Polyhedron 28 (2009) 1842–1851

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, structures and magnetic properties of two hexanuclear complexes

Chen-I Yang [a], Kai-Hung Cheng [a], Motohiro Nakano [b], Gene-Hsiang Lee [c], Hui-Lien Tsai [a,*]

[a] Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan, ROC
[b] Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan
[c] Instrumentation Center, College of Science, National Taiwan University, Taipei 106, Taiwan, ROC

ARTICLE INFO

Article history:
Available online 13 February 2009

Keywords:
Hexanuclear manganese complexes
Oximato-based ligands
Single-molecule magnets
Superparamagnets
Nanoscale magnets

ABSTRACT

The reaction of salicylaldoxime (H_2salox) with $Mn(ClO_4)_2 \cdot 6H_2O$, $NaN(CN)_2$ and NEt_3 in MeOH affords a Mn_6^{III} hexanuclear complex of $[Mn_6O_2(salox)_6(MeOH)_6(NCNCONH_2)_2]$ (**1**), while reaction of H_2salox with $MnCl_2 \cdot 4H_2O$ and NEt_4OH in EtOH affords a Mn_6^{III} hexanuclear complex of $[Mn_6O_2(salox)_6(EtOH)_4(H_2O)_2Cl_2]$ (**2**). Both complexes **1** and **2** contain a $[Mn_6^{III}(\mu_3\text{-}O)_2]^{14+}$ core, which is a known structural type in the family of Mn_6 complexes. Variable temperature magnetic susceptibilities and magnetization measurement of complexes **1** and **2** have been carried out. Exchange interactions of metal centers for complexes **1** and **2** are fitted by a full diagonalization matrix method. The fitting results indicate that both complexes **1** and **2** have the ground-state spin value of $S = 4$, and the ground state of complex **1** has the much closer energy to low-lying spin states than that of complex **2**. Magnetization measurements at 2.0–4.0 K and 10–70 kG confirm that the ground state is $S = 4$, with significant magnetoanisotropy as gauged by the D value of $-0.82\ cm^{-1}$ and $-1.18\ cm^{-1}$, for **1** and **2**, respectively. The frequency dependence of the out-of-phase component in alternating current magnetic susceptibilities for both complexes **1** and **2** indicates the slow magnetic relaxation of superparamagnetic behaviour with a U_{eff} of 27.0(1) K and $\tau_0 = 3.8(2) \times 10^{-9}$ s for complex **1**, and U_{eff} of 25.1(6) K and $\tau_0 = 4.6(1) \times 10^{-8}$ s for complex **2**.

1. Introduction

Polynuclear manganese clusters often exhibit large, and sometimes abnormally large, spin value in the ground state. This large spin value combined with a large and negative magnetic anisotropy has led some of these species to be single-molecule magnets (SMMs). SMMs are attracting extensive attention because they represent nanoscale magnetic particles of a well-defined size [1,2]. They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase signals in alternating current (ac) magnetic susceptibility measurements [3,4]. The remarkable magnetic properties of an SMM arise from its high-spin ground state (S) split by a large negative axial zero-field splitting (ZFS, D), resulting in an anisotropy energy barrier of $U = |D|S_Z^2$ [5]. The first SMM reported was $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4] \cdot 2HOAc \cdot 4H_2O$, with an $S = 10$ ground state and D value of $-0.5\ cm^{-1}$ [3]. A large number of SMMs contain Mn(III) ions due to the combination of a large number of unpaired electrons on each high-spin, near-octahedral Mn(III) ion and the Jahn–Teller (JT) distortion in the form of an axial elongation [6]. It is known, that the Mn(III) ion JT elongation plays an importance role in presence of SMMs properties, and the orientations of JT elongation affect significantly for energy barrier in some Mn_{12} systems [7]. Thus, many current routes to SMMs study in Mn(III) ion containing complexes, and exploit the associated large single-ion anisotropy [8,9]. From previous experience in employing oximato-based ligand in manganese chemistry, they have proven to be extremely successful ligands in the synthesis of new polynuclear complexes, suggesting that such groups are indeed excellent candidates for the preparation of polynuclear Mn complexes with interesting magnetic properties [10–17]. An SMM of $(NEt_4)_3[Mn_5O(salox)_3(N_3)_6Cl_2]$ with $S = 11$ from the use of azide ligand with salicylaldoxime (H_2salox) is reported, in which the end-on bridging azide mediates ferromagnetic exchange between Mn centers [18]. The azide ligand has recently been exploited in the preparation of some SMMs [19–25]. We therefore extend these studies the use of Mn(II) sources and H_2salox as chelating ligand combined with some bridging groups such as $NaN(CN)_2$. Herein, the synthesis, structures and magnetic properties of two SMMs $[Mn_6O_2(salox)_6(MeOH)_6(NCNCONH_2)_2]$ (**1**) and $[Mn_6O_2(salox)_6(EtOH)_4(H_2O)_2Cl_2]$ (**2**), built with salicylaldoxime are reported. Both complexes display magnetic relaxation.

2. Experimental

2.1. Synthesis

All solvents and reagents where used as received, no purification was necessary. All reactions were performed under aerobic conditions.

* Corresponding author. Tel.: +886 6 275 57575x65349; fax: +886 6 274 0552.
E-mail address: hltsai@mail.ncku.edu.tw (H.-L. Tsai).

0277-5387/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2009.02.001

*2.1.1. $[Mn_6O_2(salox)_6(MeOH)_6(NCNCONH_2)_2]$ (**1**)*

$Mn(ClO_4)_2 \cdot 6H_2O$ (0.623 g, 1.72 mmol) was dissolved in MeOH (50 ml). To this was added H_2salox (0.240 g, 1.710 mmol), sodium dicyanamide (0.155 g, 1.74 mmol) and Et_3N (0.176 g, 1.74 mmol) resulting in a deep green solution, which was stirred for 10 min. Vapor diffusion of Et_2O into the solution slowly produced crystals, after one week dark-green crystals were obtained. Crystals were collected by filtration, washed with MeOH, Et_2O and dried in vacuo. The yield was 48% (based on Mn). *Anal.* Calc. for $C_{52}H_{58}Mn_6N_{12}O_{22}$ (1532.74): C, 40.75; H, 3.81; N, 10.97. Found: C, 40.44; H, 3.80; N, 10.95%. IR data (KBr disk, cm^{-1}): 3413 (m), 3330 (m), 3228 (m), 2201 (m), 2169 (s), 1627 (m), 1597 (s), 1543 (m), 1473 (m), 1438 (s), 1417 (m), 1323 (w), 1277 (s), 1245 (w), 1202 (m), 1146 (w), 1121 (w), 1024 (s), 944 (w), 914 (s), 756 (s), 680 (vs), 506 (w), 483 (w), 466 (w).

*2.1.2. $[Mn_6O_2(salox)_6(EtOH)_4(H_2O)_2Cl_2]$ (**2**)*

$MnCl_2 \cdot 4H_2O$ (0.405 g, 2.05 mmol) and H_2salox (0.276, 2.00 mmol) were dissolved in EtOH (20 ml). To this was added 10 wt% water solution of NEt_4OH (1.472 g, 1.00 mmol) resulting in a deep green solution, which was stirred for 1 h. The solution was filtered to eliminate any remaining solid and the filtrate was layered with two volumes of Et_2O to slowly give well-formed dark-green crystals. After one week, crystals were collected by filtration, washed with Et_2O and dried in vacuo. The yield was 34% (based on Mn). *Anal.* Calc. for $C_{50}H_{58}Cl_2Mn_6N_6O_{21}$ (1479.55): C, 39.72; H, 3.99; N, 5.74. Found: C, 40.05; H, 4.17; N, 5.60%. IR data (KBr disk, cm^{-1}): 1597 (s), 1542 (m), 1470 (w), 1439 (m), 1327 (w), 1283 (s), 1203 (m), 1153 (w), 1119 (w), 1045 (s), 1026 (s), 918 (m), 758 (m), 677 (vs), 649 (m), 534 (w), 480 (w), 463 (w).

2.2. X-ray crystallography

Data collection parameters for complexes **1** and **2** are listed in Table 1. Diffraction measurements for complexes **1** and **2** were carried out using a Brucker Smart ApexCCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods and refined using the SHELXL-97 program [26] by full-matrix least-squares on F^2 values. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in ideal, calculated positions, with isotropic thermal parameters riding on their respective carbon atoms. Complexes **1** and **2** crystallize in the triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/n$, respectively, with a Mn_6 cluster in the asymmetric unit.

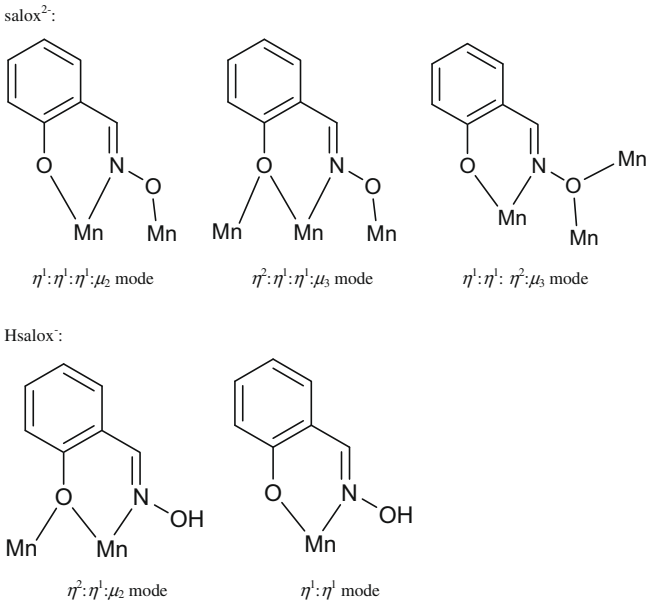
Table 1
Crystallographic data for **1** and **2**.

	1	**2**
Formula	$C_{52}H_{58}Mn_6N_{12}O_{22}$	$C_{50}H_{56}Cl_2Mn_6N_6O_{20}$
Formula weight	1532.74	1461.55
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.2280(5)	13.3510(6)
b (Å)	12.4245(7)	18.8326(8)
c (Å)	13.1243(7)	12.9116(6)
α (°)	83.418(1)	90
β (°)	68.907(1)	115.569(1)
γ (°)	72.037(1)	90
V (Å^3)	1480.20(14)	2928.5(2)
Z	1	2
T (K)	150(2)	150 (2)
Wavelength (Å)	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.719	1.657
μ (mm^{-1})	1.331	1.424
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.705, −0.860	0.590, −0.419
R_1[a], wR_2[b] (all data)	0.1036, 0.1628	0.0555, 0.0989
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0803, 0.1540	0.0413, 0.0922

[a] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for complex **1**.

1			
Mn1–O1	1.885(3)	Mn2–N2	1.998(5)
Mn1–O2	1.908(4)	Mn2–O9	2.264(5)
Mn1–O7	1.944(4)	Mn2–O8	2.282(4)
Mn1–N1	1.999(4)	Mn3–O6	1.872(4)
Mn1–N4	2.165(5)	Mn3–O1	1.887(3)
Mn1–O7	2.334(4)	Mn3–O5	1.904(4)
Mn2–O1	1.874(3)	Mn3–N3	1.994(4)
Mn2–O4	1.878(4)	Mn3–O10	2.249(4)
Mn2–O3	1.915(4)	Mn3–O2	2.523(4)
O1–Mn1–O2	169.68(16)	O1–Mn2–O8	92.79(15)
O1–Mn1–O7	90.46(15)	O4–Mn2–O8	85.35(16)
O2–Mn1–O7	90.74(15)	O3–Mn2–O8	87.16(16)
O1–Mn1–N1	89.50(16)	N2–Mn2–O8	94.51(17)
O2–Mn1–N1	88.49(17)	O9–Mn2–O8	169.07(17)
O7–Mn1–N1	175.46(17)	O1–Mn2–Mn1	30.69(10)
O1–Mn1–N4	94.42(17)	O4–Mn2–Mn1	148.85(12)
O2–Mn1–N4	95.66(17)	O3–Mn2–Mn1	63.11(11)
O7–Mn1–N4	95.88(17)	N2–Mn2–Mn1	119.38(13)
N1–Mn1–N4	88.65(18)	O9–Mn2–Mn1	95.62(13)
O1–Mn1–O7	84.36(14)	O8–Mn2–Mn1	91.85(11)
O2–Mn1–O7	85.72(14)	O6–Mn3–O1	175.80(16)
O7–Mn1–O7	80.70(15)	O6–Mn3–O5	90.19(16)
N1–Mn1–O7	94.78(15)	O1–Mn3–O5	91.46(15)
N4–Mn1–O7	176.34(16)	O6–Mn3–N3	89.31(17)
O1–Mn1–Mn2	30.49(10)	O1–Mn3–N3	88.70(16)
O2–Mn1–Mn2	144.91(12)	O5–Mn3–N3	174.89(18)
O7–Mn1–Mn2	120.19(11)	O6–Mn3–O10	86.50(16)
N1–Mn1–Mn2	59.31(13)	O1–Mn3–O10	97.20(16)
N4–Mn1–Mn2	97.00(12)	O5–Mn3–O10	94.76(17)
O7–Mn1–Mn2	83.70(9)	N3–Mn3–O10	90.28(17)
O1–Mn2–O4	178.10(17)	O6–Mn3–O2	88.85(14)
O1–Mn2–O3	93.79(15)	O1–Mn3–O2	87.05(13)
O4–Mn2–O3	85.75(16)	O5–Mn3–O2	100.58(15)
O1–Mn2–N2	88.75(16)	N3–Mn3–O2	74.33(15)
O4–Mn2–N2	91.77(17)	O10–Mn3–O2	163.98(14)
O3–Mn2–N2	176.90(17)	Mn2–O1–Mn1	118.81(18)
O1–Mn2–O9	97.70(17)	Mn2–O1–Mn3	121.19(18)
O4–Mn2–O9	84.14(17)	Mn1–O1–Mn3	119.99(18)
O3–Mn2–O9	89.11(17)	Mn1–O2–Mn3	116.28(16)
N2–Mn2–O9	88.78(18)	Mn1–O7–Mn1	99.30(15)



Scheme 1. Coordination types of salicylaldoxime.