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Toward Multifunctional Single-Molecule Magnets: Characterization of Dodecanuclear Manganese Complexes by Electrospray Ionization Mass Spectrometry

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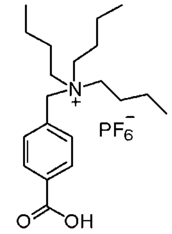
A lot of excitement surrounds the chemistry and physics of dodecanuclear manganese complexes (Mn_{12}) of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$.[2,3] The interest stems from the fact that these compounds have large-spin ground states and a significant magnetic anisotropy. The anisotropy splits in zero-field the ($2S + 1$) energy levels corresponding to different M_S, and, as S becomes large, this provides an energy barrier for the reorientation of the spins at low temperatures. As the magnetic field is cycled, the conversion between $+M_S$ and $-M_S$ sublevels is very slow and typical relaxation phenomena, like a frequency-dependent out-of-phase signal in the ac susceptibility, appear.[4] Magnetic hysteresis loops of purely molecular origin are also characteristic of these kinds of materials. A single molecule can thus be addressed with its spin "up" or "down", and this opens the way to information storage at the molecular level.[5] Besides its possible applications, Mn_{12} has attracted the attention of many physicists since it provides model systems for the study of macroscopic quantum tunneling of magnetization.[6]

The synthesis of the first Mn_{12}, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (**1**), was reported by Lis in 1980.[7] Later, **1** was found to be a useful starting material for the synthesis of different Mn_{12} complexes via ligand-exchange reactions involving other carboxylate groups. Characterization of the expected Mn_{12} usually involves X-ray crystallography. NMR studies in solution have also been reported for some simple systems.[8]

As part of a project aimed toward the synthesis of cationic single-molecule magnets that can combine with electronically active anions, we have synthesized Mn_{12} bearing quaternary ammonium substituents in the periphery. This cationic Mn_{12} has been prepared by reaction between **1** and the carboxylic acid **ZH**(PF_6)[9] (Chart 1). As the complexity of the incoming carboxylic acid increases, the techniques of characterization mentioned above are not very appropriate and there is a need for a simple method that can allow identification of isolated species and monitoring of the ligand exchange.

Chart 1. Compound **ZH**(PF_6)



Electrospray ionization mass spectrometry (ESI-MS) is a soft-ionization technique that provides an accurate determination of the molecular mass of relatively large and fragile molecules.[11] It is well suited for the analysis of ionic compounds and has been applied in the characterization of simple cationic complexes[12] and in the study of metal-ion-induced self-assembly processes.[13] Clusters like the anionic metal carbonyls $[M_6C(CO)_{16}]^{2-}$ (M = Ru, Os) and oligonuclear metal complexes have also been studied.[14] Particularly interesting in our context is the identification of the trinuclear complexes $[Cr_3O(RCOO)_6(L)_3]^+$. Fragmentation of these carboxylate-bridged compounds can be induced by increasing the cone voltage (V_C). Successive loss of terminal ligands can be detected, thus providing further structural information.[15]

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ compounds are neutral, but they can easily undergo reduction processes to form multiply charged anionic species.[8,16] Since the ESI spectrometer acts as an

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(2) (a) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873. (b) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804.

(3) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

(4) Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054.

(5) Chudnovsky, E. M. *Science* **1996**, *274*, 938.

(6) (a) Friedman, J.; Sarachik, M.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (b) Hernández, J.; Zhang, X.; Louis, F.; Bartolomé, J.; Tejada, J.; Ziolo, R. *Europhys. Lett.* **1996**, *35*, 301. (c) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.

(7) Lis, T. *Acta Crystallogr. B* **1980**, *36*, 2042.

(8) Eppley, H. J.; Tsai, H.-L.; de Vries, N.; Folting, K.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 301.

(9) **Preparation of (4-Carboxybenzyl)tributylammonium hexafluorophosphate, ZH(PF_6). ZH**Br[10] (8.7 g, 21.8 mmol) was dissolved in the minimum amount of hot water and filtered to remove an insoluble residue. The solution was slowly added over a stirred water solution of KPF_6 (8 g, 43.4 mmol). A white fine powder precipitated. The product was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and the solvent was evaporated to obtain a white solid. Yield: 70%. Elem. anal. Found (calcd): C, 51.47 (51.61); H, 7.39 (7.36); N, 3.12 (3.01). ^1H NMR (CD_3CN): δ 8.1 (d, 2H), 7.6 (d, 2H), 4.4 (s, 2H), 3.1 (t, 2H), 1.8 (q, 2H), 1.4 (m, 2H), 1 (t, 3H). **Preparation of $[Mn_{12}O_{12}(Z)_{16}](PF_6)_{16}\cdot 2ZH(PF_6)$.** The complex was prepared by the well-known ligand-exchange method reported for the benzoate analogue by using **ZH**(PF_6) instead of benzoic acid.[2b] Yield: 23%. Elem. anal. Found (calcd): C, 46.65 (46.57); H, 6.88 (6.56); N, 2.70 (2.72).

(10) (4-Carboxybenzyl)tributylammonium bromide was prepared by a slight modification of the procedure previously reported for the triethylammonium analogue. Yield: 73%. Lu, M. Y.; Bao, R.; Liu, W.; Li, Y. *J. Org. Chem.* **1995**, *60*, 5341.

(11) (a) Hofstadler, S. A.; Bakhtiar, R.; Smith, R. D. *J. Chem. Educ.* **1996**, *73*, A82. (b) Fenn, J. B. Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64. (c) Jardine, I. *Nature* **1990**, *345*, 747.

(12) Katta, V.; Chowdbury, S. K.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 319.

(13) (a) Leize, E.; Van Dorsselaer, A.; Krämer, R.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 990. (b) Romero, F. M.; Ziessel, R.; Dupont-Gervais, A.; Van Dorsselaer, A. *Chem. Commun.* **1996**, 551.

(14) Johnson, B. F. G.; McIndoe, J. S. *Coord. Chem. Rev.* **2000**, *200*−*202*, 901.

(15) (a) van den Bergen, A.; Colton, R.; Percy, M.; West, B. O. *Inorg. Chem.* **1993**, *32*, 3408. (b) Palii, S. P.; Richardson, D. E.; Hansen, M. L.; Iversen, B. B.; Larsen, F. K.; Sîngerean, L.; Timco, G. A.; Gerbeleu, N. V.; Jennings, K. R.; Eyler, J. R. *Inorg. Chim. Acta* **2001**, *319*, 23.

10.1021/ic0155481 CCC: \$20.00

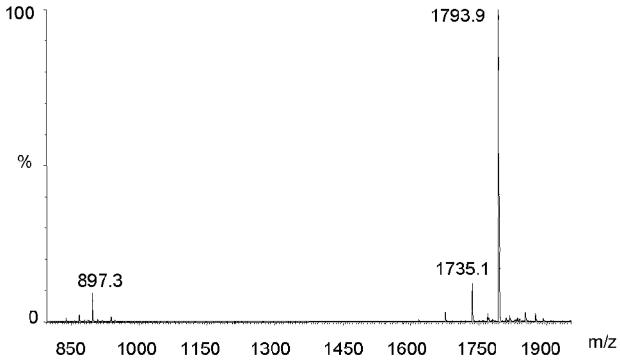

Figure 1. ESI-MS spectrum (negative mode) of a CH_3CN solution of **1**. The cone voltage is −25 V.

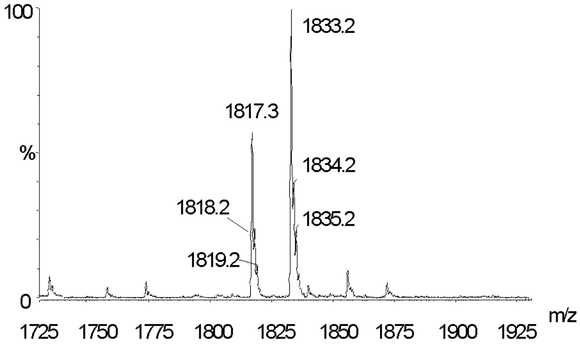

Figure 2. ESI-MS spectrum (positive mode) of a CH_3CN solution of **1**. The cone voltage is 25 V.

electrochemical cell, neutral Mn_{12} could, in principle, be reduced in situ and detected in the negative mode.

Figure 1 shows that this is indeed the case. The ESI-MS (negative mode) analysis[17] of a solution of **1** in CH_3CN shows the presence at 1794 Da of the molecular peak corresponding to $[Mn_{12}O_{12}(O_2CCH_3)_{16}]$. Fragmentation of this entity by successive loss of acetate ligands is accompanied by one-electron reduction to give peaks at 1735 and 1676 Da. A signature for a doubly reduced species of the type $[Mn_{12}O_{12}(O_2CCH_3)_{16}]^{2-}$ is present at 897 Da.

Characterization of **1** is also possible in the positive mode (Figure 2). Interestingly, the main peaks (1833.2 and 1817.3 Da) correspond to species containing potassium and/or sodium ions, presumably from traces of these alkali metals in the solutions undergoing electrospray ionization. Assignments of other peaks observed in the spectrum are gathered in Table S2 (Supporting Information). The majority of the peaks arise from species in which the core, $[Mn_{12}O_{12}(O_2CCH_3)_{16}]$, has remained intact. Loss of acetate ligands accounts for the other minor peaks observed in the spectrum. These fragmentations are favored at high cone voltages.

ESI-MS is also a valuable method for monitoring the course of the ligand-exchange reaction. Treatment of **1** with an excess of **ZH**(PF_6) yields a distribution of species of the type $[Mn_{12}O_{12}(O_2CCH_3)_{16-n}(\mathbf{Z})_n](PF_6)_n$ ($n = 13-15$). These species can be precipitated and retreated with an excess of **ZH**(PF_6) to afford a completely substituted compound. The spectrum of pure $[Mn_{12}O_{12}(\mathbf{Z})_{16}](PF_6)_{16}\cdot 2\mathbf{ZH}(PF_6)$ (Figure 3) is more complicated than that of the parent compound, **1**. At low cone voltages, formation of adducts with the free acid can be detected. Besides redox processes, multiple fragmentations due to loss of the zwitterionic ligand (**Z**) and/or hexafluorophosphate anions are also seen. The peak at higher *m*/*z* ratio (2567 Da) corresponds to a reduced species of the type $[[Mn_{12}O_{12}(\mathbf{Z})_{16}](PF_6)_{12}]^{3+}$. Successive loss of **Z**(PF_6) anions gives peaks at 2412 and 2258 Da. The mass range between 1600 and 1900 Da is dominated by the presence of tetrapositive ions derived from a $[[Mn_{12}O_{12}(\mathbf{Z})_{16}](PF_6)_{11}]^{4+}$ fragment. Loss of hexafluorophosphate yields another series of peaks that is visible in the 1100−1500 Da region of the spectrum. Significant values corresponding to the different pseudomolecular peaks are given as Supporting Information.

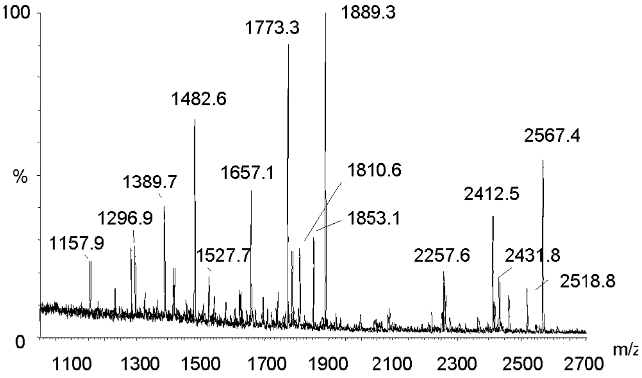

Figure 3. ESI-MS spectrum (positive mode) of a CH_3CN solution of $[Mn_{12}O_{12}(\mathbf{Z})_{16}](PF_6)_{16}$. The cone voltage is 75 V.

Preliminary measurements of the ac magnetic susceptibility of $[Mn_{12}O_{12}(\mathbf{Z})_{16}](PF_6)_{16}\cdot 2\mathbf{ZH}(PF_6)$ have been performed in the 2−10 K temperature range. The frequency-dependent out-of-phase signal observed around 4 K confirms the presence of the dodecanuclear complex. From the magnetic measurements at different frequencies, an activation barrier of 53 K has been estimated. This value is in good agreement with the previously reported systems. The field dependence of the magnetization at 2 K shows the presence of a hysteresis loop with a very small coercive field, $H_C = 25$ G.

Finally, it is worth noting that these cationic Mn_{12} compounds can be useful precursors for the deposition of single-molecule magnets onto metal and metal oxide surfaces.

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Supporting Information Available: Tables S1−S3 listing the values corresponding to the different peaks observed in the spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Soler, M.; Chandra, S. K.; Ruiz, D.; Davidson, E. R.; Hendrickson, D. N.; Christou, G. *Chem. Commun.* **2000**, 2417.

(17) ESI mass spectra were recorded on a Micromass Quattro LC instrument using nitrogen as drying and nebulizing gas.