Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 170–171

Mendeleev Communications

Reduction fragmentation of the $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ oxocarboxylate cluster to $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]$

Lyudmila A. Kushch, Gennadii V. Shilov, Roman B. Morgunov and Eduard B. Yagubskii*

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 522 3507; e-mail: yagubski@icp.ac.ru

DOI: 10.1016/j.mencom.2009.05.021

The reaction of the $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ cluster with tetrathiotetracene triiodide has been studied and, for the first time, reduction fragmentation of Mn_{12} cluster to Mn_6 cluster has been found.

Over the past decade, great interest has been devoted to high-spin transition metal clusters [single-molecule magnets (SMMs)], which show unusual mesoscopic magnetic properties on a scale of one molecule (superparamagnetism, strong magnetic anisotropy, blocking and quantum tunneling of magnetization *etc.*).[1] The wide family of SMMs is that of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ oxocarboxylate clusters ($Mn_{12}O_2CR$).[2] Some of these clusters (R = Et, Ph, C_6F_5, CH_2Cl and $CHCl_2$) oxidize the iodide ion and form mono-, di- and trianions (depending on R), which were isolated as their salts with tetraalkylammonium and tetraphenylphosphonium cations. These anionic clusters retain properties of SMMs.[2,3] It was of interest to use anionic clusters of this family as counterions to synthesize electroconducting radical cation salts based on organic π-donors. It is known that tetrathiotetracene (TTT, naphthoceno[5,6-*c*,*d*:11,12-*c*′,*d*′]bis[1,2]dithiol) is a strong electron donor and it forms high conducting radical cation salts with the triiodide ion.[4] We studied the reaction of tetrathiotetracene triiodide $[(TTT)_2I_3]$ (0.9×10^{-2} mmol) with the $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ cluster (1.8×10^{-2} mmol) in acetonitrile (20 ml) at room temperature. The reaction was monitored by periodically adding hexane to the reaction solution. Hexane was used to extract iodine evolved in the reaction. The evolution of iodine was accompanied by the gradual dissolution of starting $(TTT)_2I_3$ in acetonitrile. The process was considered to be accomplished when a fresh portion of hexane was not colored by iodine. Then, the solution was evaporated dry, the precipitate was dissolved in dichloromethane, and hexane was added slowly to the solution. The resulting solution was stored for 24 h in a refrigerator, and a red brown crystalline precipitate formed. The analysis of the electronic and IR spectra of the precipitate showed that neither TTT nor its cationic forms ($TTT^{+\bullet}$, TTT^{2+}) are involved in the composition of the product. The complete X-ray analysis of the crystals showed that the reaction is accompanied by the reduction fragmentation of the Mn_{12} cluster to the Mn_6 cluster $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]\cdot CH_2Cl_2$.[†] The average oxidation state of Mn ions changes from +3.33 in Mn_{12} $[(Mn^{3+})_8(Mn^{4+})_4]$ to +2.33 in Mn_6 $[(Mn^{3+})_2(Mn^{4+})_4]$. When selecting crystals of the Mn_6 cluster suitable for X-ray analysis, we found separate crystals, which showed another diffraction picture. However, it was impossible to solve the structure of these crystals because of their low stability and poor quality. Though Mn_6 oxocarboxylate clusters are widely known,[5–10] the cluster with a dichloroacetate ligand was prepared for the first time. The molecular structure of the complex is typical of such clusters and involves a $[(Mn^{3+})_2(Mn^{2+})_4O_2]^{10+}$ core comprising two $[Mn_4O]$ tetrahedra sharing Mn(1)–Mn(2) edge (Figure 1). The Mn(1)–Mn(2) (2.794 Å) distance is the shortest metal–metal distance in the complex (3.182–3.190 Å). Each oxygen μ_4 atom [O(3) and O(9)] located in the centers of tetrahedra coordinates to two inner Mn atoms (1, 2) and two outer Mn atoms. The O(1)C(1)O(14) and O(18)C(6)O(4) carboxylate bridges link outer Mn atoms only, while the O(21)C(2)O(22), O(13)C(7)O(10), O(16)C(9)O(15) and O(6)C(19)O(19) bridges coordinate to both outer and inner Mn atoms. The other four O(17)C(4)O(5), O(11)C(3)O(8), O(20)C(8)O(2) and O(7)C(5)O(12) carboxylate ligands are μ_3 bridging ones. In each particular

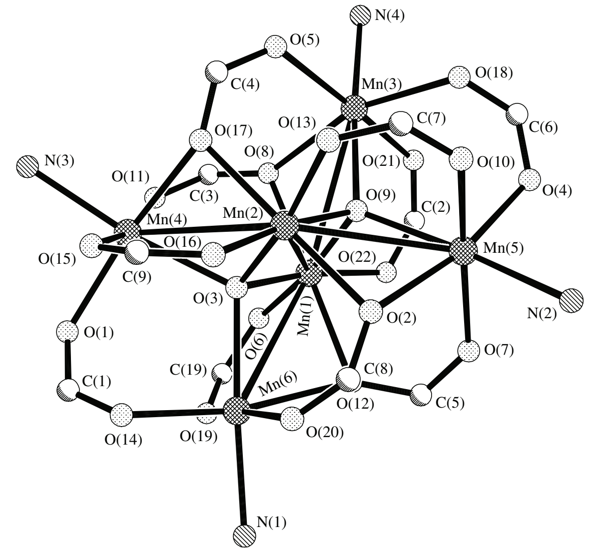

Figure 1 ORTEP drawing of $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]$ cluster. For clarity, only the O–C–O fragments of the carboxylate ligands and nitrogen atoms of terminal MeCN molecules are shown.

[†] *Crystal data* for $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]\cdot CH_2Cl_2$ were collected on a Bruker P4 four-circle diffractometer with a graphite monochromator for MoKα radiation $\lambda = 0.71073$ Å. At $T = 200(2)$ K: $C_{29}H_{24}Cl_{22}Mn_6N_4O_{22}$, $M_r = 1890.06$, monoclinic, space group $P2_1/n$, $a = 18.050(10)$, $b = 19.885(11)$ and $c = 18.579(9)$ Å, $\beta = 92.91(2)°$, $V = 6660(6)$ Å^3, $d_{calc} = 1.885$ g cm^{-3}, $Z = 4$, $\mu = 2.053$ mm^{-1}. A red-brown plate-shaped crystal was 0.15×0.1×0.05 mm in size. The total number of collected reflections up to $\theta = 25.02°$ was 11301, 9382 of which were independent and among them 2895 reflections $[I > 2\sigma(I)]$ were observed. The structure was solved by a direct method and refined to $R_{obs} = 0.1186$ by the least-squares method using SHELXTL program packages. High R-factor value is due to low stability of the crystals.

CCDC 690343 contains 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. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2009.

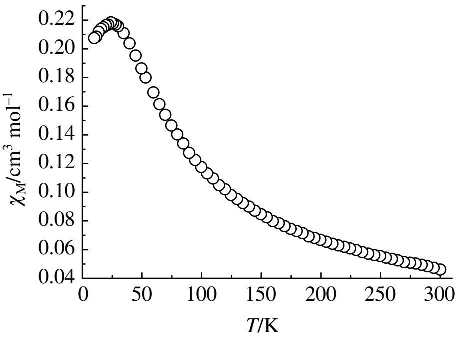

Figure 2 Temperature dependence of magnetic susceptibility (χ_M) for the product of the reaction between TTT_2I_3 and $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$, χ_M is molar susceptibility calculated to mole of $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]$; measured in a field of 1 T.

ligand, one oxygen atom is a μ_2 bridging one between outer and inner Mn atoms and the other one coordinates in a conventional way with the other outer Mn atom. The analysis of bond lengths of Mn centers in the cluster showed that the Mn–O(carboxylate) distance is 1.96 Å for the inner Mn(1) and Mn(2) atoms, while it is 2.18 Å for the outer Mn(3), Mn(4), Mn(5) and Mn(6) to evidence for a mixed-valence state of Mn atoms characteristic of such a type clusters: the inner Mn(1) and Mn(2) centers are in the 3+ oxidation state, while the outer ones are in the 2+ oxidation state. The Mn–O (μ_4) distances for the inner and outer Mn centers are even more different (1.90 Å *vs.* 2.21 Å). The composition of the cluster involves one solvated CH_2Cl_2 molecule, which is disordered in a crystal. The cluster easily loses solvated solvent resulting in a loss of crystallinity. Magnetic properties of the reaction product are typical of Mn_6 oxocarboxylate clusters (Figure 2). The magnetic susceptibility at room temperature and at the maximum (25 K) calculated to mole of $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]$ are close to χ_M for other Mn_6 clusters, namely, $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$,[10] $[Mn_6O_2(O_2CCCl_3)_{10}(H_2O)_3(PhCH_2OH)]$[9] and $[Mn_6O_2(O_2CPh)_{10}(py)_2(MeCN)_2]\cdot 2H_2O$.[6] Magnetic susceptibility increases with lowering temperature to attain a maximal value at ~25 K and then drops (Figure 2). Such a behavior of χ is characteristic of Mn_6 clusters in which strong antiferromagnetic couplings take place.[6,9,10] Thus, the analysis of magnetic properties showed that the major product of the reaction between $(TTT)_2I_3$ and $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ is the $[Mn_6O_2(O_2CCHCl_2)_{10}(MeCN)_4]$ cluster.

In conclusion, we were the first to find the reduction fragmentation of Mn_{12} clusters to Mn_6 clusters. Available publications report only the reduction of oxocarboxylate Mn_{12} clusters to Mn_8 or Mn_3 clusters in reactions with phenol, pyridine-2,6-dimethanol and trichloroacetic acid.[9,11] Clusters of the $Mn_{12}O_2CR$ family comprising electron acceptor substituents in the carboxyl ligand are strong oxidants [E^1(R = CH_2CHCl_2) = = +0.91 V *vs.* ferrocene]. The $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ cluster reacts with $(TTT)_2I_3$ to oxidize the triiodide ion to elemental iodine and forms the $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]^-$ anion, which undergoes reduction fragmentation when reacting with TTT. Tetrathiotetracene, in turn, when reacting with a strong oxidant probably undergoes deep conversion, which is accompanied by cleavage of the S–S bond as it was observed in the reaction of a Se analogue of TTT (TSeT) with HgI_2.[12] The data of elemental analysis indicate a small amount of sulfur in the reaction product; this is evidence for the formation of Mn complexes with the fragments of the TTT donor molecule. However, we were unable to identify these complexes because of their low stability. The trend in the chemistry of Mn_{12} clusters related to the study of their reactions with π-donors (tetrathiafulvalene derivatives and polynuclear aromatic hydrocarbons) is promising in respect to the synthesis of new Mn clusters with interesting structural and magnetic properties.[13]

This work was supported by the Russian Foundation for Basic Research (grant no. 06-03-32433).

References

1 D. Gatteschi and R. Sessoli, *Angew. Chem.*, 2003, **42**, 268.
2 G. Christou, *Polyhedron*, 2005, **24**, 2065.
3 R. Bagai and G. Christou, *Inorg. Chem.*, 2007, **46**, 10810.
4 I. F. Schegolev and E. B. Yagubskii, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, 1982, vol. 2, p. 385.
5 A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1986, 1587.
6 A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1989, **28**, 1915.
7 A. S. Batsanov, Yu. T. Struchkov, G. A. Timko, N. V. Gerbeleu, O. S. Manole and S. V. Grebenko, *Koord. Khim.*, 1994, **20**, 604 (in Russian).
8 M. A. Halcrow, W. E. Streib, K. Folting and G. Christou, *Acta Crystallogr.*, 1995, **C51**, 1263.
9 J. Kim and H. Cho, *Inorg. Chem. Commun.*, 2004, 122.
10 K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab and V. V. Pavlishchuk, *Inorg. Chem.*, 2005, **44**, 5903.
11 C. Boskovich, J. C. Huffman and G. Christou, *Chem. Commun.*, 2002, 2502.
12 V. F. Kaminskii, E. E. Kostyuchenko, R. P. Shibaeva, E. B. Yagubskii and A. V. Zvarykina, *J. Phys. C3*, 1983, **44**, C-1167.
13 E. B. Yagubskii, L. A. Kushch and R. B. Morgunov, *Abstracts of IV International Conference 'High-spin Molecules and Molecular Magnets'*, Ekaterinburg, October 14–19, 2008, p. 60.

Received: 8th October 2008; Com. 08/3225