

MIXED-VALENT TETRANUCLEAR $Mn^{II}Mn^{III}_3$ COMPLEX WITH 1,3-DIAMINO-2-HYDROXYPROPANE- N,N',N'',N''' -TETRAACETIC ACID

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Abstract. Mixed-valent tetranuclear $Mn^{II}Mn^{III}_3$ complex with 1,3-diamino-2-hydroxypropane- N,N',N'',N''' -tetraacetic acid (H_5dhpta), $Ca_2[Mn_4\{\mu-OHO\}(dhpta)_2(CH_3COO)_2]$, was synthesized and characterized by elemental analysis, IR and UV-vis-NIR spectroscopy, and temperature dependence of magnetic susceptibilities (4.5–300 K). Single-crystal X-ray crystallography revealed a trapezoid tetranuclear core with μ -(OHO), μ -alkoxido, μ -acetato bridges. Magnetic data analysis showed considerable antiferromagnetic interactions among these four manganese atoms with $J(Mn^{II}-Mn^{III})$ of -35.02 cm^{-1} , $J'(Mn^{III}(Mn^{II})-Mn^{III})$ of -4.82 cm^{-1} , and $J''(Mn^{II}-Mn^{III})$ of -4.61 cm^{-1} .

Keywords: manganese complex, tetranuclear complex, magnetic property, mixed-valent complex.

Introduction

Tetranuclear manganese complexes have received much attention as model complexes of tetranuclear manganese center of oxygen-evolving complex (OEC) since such system was discovered in the active site of OEC of photosystem II [1-4]. Especially, mixed metal complexes with calcium ions are most interesting in relation to the OEC active site. We have engaged in chemistry of manganese complexes, paying attention to their magnetic properties with a variety of unpaired electrons depending on the oxidation state of manganese ion. So far, we and others synthesized some manganese complexes from mononuclear to tetranuclear and polynuclear species by the use of organic ligands [5-30]. Gorun *et al.* reported that tetranuclear and hexadecanuclear manganese complexes with barium or calcium ions can be isolated by the use of polydentate organic ligand, 1,3-diamino-2-hydroxypropane- N,N',N'',N''' -tetraacetic acid (H_5dhpta) shown in Figure 1 [31-33]. In this study, we examined reaction of H_5dhpta with manganese salt by the use of calcium acetate as counter ion in the hope of obtaining new polynuclear manganese complexes. We isolated a tetranuclear manganese complex with calcium

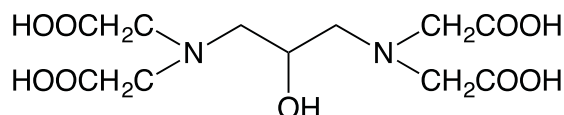


Figure 1. Polydentate organic ligand, H_5dhpta .

ions similar to Gorun's tetranuclear manganese complex. The isolated complex was characterized by elemental analysis, IR and UV-vis-NIR spectroscopies, measurement of temperature dependence of magnetic susceptibilities (4.5–300 K), and single-crystal X-ray crystallography. Herein, we report on the crystal structure, spectral features, and magnetic property of this complex.

Experimental

All reagents and solvents were obtained from commercial sources and were used without further purification.

$Ca_2[Mn_4\{\mu-OHO\}(dhpta)_2(CH_3COO)_2] \cdot 13H_2O$ (**1**)

Calcium acetate monohydrate (23 mg, 0.15 mmol) and H_5dhpta (32 mg, 0.10 mmol) were dissolved in 4.5 mL of H_2O . To this solution was added a methanol solution (3 mL) of manganese(II) chloride tetrahydrate (40 mg, 0.20 mmol). After the pH of the solution was brought to *ca.* 8 with 1 M NaOH solution, 0.1 mL of 30% H_2O_2 was added dropwise with stirring, giving a dark brown solution. N,N -Dimethylformamide (10 mL) was layered onto this solution and the mixture was allowed to stand at room temperature for several days. Dark brown crystals separated, and were collected by filtration, washed with small amount of methanol, and dried *in vacuo*. Yield: 25 mg (38%). Anal. Found: C, 23.81; H, 4.71; N, 4.61%. Calcd. for $C_{26}H_{59}Ca_2Mn_4N_4O_{37}$: C, 23.66; H, 4.51; N, 4.25%. IR (KBr): $\nu(OH)$ 3381, $\delta(H_2O)$ 1616, $\nu_{as}(CO_2^-)$ 1560sh, $\nu_s(CO_2^-)$ 1400. Diffuse reflectance spectrum: λ_{max} 292, 478, 566(sh), 858, 1096(sh) nm.

Measurements: Elemental analyses for carbon, hydrogen, and nitrogen were done using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5–300 K. The susceptibilities were

corrected for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_{\text{M}}T}$, where χ_{M} is the molar magnetic susceptibility per mole of tetranuclear manganese unit.

X-Ray Crystallography: Preliminary X-ray diffraction data were taken by a Rigaku R-AXIS RAPID diffractometer using graphite-monochromated Mo K α radiation at 200 K. X-Ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer (Mo K α radiation) at 90 K and indexed using the SMART software. Crystal data and details concerning data collection are given in Table 1. The cell parameters were refined by full-matrix least-squares on F^2 . Integrated intensity information for each reflections was obtained and corrected using the SAINT+ program package including the reduction program SAINT and the empirical absorption correction program SADABS. The structure was solved using the SHELXTL program. The structure was solved by direct methods, and the residual non-hydrogen atoms were located by D-Fourier synthesis. All of non-hydrogen atoms were refined by full-matrix least-squares on F^2 . One of the two acetato groups was found to be disordered into two positions with half occupations. The hydrogen atoms except for those of water molecules were inserted at their ideal positions and fixed there. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package. CCDC 996784 for **1** contains supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (internet.) +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1

Crystal and experimental data.

Parameter	Value
Chemical formula	C ₂₆ H ₆₇ Ca ₂ Mn ₄ N ₄ O ₄₁
Formula weight	1391.76
Temperature, (K)	90
Crystal system	monoclinic
Space group	$P2_1/m$
Z	2
a, (Å)	11.291(2)
b, (Å)	20.601(4)
c, (Å)	11.563(2)
β , (°)	98.678(3)
V, (Å ³)	2658.7(9)
D _x , (g/cm ³)	1.738
Radiation: Mo K α , λ , (Å)	0.71073
μ (Mo K α), (mm ⁻¹)	1.235
F, (000)	1438
Crystal size, (mm ³)	0.73 x 0.64 x 0.10
No. of reflections collected	15723
No. of independent reflections	6157
θ range for data collection, (°)	1.81 - 28.22
Data/Restraints/Parameters	6157/0/371
Goodness-of-fit on F^2	1.050
R indices [$I > 2\sigma(I)$]	R1 = 0.0832, wR2 = 0.2275
R indices (all data)	R1 = 0.1033, wR2 = 0.2427
$(\Delta/\sigma)_{\text{max}}$	0.000
$(\Delta\rho)_{\text{max}}$, (eÅ ⁻³)	2.547
$(\Delta\rho)_{\text{min}}$, (eÅ ⁻³)	-1.957
Measurement	Bruker Smart APEX CCD diffractometer
Program system	SHELXTL
Structure determination	Direct methods (SHELXS-97)
Refinement	full matrix least-squares (SHELXL-97)
CCDC deposition number	996784

Results and discussion

Reaction of manganese(II) chloride tetrahydrate with the polydentate ligand H_3dhpta in the presence of calcium ions gave dark brown crystals. The formulation of the mixed-metal system of tetranuclear $Mn^{II}Mn^{III}_3$ complex with calcium(II), $Ca_2[Mn_4\{\mu-OHO\}(dhpta)_2(CH_3COO)_2]$, was confirmed by the elemental analyses, infrared and electronic spectroscopies, single-crystal X-ray structure analysis, and magnetic susceptibility measurement. The analytical data were obtained from the dried sample containing different amount of crystal water molecules from the single crystals for X-ray structure analysis. In the infrared spectra of **1**, one strong shoulder band at 1560 cm^{-1} and one strong band at 1400 cm^{-1} may be assigned to antisymmetric and symmetric stretching vibrations of the *syn-syn* acetato bridges [34], respectively, as shown in Figure 2. The broad bands at 3381 and 1616 cm^{-1} in **1** may be attributed to $\nu(OH)$ stretching band and $\delta(H_2O)$ bending mode of water molecules, respectively [34].

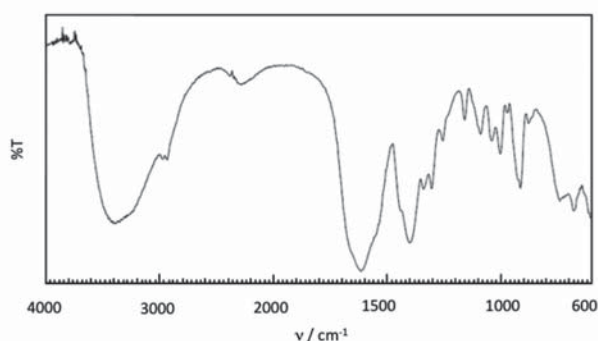


Figure 2. Infrared spectra of **1**.

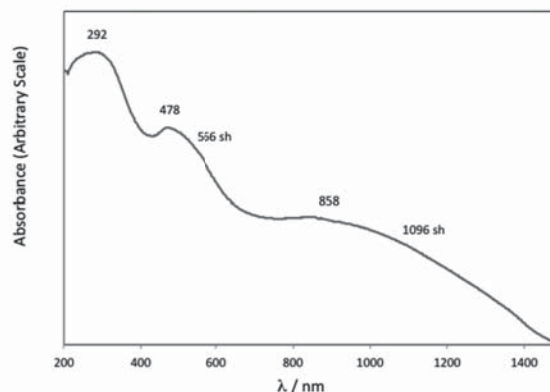


Figure 3. Diffused reflectance spectra of **1**.

The diffused reflectance spectra of **1** are shown in Figure 3. Two or three broad absorption bands around 292 and 478 (possibly, and 566 shoulder) nm in solid can be attributed to LMCT charge-transfer transitions in origin [5,6,8]. A broad band at 858 nm with shoulder at 1096 may be due to d-d transitions of manganese(III) ions [5,6,8]. The spectral feature is in harmony with the mixed-valent state of the present complex, because d-d transitions of manganese(II) are spin-forbidden and the intervalence bands of the mixed-valence should be in the broad band in the NIR region.

Single crystals of **1** were obtained by crystallization from the reaction solution. X-ray crystal structure analysis revealed that the present complex has a tetranuclear manganese core similar to Gorun's structure [32]. The structure of the tetranuclear complex drawn by ORTEP is shown in Figure 4. The four manganese atoms are located in a trapezoid form. The molecule has a crystallographic mirror plane intersecting the O13, O14, C12, C13, and H(O14) atoms. The Mn1 atom is coordinated by two monodentate acetato-oxygen atoms (O1, O3), amino-nitrogen atom (N1), and alkoxido-oxygen atom (O5) of $dhpta^{5-}$, one acetato-oxygen atom (O10) of *syn-syn*-bridging acetate ion, and oxido-oxygen atom (O13) in an axially compressed octahedral geometry, suggesting the Jahn-Teller distortion due to Mn^{III} , whereas the Mn2 atom is coordinated by two monodentate acetato-oxygen atoms (O6, O8), amino-nitrogen atom (N2), and alkoxido-oxygen atom (O5) of $dhpta^{5-}$, one acetato-oxygen atom (O11 or O12') of *syn-syn*-bridging acetate ion, and hydroxido-oxygen atom (O14) in a distorted octahedral geometry. The bond distances around the Mn2 atom are mostly longer than those of the Mn1 atom in accordance with the mixed-valence $Mn^{II}Mn^{III}$ state of the Mn2 and Mn2' atoms.

Temperature dependence of effective magnetic moments is shown in Figure 5. The magnetic moment of **1** is $9.72 \mu_B$ at 300 K per tetranuclear $Mn^{II}Mn^{III}_3$ unit, which is lower than the spin-only value ($10.34 \mu_B$). The magnetic moments gradually decrease with lowering of temperature until reaching $3.74 \mu_B$ at 4.5 K, being typical of antiferromagnetic behavior [3, 11-14, 17-20, 25-28]. The magnetic data were analyzed with magnetic susceptibility equation based on the Heisenberg model $H = -JS_{31} \cdot S_{32} - J'(S_{31} \cdot S_{21} + S_{31} \cdot S_{33} + S_{32} \cdot S_{21} + S_{32} \cdot S_{33}) - J''S_{21} \cdot S_{33}$ by a scheme shown in Figure 6 considering the mirror symmetry of this system. The g value was treated as isotropic and $g(Mn^{III}) = g(Mn^{II})$. Best fitting curve was obtained with the parameters; $J = -35.02 \text{ cm}^{-1}$, $J' = -4.82 \text{ cm}^{-1}$, $J'' = -4.61 \text{ cm}^{-1}$, $g = 2.08$, and $N\alpha = 2500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. This result shows that a strong antiferromagnetic interaction is operating between the two Mn^{III} atoms ($Mn1-Mn1'$) with weak antiferromagnetic interactions between $Mn^{III}-Mn^{II}(Mn^{III})$ ($Mn1-Mn2$, $Mn1-Mn2'$, $Mn1'-Mn2$, $Mn1'-Mn2'$) or $Mn^{II}-Mn^{III}$ ($Mn2-Mn2'$) atoms, being consistent with the wide angles of the bridging groups ($Mn1-O13-Mn1'$ $137.7(3)^\circ$, $Mn2-O14-Mn2'$ $136.0(4)^\circ$, $Mn1-O5-Mn2$ $132.85(18)^\circ$) between these manganese atoms preferring antiferromagnetic interaction for the present complex.

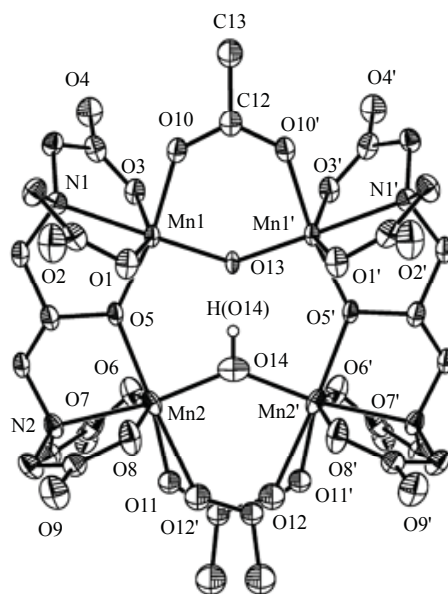


Figure 4. ORTEP drawing of the structure of the tetranuclear manganese complex anion showing the 50% probability level thermal ellipsoids.

Selected bond lengths (Å) and angles (°): Mn1···Mn1' 3.382(2), Mn2···Mn2' 3.565(2), Mn1···Mn2 3.719(1), Mn1-O1 2.150(4), Mn1-O3 2.188(4), Mn1-O5 1.953(4), Mn1-O10 1.969(4), Mn1-O13 1.813(2), Mn1-N1 2.114(4), Mn2-O5 2.103(4), Mn2-O6 2.172(4), Mn2-O8 2.133(4), Mn2-O12' 2.323(11), Mn2-O11 1.851(9), Mn2-O14 1.923(3), Mn2-N2 2.193(4), Mn1-O13-Mn1' 137.7(3), Mn2-O14-Mn2' 136.0(4), Mn1-O5-Mn2 132.85(18). Prime denotes the equivalent position (x, 1/2-y, z).

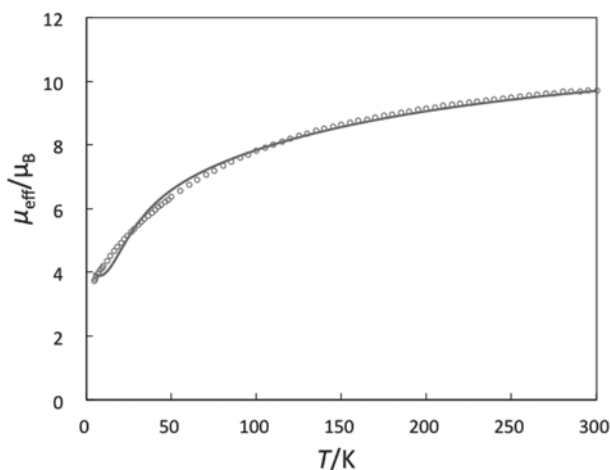


Figure 5. Temperature dependence of magnetic moment of **1**.

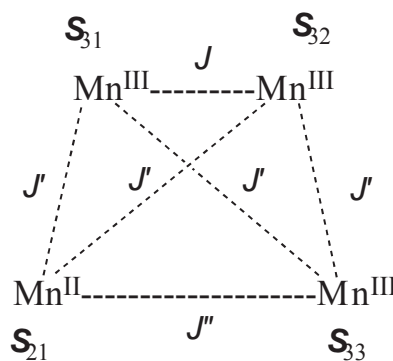


Figure 6. Magnetic interactions in trapezoid tetranuclear Mn^{II}Mn^{III}₃ core.

Conclusions

By using 1,3-diamino-2-hydroxypropane-*N,N',N'',N'''*-tetraacetic acid, a tetranuclear mixed-valent Mn^{II}Mn^{III}₃ complex, Ca₂[Mn₄{μ-OHO}(dhpta)₂(CH₃COO)₂], was isolated. The crystal structure revealed a trapezoid tetranuclear core with μ-(OHO), μ-alkoxido, μ-acetato bridges. In accordance with the structural feature, a considerable antiferromagnetic interaction was observed for the present complex.

Acknowledgements

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