一个新的双核双(μ-氧桥)锰(Ⅲ/Ⅳ)配合物的合成、结构和性质

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二价锰盐和 1, 4, 8, 11-环十四四氮烷(cyclam)在溶液中自组装生成双核双(μ-氧桥)锰(Ⅲ/Ⅳ)配合物:[(cyclam)MnO]$_2$(ClO$_4$)$_2$(NO$_3$)。该配合物被晶体结构表征,低温 EPR 表明其具有 16 条 Mn(Ⅲ)/Mn(Ⅳ)二聚体的特征信号。磁性研究确认有强的反铁磁性,$J/k = -680$K, $g = 2.0$。

关键词: 锰配合物 晶体结构 EPR 磁性
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Synthesis, Structure and Properties of a New Dinuclear Bis(μ-oxo) Manganese(Ⅲ/Ⅳ) Complex

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The dinuclear bis(μ-oxo) manganese(Ⅲ, Ⅳ) complex, [(cyclam)MnO]$_2$(ClO$_4$)$_2$(NO$_3$) (cyclam = 1, 4, 8, 11-tetraazacyclotetradecane), was self-assembled by the reaction of Mn^{2+} with 1, 4, 8, 11-tetraazacyclotetradecane in aqueous medium. This compound was structurally characterized and the typical 16 line signal for a bis(μ-oxo) Mn(Ⅲ)/Mn(Ⅳ) dimer was observed in the low temperature EPR spectra. The magnetic susceptibility studies suggest that the compound is strong antiferromagnetic with $J/k = -680$K for $g = 2.0$.

Keywords: manganese complex crystal structure EPR magnetic properties

0 Introduction

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国家自然科学基金资助项目(No. NSF 29823001)。
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It is well known that tetranuclear manganese center in photosystem Ⅱ (PSII) in green plants plays an essential role in oxidation of water to molecular oxygen[1~3]. Recent EPR studies of the S_2 state in PSII also suggest that the S_2 state exhibits an unusual sixteen-line EPR spectrum, which is in the mixed balance state of manganese (Ⅲ) and manganese (Ⅳ) ions, and consists of two dinuclear di-μ-oxo-dimanganese cores ($2[Mn_2(O)_2]$)[2, 3]. In addition, EXAFS studies pointed out that nitrogen and/or oxygen atoms participate in acting as terminal ligand around the $[Mn_2(O)_2]$ core[4, 5]. Lately several di-μ-oxo-dimanganese(Ⅲ, Ⅳ) complexes with a terminal N_4 donor set have been reported as model complexes for the S_2 state[6~12]. Interest in complexes of this general type stems more from their potential use as two-electron oxidation electrocatalysts. Gref et al[13] have electrochemically oxidized alcohols and ethers in a condition of the presence of both the bpy and phen complexes (bpy = 2, 2' -bipyridine, phen = 1, 10-phenanthroline), and Ramaraj et al[14] have shown that the bpy complex oxidizes water *via* a chemical oxidant such as cerium (Ⅳ) ion. Consequently, various synthetic efforts have been made to obtain di-μ-oxo-dimanganese compounds with desired electrochemical properties, with an expectation of producing useful catalytic complexes. But most of the synthetic methods involve the oxidation of Mn (Ⅱ) precursors using persulfate, permanganate, hydrogen peroxide, or dioxygen[15~18]. In this paper we represented that a new mixed-valence Mn (Ⅲ) -Mn (Ⅳ) bis(μ-oxo) compound $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$ can be obtained through self-assembly from aqueous solution. Its magnetic susceptibilities and exchange couplings are also reported and interpreted.

1 Experimental

1.1 Materials and measurements

Reagents and solvents were chemical grade and were used without further purification. The cyclam ligand was prepared according to literature methods[16]. Elemental analyses were performed at the Perkin-Elmer 240C analytic instrument. IR spectrum was recorded on a Nicolet 170SX FT-IR spectrophotometer. Magnetic susceptibility was measured on a SQUID magnetometer (MPMS-7), from 300 to 5K at a field of 10KOe. UV-Vis spectra were performed with SHIMADZU UV 3100 spectrophotometry. The concentration in water was 2.5×10^{-5} mol · L^{-1}. X-Band EPR spectra were recorded on a Varian Model E109 spectrometer equipped with a low-temperature Dewar.

1.1.1 $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$

To a solution of 0.42g(2.1mmol) of cyclam in 10mL CH_3OH was added with a solution of 0.574g(2.0mmol) of $Mn(NO_3)_2 \cdot 6H_2O$ in 8mL of water. The solution changed quickly from colorless to red-brown and lastly a color of dark blue appeared. To the resulting dark blue solution, a solution of 0.37g(3.0mmol) of $NaClO_4$ in 5mL of water was added. The solution was stood undisturbedly for one day, then the plate-type dark green crystals, suitable for X-ray analysis, were obtained. The crystals were stable in the air. Anal. Calcd. for $C_{20}H_{48}Cl_2Mn_2N_9O_{13}$: Mn, 13.68; C, 29.90; H, 6.02; N, 15.69%. Found: Mn, 14.00; C, 29.65; H, 5.78; N, 15.47%.

Caution! Perchlorate salts are potentially explosive and should be handled in a small amount.

1.1.2 X-ray structure determination

A single crystal, with dimensions 0.38 × 0.36 × 0.12mm, was put on a Siemens SMART CCD diffractometer. Intensity data were collected at room temperature using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$Å) with a detector distance of 4 cm and swing angle of −35°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) and each exposure of 30s covered 0.3° in ω. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL. A summary of the crystal data collection and refinement parameters for compounds $[(\text{cyclam})\text{MnO}]_2(\text{ClO}_4)_2(\text{NO}_3)$ was given in Table 1.

Table 1　Crystal Data and Structure Refinement for $[(\text{cyclam})\text{MnO}]_2(\text{ClO}_4)_2(\text{NO}_3)$

empirical formula	$C_{20}H_{48}Cl_2Mn_2N_9O_{13}$
formula weight	803.45
temperature	293(2)K
wavelength	0.71073Å
crystal system	monoclinic
space group	$C2/c$
unit cell dimensions	$a = 19.9616(4)$Å
	$b = 13.8047(4)$Å
	$c = 12.1531(3)$Å
	$\beta = 90.508(1)°$
volume	3348.82(14)Å^3
Z, calculated density	4, 1.594Mg·m^{-3}
absorption coefficient	0.986mm^{-1}
$F(000)$	1676
crystal size	0.38 × 0.36 × 0.12mm
θ range for data collection	2.45 to 27.50°
limiting indices	$-25 < h < 25$, $-17 < k < 17$, $-11 < l < 15$
reflections collected/unique	11565/3823[R(int) = 0.0344]
completeness to $\theta = 27.50$	99.4%
absorption correction	empirical
max. and min. transmission	0.8908 and 0.7057
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3823/0/209
goodness-of-fit on F^2	1.070
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0493$, w$R_2 = 0.1419$
R indices (all data)	$R_1 = 0.0564$, w$R_2 = 0.1495$
largest diff. peak and hole	0.801 and −0.538e·Å^{-3}

2　Results and discussion

2.1　Description of the Structure

The structure of $[(\text{cyclam})\text{MnO}]_2(\text{ClO}_4)_2(\text{NO}_3)$ is represented in Fig. 1 and Fig. 2. Principal distances and angles for this complex are listed in Table 2. It consists of apparently centrosymmetric binuclear $[(\text{cyclam})\text{MnO}]^{3+}$ cations, two perchlorate and one nitrate anions.

The geometry about each manganese center is roughly octahedral, the ligating atoms being two *cis* oxo-bridges and four nitrogen atoms from the cyclam ligand. The *trans* angles at Mn fall in the range 158.6(2) to 174.1(2)°, with the greatest deviation from linearity occurring at the intra-ligand

Table 2 Bond Lengths (Å) and Angles (°) for [(cyclam)MnO]$_2$(ClO$_4$)$_2$(NO$_3$)

Mn(1)-O(1)	1.829(2)	Mn(1)-O(1)^a	1.826(2)	Mn(1)-N(1)	2.114(2)
Mn(1)-N(2)	2.185(3)	Mn(1)-N(3)	2.125(2)	Mn(1)-N(4)	2.217(3)
Mn(1)-Mn(1)^a	2.740(1)	O(1)-Mn(1)^a	1.826(2)		
O(1)^a-Mn(1)-O(1)	82.90(8)	O(1)^a-Mn(1)-N(1)	173.95(9)	O(1)-Mn(1)-N(1)	91.07(9)
O(1)^a-Mn(1)-N(3)	91.74(9)	O(1)-Mn(1)-N(3)	174.34(9)	N(1)-Mn(1)-N(3)	94.30(9)
O(1)^a-Mn(1)-N(2)	95.60(9)	O(1)-Mn(1)-N(2)	98.41(1)	N(1)-Mn(1)-N(2)	85.69(1)
N(3)-Mn(1)-N(2)	80.24(1)	O(1)^a-Mn(1)-N(4)	99.97(9)	O(1)-Mn(1)-N(4)	98.00(9)
N(1)-Mn(1)-N(4)	80.37(1)	N(3)-Mn(1)-N(4)	84.70(1)	N(2)-Mn(1)-N(4)	158.61(1)
O(1)^a-Mn(1)-Mn(1)^a	41.49(6)	O(1)-Mn(1)-Mn(1)^a	41.41(6)	N(1)-Mn(1)-Mn(1)^a	132.48(7)
N(3)-Mn(1)-Mn(1)^a	133.21(7)	N(2)-Mn(1)-Mn(1)^a	99.36(7)	N(4)-Mn(1)-Mn(1)^a	102.02(7)
Mn(1)^a-O(1)-Mn(1)	97.10(8)				

^{a}Symmetry transformations used to generate equivalent atoms: $-x+1/2$, $y+1/2$, $-z+1$

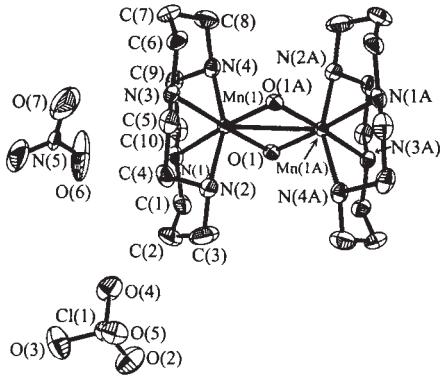

Fig. 1 Molecular structure of [(cyclam)MnO]$_2$(ClO$_4$)$_2$(NO$_3$)

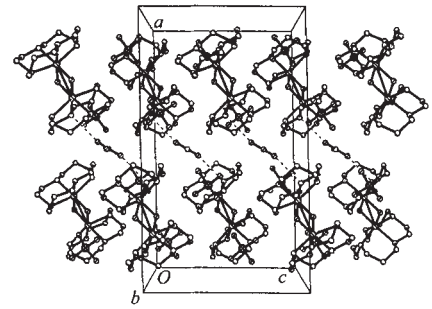

Fig. 2 Packing diagram of [(cyclam)MnO]$_2$(ClO$_4$)$_2$(NO$_3$) in the unit cell down to *b* axis

N(4)-Mn-N(2) angle defined by the two axial nitrogen atoms. The four chelating N-Mn-N angles fall in the range 80.2(2) to 85.4(2)°, with an average value of 82.2(3)°. The Mn-Mn separation of 2.7398(7)Å is compared with the values for other di-μ-oxo dimanganese complexes. The Mn-O-Mn bond angle of 97.10(8)° can be compared with the other reported values, which range from 94.0 to 96.6°. The presence of the crystallographic inversion center in the middle of the dimer causes the two manganese centers to be crystallographically equivalent. While this could indicate that the two manganese centers are chemically equivalent, and that the complex is delocalized, it could also be due to a static disorder resulting from the crystallographic superposition of an equal number of Mn (Ⅲ) -Mn (Ⅳ) and Mn (Ⅳ) -Mn (Ⅲ) cations, or from a dynamic disorder due to rapid (on the crystallographic time scale) electron transfer between the two manganese centers. Burgi and coworkers[15] noted an analogous crystallographic symmetry in the phen complex, where the dimmer has apparent C_2 symmetry leading to crystallographically equivalent manganese centers, and their excellent and detailed analysis need not be repeated here. Hence, we conclude that the two sites are chemically inequivalent, and this compound exhibits a static disorder in the crystals due to superposition of the Mn (Ⅲ) and Mn (Ⅳ) ends of the cation.

2.2 EPR Spectrum

The EPR spectrum of $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$ was recorded at 110K(Fig. 3) . The powder EPR spectrum exhibits the expected sixteen-line pattern centered near $g = 2.0$. Such a sixteen-hyperfine pattern is expected for an antiferromagnetically coupled Mn(Ⅲ, Ⅳ) dimmer with a spin state of 1/2 where two manganese ions are not equivalent. Preliminary computer simulation of the multiline spectrum yielded the spectral parameters: $g = 2.07$, $A_1 = 234.2 \times 10^{-4}$ and $A_2 = 78.2 \times 10^{-4}cm^{-1}$. The EPR results indicate that the complex is in a trapped mixed valence state.

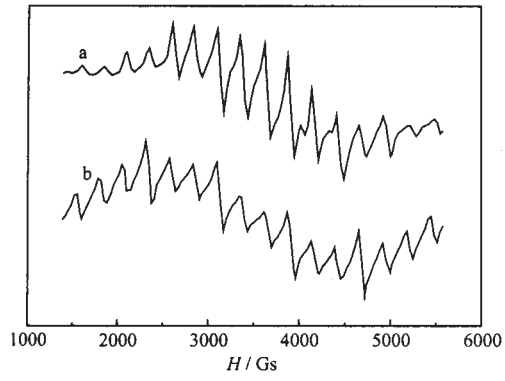

Fig. 3 X-band EPR spectrum of $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$ at 110 K (a) and a simulated spectrum (b) obtained with the parameters described in the text

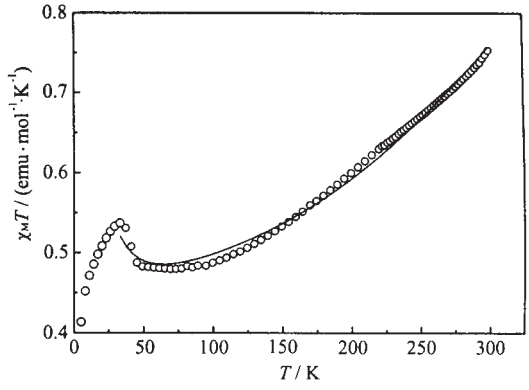

Fig. 4 Thermal variation $\chi_M T$(°) of compound $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$

2.3 Magnetic Properties

The molar magnetic susceptibility χ_M of $[(cyclam)MnO]_2(ClO_4)_2(NO_3)$ was measured as a function of the temperature T. The results are shown in Fig. 4 in the form of $\chi_M T$ versus T plot. $\chi_M T$ value decreases from 0.75emu · mol^{-1} · K at 299K to a minimum of 0.48emu · mol^{-1} · K at 70K. This is characteristic of an antiferromagnetic coupling between the electronic spins of the Mn (Ⅳ) and Mn (Ⅲ) ions which produces a spin $S = 1/2$ ground state. The decrease at low temperature was attributed to interactions between the residual spins which can lead to a long-range three dimensional magnetic ordering and spontaneous magnetization at low temperatures. The susceptibility was calculated as

$$\chi_M T = (N\beta^2 g^2 T/3k(T+\theta))(\sum S(S+1)(2S+1) \times \exp(JS(S+1)/2kT)) / (\sum (2S+1)\exp(JS(S+1)/2kT))$$

The best fit was obtained by setting $g = 2$ for $J/k = -680$K and $\theta = 7.8$K, TIP $= 92 \times 10^{-6}$.

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