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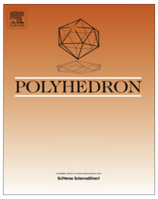

Synthesis, structure, and magnetic properties of a tetradecanuclear manganese complex

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ABSTRACT

A new $[Mn_{14}(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4(L)_4(O_2CPh)_{14}(OMe)_2]\cdot 2CH_2Cl_2$ (**1**·2CH$_2$Cl$_2$) cluster, where H$_2$L = *N*-salicylidene-*o*-aminophenol, was synthesized by reacting the $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ precursor with tridentate ligands. The structure of the tetradecanuclear complex features a $[Mn^{II}{}_6Mn^{III}{}_8(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4]^{24+}$ core which is comprised of a non-planar rod-like $[Mn^{II}{}_2Mn^{III}{}_6(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_2]^{12+}$ unit, with both sides bonded in the form of a $[Mn^{II}{}_2Mn^{III}(\mu_3\text{-}OH)]^{6+}$ triangle. Direct current (dc) magnetic susceptibility measurements of the complex indicate the existence of intramolecular antiferromagnetic interactions between the metal ions, with a ground state of $S = 2$. The complex exhibits frequency-dependent out-of-phase signals in alternating current (ac) magnetic susceptibility measurements, suggesting slow magnetic relaxations.

1. Introduction

The synthesis and characterization of 3d transition metal complexes with various nuclearities and structure topologies are of interest because of their fascinating physical properties and interesting structures [1–18]. The uses of suitable types of ligands and appropriate reaction conditions have allowed the formation of a variety of high nuclear complexes. There are many examples of high nuclearities in the field of manganese chemistry [6–17]. The synthesis of such complexes involves the use of multinuclear clusters as starting materials. Some of the most successful starting materials employed for these reactions arise from the $[Mn_3O(O_2CR)_6(L)_3]^{n+}$ ($n = 0,\ 1$; R = various; L = terminal ligands) family, which have afforded a variety of new high nuclear complexes, such as Mn$_9$ [19], Mn$_{21}$ [11], and Mn$_{22}$ [13], and all of these manganese clusters show single-molecule magnet (SMM) behaviors. For example Mn$_{21}$ [10], Mn$_{22}$ [12], Mn$_{30}$ [15], and Mn$_{84}$ [17], which have pleasing structures, are synthesized from reactions using the mixed-valence SMM archetype $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = various) family as the starting materials. The mixed-valence $[Mn_6O_2(Piv)_{10}(4\text{-}Me\text{-}py)_{2.5}(PivH)_{1.5}]$ [20] (PivH = ^{t}BuCO$_2$H, 4-Me-py = 4-methylpyridine) can be used as the starting material, and has been shown to be a good candidate for the synthesis of Mn–Ln complexes [20,21]. In this study, we used the $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ [22] complex as the starting material to synthesize a $[Mn_{14}(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4(L)_4(O_2CPh)_{14}(OMe)_2]\cdot 2CH_2Cl_2$ (**1**·2CH$_2$Cl$_2$) cluster, where H$_2$L = *N*-salicylidene-*o*-aminophenol (Scheme 1). Only a few mixed-valance Mn$_{14}$ clusters have been reported to date, and their oxidation states have been determined to be $Mn^{II}{}_{14}$, $Mn^{II}{}_{12}Mn^{III}{}_2$, $Mn^{II}{}_{10}Mn^{III}{}_4$, $Mn^{II}{}_8Mn^{III}{}_6$, $Mn^{II}{}_4Mn^{III}{}_{10}$, and $Mn^{II}{}_2Mn^{III}{}_{12}$ [23–29]. The Schiff base compound H$_2$L, which functions as a proligand [30–32], is prepared *in situ* by the condensation of 2-amino phenol and salicylaldehyde and is used in the synthesis of mononuclear complexes [33–38], a trinuclear complex [38] and heterometallic complexes [39]. In the present study, this ligand was used in the preparation of a new tetradecanuclear $Mn^{II}{}_6Mn^{III}{}_8$ structure. The synthesis, structure, and magnetic properties of complex **1**·2CH$_2$Cl$_2$ are reported below.

2. Experimental

2.1. Synthesis

All solvents and reagents were purchased from commercial sources and were used without further purification. All reactions were performed under aerobic conditions. The starting material, $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$, was prepared following a procedure described in the literature [22].

2.1.1. Synthesis of $[Mn_{14}(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4(L)_4(O_2CPh)_{14}(OMe)_2]\cdot 2CH_2Cl_2$ (**1**·2CH$_2$Cl$_2$)

Method A: $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ (320.8 mg, 0.172 mmol) was dissolved in CH$_2$Cl$_2$ (40 mL), followed by the addition of 2-amino phenol (42.1 mg, 0.386 mmol), and salicylaldehyde (46.2 mg, 0.378 mmol) dissolved in MeOH (5 mL) was then added,

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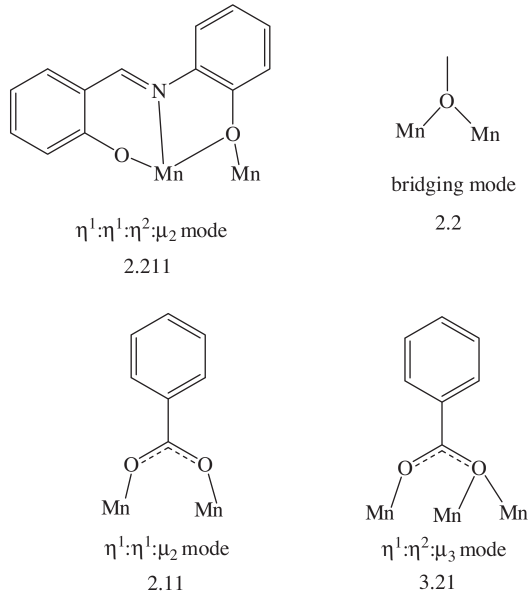

Scheme 1. Coordination modes of L^{2-}, benzoate, and methanol groups within complex $\mathbf{1}\cdot 2CH_2Cl_2$.

Table 1
Crystallographic data for $\mathbf{1}\cdot 2CH_2Cl_2$.

	$\mathbf{1}\cdot 2CH_2Cl_2$
Formula	$C_{154}H_{120}Cl_4Mn_{14}N_4O_{46}$
Mw	3673.50
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	14.715(2)
b (Å)	17.578(3)
c (Å)	18.497(3)
α (°)	114.225(2)
β (°)	109.864(2)
γ (°)	101.070(2)
V (Å^3)	3784.6(11)
Z	1
λ (Å)	0.71073
T (K)	150(2)
F (000)	1858
D_{calc} (g cm^{-3})	1.612
μ (mm^{-1})	1.279
Measured/independent reflections	44824/18232
R_{int}	0.0246
Goodness-of-fit (GOF) on F^2	1.108
Maximum and minimum transmission	0.7457, 0.6370
Data/restraints/parameters	18232/0/1006
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0451, 0.1350
R_1[a], wR_2[b] (all data)	0.0589, 0.1429
Largest difference peak and hole (e Å^{-3})	1.300, −1.541

[a] $R_1 = (\Sigma||F_O|-|F_C||)/\Sigma|F_O|$.
[b] $wR_2 = [\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]]^{1/2}$.

resulting in a brown solution, which was stirred for 30 min and subsequently filtered. The diffusion of Et_2O vapors into the solution slowly produced crystals, and after three weeks, well-formed brown chunk crystals formed. The yield was 11.4% (based on Mn). The single crystal, employed for crystallography and maintained in contact with the mother liquor to avoid solvent loss, was defined as $\mathbf{1}\cdot 2CH_2Cl_2$. *Anal.* Calc. for $\mathbf{1}\cdot 2CH_2Cl_2$ ($C_{154}H_{120}Cl_4Mn_{14}N_4O_{46}$): C, 50.35; H, 3.29; N, 1.53. Found: C, 50.55; H, 3.71; N, 1.45%. Two CH_2Cl_2 solvated molecules in the crystal were removed, when a powdered sample of $\mathbf{1}\cdot 2CH_2Cl_2$ was dried under a vacuum for 2 days. *Anal.* Calc. for $\mathbf{1}\cdot(C_{152}H_{116}Mn_{14}N_4O_{46})$: C, 52.11; H, 3.34; N, 1.60. Found: C, 51.25; H, 3.46; N, 1.65%. IR data (KBr disk, cm^{-1}): 3435 (br), 3064 (w), 3025 (w), 2928 (w), 1604 (s), 1537 (s), 1482 (m), 1466 (w), 1398 (s), 1304 (m), 1255 (m), 1225 (w), 1176 (w), 1149 (w), 1127 (w), 1069 (w), 1026 (w), 1003 (w), 926 (w), 840 (w), 793 (w), 741 (w), 718 (s), 675 (w), 642 (w), 607 (m), 549 (w), 459 (w).

Method B: The Schiff base compound H_2L was prepared following a procedure described in the literature [40]. $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ (323.7 mg, 0.173 mmol) was dissolved in CH_2Cl_2 (40 mL), followed by the addition of H_2L (80.6 mg, 0.378 mmol) dissolved in MeOH (5 mL) was then added, resulting in a brown solution, which was stirred for 30 min and subsequently filtered. The diffusion of Et_2O vapors into the filtrate slowly produced crystals, and after a month, well-formed brown chunk crystals formed. The yield was 17.7% (based on Mn). The lattice constants of the crystals were measured by X-ray diffraction to determine identity.

2.2. X-ray crystallography

Data collection parameters are listed in Table 1. Diffraction measurements for complex $\mathbf{1}\cdot 2CH_2Cl_2$ were carried out using a Bruker SMART APEXII CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Cell parameters were retrieved and refined using the Bruker SAINT software on all reflections. Data reduction was performed with the Bruker SAINT software. The structure was solved using direct methods and refined using the SHELXS-97 [41] program with 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, except for H3A and H22A on μ_3-OH, which were located in a difference map.

2.3. Physical measurements

Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet 380 FTIR spectrometer in 400–4000 cm^{-1} range. The elemental analyses for C, H and N were carried out with an Elementar vario EL III analyzer. Variable-temperature dc magnetic susceptibility measurements were collected on a microcrystalline sample, restrained in eicosane to prevent torquing, on a Quantum Design MPMS SQUID VSM equipped with a 7.0 Tesla magnet and operating in the temperature range of 1.8–300.0 K. Variable-temperature ac magnetic susceptibility measurements were carried out on a Quantum Design PPMS-9 magnetometer equipped with a 9.0 Tesla magnet and operating in the range of 1.8–300.0 K. Diamagnetic corrections were estimated from Pascal's constants [42] and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility of the compound.

3. Results and discussion

3.1. Synthesis

The Schiff base proligand H_2L was prepared *in situ* by the condensation of 2-amino phenol and salicylaldehyde in a 1:1 ratio in methanol. The reaction of $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ in dichloromethane with salicylaldehyde and 2-amino phenol in methanol resulted in the formation of a brown solution. The resulting mixture was stirred at room temperature for a further 30 min and subsequently filtered. The filtrate was slowly diffused with Et_2O vapors to produce brown chunk crystals of complex **1** with the formula $[Mn_{14}(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4(L)_4(O_2CPh)_{14}(OMe)_2]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$), in a 11.4% yield. Complex $\mathbf{1}\cdot 2CH_2Cl_2$ could also have been prepared by reacting the $[Mn_6O_2(O_2CPh)_{10}(DMF)_4]$ with H_2L in CH_2Cl_2/MeOH (40 mL/5 mL). The resulting solution was filtered and the