χ_M) 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 $\chi_M T$ 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 cm^3 K mol^{-1} expected for two Mn^{II} and six Mn^{III} noninteracting ions. The measurements show a continuous decrease to $\chi_M T$ values of 4.51 (**2**) and 1.52 (**1**) cm^3 K mol^{-1} down to 2.0 K, indicating the presence of dominant antiferromagnetic interactions. Preliminary analysis of the magnetic data[20] indicates that there is weak antiferromagnetic coupling between the central $S = 3$ butterfly $\{Mn^{III}{}_4(\mu_3\text{-}O)_2\}^{8+21}$ and the two $S = {}^1/_2$ $\{Mn^{II}Mn^{III}(\mu\text{-}OR)(\mu\text{-}OR')\}^{3+}$ 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 Mn_8 units in **1**.

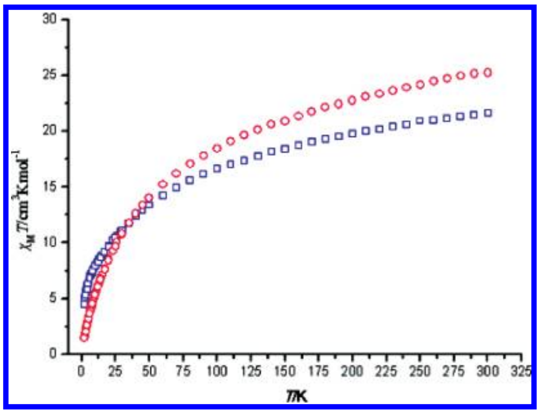


Figure 3. $\chi_M T$ vs T plots for complexes **1** (circles) and **2** (squares) in the 5−300 K temperature range.

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 $EtCO_2^-$ ligand and its flexibility in participating in two different ligation modes (η^1:η^1:μ and η^1:η^1) 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.

Acknowledgment. Financial support from the Cyprus Research Promotion Foundation (Grant TEXNO/0506/06 to A.J.T.), the CICYT (Project CTQ2009-07264 to A.E.), and the programme PYTHAGORAS I (Grant b.365.037 to S.P.P.) is gratefully acknowledged. We also acknowledge the provision of time at the Advanced Light Source synchrotron, which is supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Enegry under Contract DE-AC02-05CH11231.

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.

---

(19) For example, see:Milios, C. J.; Inglis, R.; Vinslava, A.; Prescimone, A.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *Chem. Commun.* **2007**, 2738.

(20) Details will be reported in a forthcoming full paper.

(21) Libby, E.; McCusker, J. K.; Schmitt, E. A.; Folting, K.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1991**, *30*, 3486.