Construction of a mixed valence trinuclear $Mn^{II}Mn^{III}Mn^{II}$ aggregate into a large macrocyclic ligand†

Atsushi Yoshino,[a] Tatsuya Miyagi,[a] Eiji Asato,*[a] Masahiro Mikuriya,[b] Yoshiteru Sakata,[c] Ken-ichi Sugiura,[c] Kentaro Iwasaki[d] and Shojun Hino[d]

[a] *Department of Chemistry, Biology and Marine Science, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan. E-mail: asato@sci.u-ryukyu.ac.jp*
[b] *Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 622-8501, Japan*
[c] *The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[d] *Faculty of Engineering, Chiba University, Inagaku, Chiba, 263-8522, Japan*

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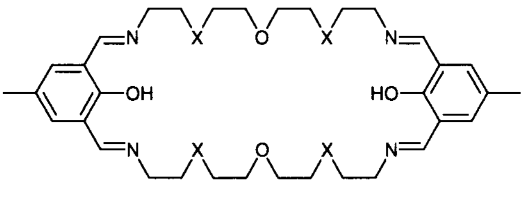
A Schiff-base [2 + 2] macrocycle obtained by the reaction of 2,6-diformyl-4-methylphenol with 1,11-diamino-3,9-dimethyl-3,9-diazo-6-oxaundecane encapsulates three manganese ions into its cavity; EPR, UV–VIS–NIR, XPS spectroscopic data, X-ray crystallography and magnetic measurements showed that the metal ions are in a mixed valence state (II, III, II) which is rare for trimanganese systems.

Polynuclear manganese complexes are now receiving increased attention from a wide area of science, including chemistry, biology and physics. Representative target molecules fascinating synthetic inorganic chemists are tetranuclear aggregates as models of the oxygen-evolving complex (OEC) of photosystem II[1] and 'high spin Mn-clusters'[2] potentially applicable to future molecular devices. Most commonly, these complexes are synthesized utilizing self-assembling properties of manganese ions, where the metal ions are bridged by O^{2-} units and externally capped with multidentate ligands.[3] Our approach to Mn-aggregated systems has started with specially designed polynucleating macrocycles. For example, the macrocycle $(L^1)^{2-}$ functions as a tetranucleating ligand for Zn^{II},[4] but did not give any manganese complexes, probably owing to poor affinity of the ether oxygen towards this metal ion. Thus, we have prepared a new macrocycle H_2L^2, to enhance binding ability by substituting the ether units with tertiary amine groups. We report herein, the synthesis and characterization of a novel mixed valence $Mn^{II}Mn^{III}Mn^{II}$ trimanganese subunit formed within the macrocycle.



X = O : H_2L^1, X = NMe : H_2L^2

1,11-Diamino-3,9-dimethyl-3,9-diazo-6-oxaundecane (daud) as a precursor for H_2L^2 was prepared in a four-step synthesis with an overall yield of *ca.* 30%.† All products obtained at each step were identified by ^1H NMR spectroscopy.

The metal-templated Schiff-base condensation of 2,6-diformyl-4-methylphenol (dfmp) with the diamine in methanol was carried out in open-air using $Mn(ClO_4)_2\cdot 6H_2O$ as the template core in the presence of triethylamine (NEt_3). The reaction using a mole ratio of dfmp : daud : Mn : NEt_3 = 2 : 2 : 4 : 2 gave dark-brown microcrystals formulated as $[Mn_3(L^2)(\mu\text{-OMe})_2](ClO_4)_3$ **1**.‡ The [2 + 2] Schiff-base macrocyclization and formation of the trinuclear Mn_3 unit were supported by detection of the strongest peak in its electrospray mass spectrum (*m/z* 305.8) corresponding to the trication for an acetonitrile solution of the complex. A mixed valence state (two Mn^{II} and one Mn^{III}) expected from the formula is evident from spectroscopic data (EPR, UV–VIS-NIR and XPS). An X-band solid-state EPR spectrum of **1** at 25 °C showed two sets of overlapped six-line signals at $g \approx 2.00$ with $A \approx 0.87$ mT, suggesting the presence of two magnetically uncoupled Mn^{II} ions. The electronic spectrum of the complex in methanol showed a very broad peak centered at *ca.* 1005 nm (ε = 142 $dm^3\ mol^{-1}\ cm^{-1}$) and a shoulder at *ca.* 550 nm (ε = 280 $dm^3\ mol^{-1}\ cm^{-1}$), tentatively attributed to $^5B_{1g} \rightarrow {}^5A_{1g}$ and $^5B_{1g} \rightarrow {}^5B_{2g}$ transitions of high-spin Mn^{III} species, respectively, while no strong absorption assignable to an intervalence charge transfer was observed in the visible or near-IR region. The XPS spectrum of **1** exhibited two peaks at 641.5 and 653.3 eV, which were attributed to Mn $2p_{3/2}$ and Mn $2p_{1/2}$ core ionization potentials from each manganese. Although these values do not agree with those of Mn^{2+} or Mn^{3+} ionized states, the spectral envelope as well as the peak positions can be reproduced by superposition of corresponding spectra of $[Mn^{II}(TPP)]\cdot py$ and $[Mn^{III}(TPP)]Cl$ (TPP = 5,10,15,20-tetraphenylporphyrinate) with a 2 : 1 intensity ratio.

Recrystallization of **1** from wet methanol gave needle-like single crystals as the monohydrate (**1**$\cdot H_2O$), the structure of which (Fig. 1) was determined by X-ray crystallography.§ The three manganese ions are encapsulated into the macrocycle in a bent-chain form with an angle of 129.45(6)° for Mn(1)–Mn(2)–Mn(3). Each of the two facing phenoxide moieties bridges a pair of adjacent manganese ions which are further bridged by an exogenous methoxide ion. The two terminal manganese centers, Mn(1) and Mn(3), have essentially the same coordination geometry being significantly distorted octahedral with average Mn–O,N bond distances of 2.245 and 2.230 Å, respectively, comparable with typical Mn(II)–O,N distances.[5] The central Mn(2) has an elongated octahedral geometry where its axial positions are occupied by the two phenoxide oxygen atoms [Mn(2)–O(1) 2.134(6) Å, Mn(2)–O(3) 2.137(6) Å]. These distances are significantly longer than the four basal Mn–O,N bonds [av. Mn–O,N = 1.962 Å], thus revealing a Jahn–Teller distortion expected for a high spin Mn^{III} species. Thus, we concluded that the three metal ions in the macrocycle are in a mixed valence state $Mn^{II}Mn^{III}Mn^{II}$.

The value of μ_{eff} = 9.968 μ_B at 300 K for powder sample **1** is close to the spin-only value of 9.695 μ_B expected for three spin systems of S = 5/2; S = 4/2; S = 5/2, indicating that all the

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† Electronic supplementary information (ESI) available: synthetic route to diamine (daud) and ^1H NMR data for all products obtained at each step. See http://www.rsc.org/suppdata/cc/b0/b003479gl

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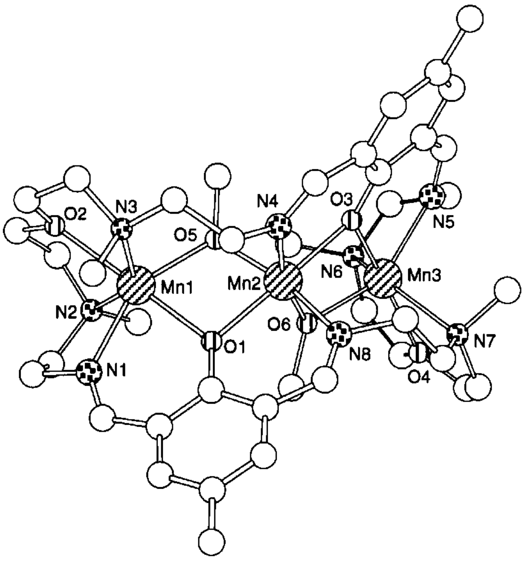

Fig. 1 Perspective view of the $[Mn_3(L^2)(\mu\text{-}OMe)_2]^{3+}$ cation; Selected distances (Å) and angles (°): Mn(1)–O(1) 2.192(6), Mn(1)–O(2) 2.217(6), Mn(1)–O(5) 2.085(5), Mn(1)–N(1) 2.178(8), Mn(1)–N(2) 2.393(8), Mn(1)–N(3) 2.403(8), Mn(2)–O(1) 2.134(6), Mn(2)–O(3) 2.137(6), Mn(2)–O(5) 1.913(5), Mn(2)–O(6) 1.899(7), Mn(2)–N(4) 2.015(7), Mn(2)–N(8) 2.022(8), Mn(3)–O(3) 2.172(6), Mn(3)–O(4) 2.200(7), Mn(3)–O(6) 2.085(7), Mn(3)–N(5) 2.16(1), Mn(3)–N(6) 2.35(1), Mn(3)–N(7) 2.41(1), Mn(1)–Mn(2) 3.235(2), Mn(2)–Mn(3) 3.218(2); Mn(1)–Mn(2)–Mn(3) 129.45(6), Mn(1)–O(1)–Mn(2) 96.8(2), Mn(1)–O(5)–Mn(2) 108.0(2), Mn(2)–O(3)–Mn(3) 96.6(2), Mn(2)–O(6)–Mn(3) 107.7(3).

metal ions are in the high-spin state. The μ_{eff} value increases with decreasing temperature up to a maximum value of 13.96 μ_B at *ca.* 6 K (Fig. 2). The drop in μ_{eff} below 6 K suggests a zero-field splitting of Mn^{II} and Mn^{III} ions or an intermolecular antiferromagnetic coupling. The magnetic data were analyzed with the Van Vleck equation including a correction term θ based on the Heisenberg model [$\mathscr{H} = -2(J_{12}S_1{\cdot}S_2 + J_{23}S_2{\cdot}S_3 + J_{13}S_1{\cdot}S_3)$; $S_1 = S_3 = 5/2$, $S_2 = 4/2$, $J_{12} = J_{23} = J$, $J_{13} = J'$], leading to the best-fitting parameters $g = 2.01(1)$, $J = +1.83(5)$ cm^{-1}, $J' = 0$ cm^{-1}, $\theta = -1.03(4)$ K. The result indicates that weak ferromagnetic interactions operate between the adjacent Mn^{II}–Mn^{III} pairs while interactions between the terminal ions are negligible. Structural data on oxygen-bridged $Mn^{II}Mn^{III}$ pairs showing ferromagnetic interaction remain scarce. However, observed Mn^{II}–O–Mn^{III} angles [96.8 and 108.0° for Mn(1)–Mn(2); 96.6 and 107.7° for Mn(2)–Mn(3)] are comparable to the angles (97.1 and 102.4°) reported for a mixed valence dinuclear $Mn^{II}Mn^{III}$ complex exhibiting $J = +0.89$ cm^{-1}.[6] Magnetically coupled Mn^{II} clusters with high nuclearity, *e.g.* Mn^{II}_5[7] and Mn^{II}_9,[8] often show interesting electrochemical properties. A cyclic voltammogram of **1** in methanol (1.0 mM, 0.1 M NEt_4ClO_4) indeed exhibited a quasi-reversible one-electron reduction wave at $E_{1/2} = -0.14$ V with $\Delta E_p = ca.$ 70 mV (glassy carbon working electrode, Pt counter electrode, $Ag^+/AgCl$ reference electrode), which was tentatively attributed to the formation of the Mn^{II}_3 species. However, all attempts to isolate this species by chemical or electrochemical reduction were unsuccessful. Finally it should be emphasized that the metal-templated reaction in Ar atmosphere with the same stoichiometry as that for **1** yielded a yellow powder formulated as $[Mn_2(L^2)](ClO_4)_2{\cdot}H_2O{\cdot}2MeOH$ **2**.¶

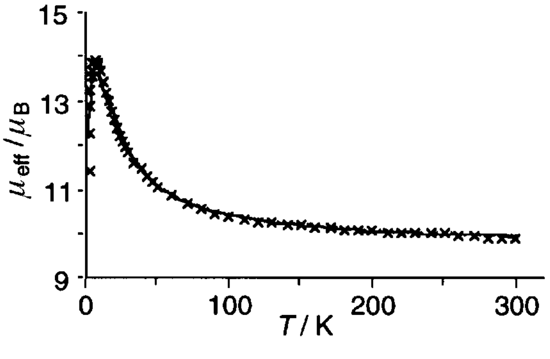

Fig. 2 Plot of μ_{eff} *vs.* *T* for a powdered sample of **1**.

In conclusion, a new Schiff-base macrocycle $(L^2)^{2-}$ obtained by the Mn-templated reaction afforded a novel $Mn^{II}Mn^{III}Mn^{II}$ complex, which is very rare[9] for mixed valence trimanganese systems in contrast to the many Mn^{II}_3[10] and $Mn^{III}Mn^{II}Mn^{III}$[11] complexes that have been reported. In addition to EPR, UV–VIS–NIR and XPS spectroscopic evidence, the X-ray structure and the magnetic behavior finally establish that the mixed valence state is of class I type in the Robin–Day classification.[12] In principle, the macrocycle could incorporate further aggregated cores ($n > 3$), since a closely related ligand $(L^1)^{2-}$ is known to afford two types of tetrazinc complex.[4] Approaches to highly aggregated systems are now scheduled and in progress in our laboratory.

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Notes and references

‡ Anal. $C_{40}H_{64}N_8O_{18}Cl_3Mn_3$. Calc.: C, 39.50; H, 5.30; N, 9.21; Cl, 8.76. Found: C, 39.26; H, 4.96; N, 9.21; Cl, 8.56%. UV-VIS [MeOH; $\lambda_{max/nm}$ (ε/dm^3 mol^{-1} cm^{-1})], 1005 (142), 550 (280), 397 (12 000), 260 (17 300)

§ *Crystal data* for $C_{40}H_{66}N_8O_{19}Cl_3Mn_3{\cdot}H_2O$ **1**·H_2O: M = 1234.18, orthorhombic, $a = 32.315(4)$, $b = 23.461(3)$, $c = 13.750(3)$ Å, $U = 10424(2)$ Å^3, $T = 163$ K, space group *Pbca* (no. 61), $Z = 8$, μ(Mo-Kα) = 9.49 cm^{-1}, Of the 9708 which were collected, 4140 reflections with $I > 3\sigma(I)$ were used for calculation. The structure was solved by direct methods and refined using full-matrix least-squares procedures. All hydrogen atoms were located on the calculated positions. Refinement converged with $R_1 = 0.077$ and $R_w = 0.095$ [$w = 1/\sigma^2(F_o)$].

CCDC 182/1701. See http://www.rsc.org/suppdata/cc/b0/b003479g/ for crystallographic files in .cif format.

¶ Anal. $C_{38}H_{68}N_8O_{15}Cl_2Mn_2$. Calc.: C, 44.41; H, 6.34; N, 10.36; Cl, 6.55. Found: C, 44.51; H, 6.13; N, 10.61; Cl, 6.23%.

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