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Synthesis and Crystal Structures of Manganese(IV) Complexes with Tridentate Schiff Bases[1]

D. L. Peng

Key Laboratory of Surface & Interface Science ofHenan, School of Material & Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002 P.R. China

e-mail: pengdonglai@yahoo.cn

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Abstract—The complexes with the formulae $[Mn(L^1)_2] \cdot 0.5H_2O$ (**I**) and $[Mn(L^2)_2]$ (**II**), where L^1 and L^2 are the dianionic form of 2,4-dichloro-6-[(2-hydroxyethylimino)methyl]phenol and 2-{[1-(3-ethoxy-2-hydroxyphenyl)methylidene]amino}-2-methylpropane-1,3-diol, respectively, were obtained and characterized by elemental analysis and IR spectroscopy. The crystal structures of complexes **I** and **II** were determined using X-ray diffraction. The crystal of **I** is orthorhombic space group *Fdd*2: $a = 24.170(2)$, $b = 32.021(3)$, $c = 11.352(2)$ Å, $V = 8785.9(19)$ Å^3, $Z = 8$. The crystal of **II** is monoclinic space group *C*2/*c*: $a = 13.931(4)$, $b = 18.381(5)$, $c = 12.444(5)$ Å, $\beta = 121.980(3)°$, $V = 2702.9(15)$ Å^3, $Z = 4$. The Mn atom in each of the complexes is in an octahedral coordination.

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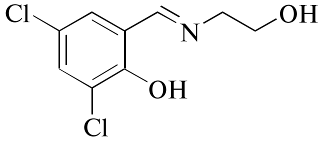
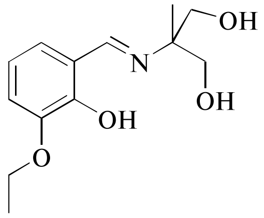
INTRODUCTION

Schiff bases have been widely studied in coordination chemistry mainly due to their facile syntheses, easily tunable steric, electronic properties and good solubility in general solvents [1–3]. Transition metal complexes derived from N and O-containing multidentate Schiff bases are of particular interest because of their versatile structures and wide applications [4–6]. In addition, the hydroxy-containing Schiff bases and their complexes have been proved to have interesting biological activities, such as antibacterial, antiviral, antifungal, and anticancer [7–9]. Manganese is an essential component of various biological redox processes, as in catalases [10–12], and in photosynthesis by oxidizing water to dioxygen [13]. In the processes, the intermediate generated has manganese in its +4 oxidation state and hence the studies associated with Mn(IV) are important in the coordination and biomimetic chemistry. The manganese Schiff base complexes have also received considerable attention for their application in catalytic and bioinorganic chemistry [14–16]. In this paper, we describe the synthesis and structures of two new manganese(IV) complexes, $[Mn(L^1)_2] \cdot 0.5H_2O$ (**I**) and $[Mn(L^2)_2]$ (**II**), where L^1 and L^2 are the dianionic form of the tridentate Schiff bases 2,4-dichloro-6-[(2-hydroxyethylimino)methyl]phenol (H_2L^1) and 2-{[1-(3-ethoxy-2-hydroxyphenyl)methylidene]amino}-2-methylpropane-1,3-diol (H_2L^2).



(H_2L^1)



(H_2L^2)

EXPERIMENTAL

Materials and methods. The infrared spectra of the compounds were recorded on a PerkinElmer RX 1 FT-IR spectrophotometer with KBr discs. Elemental analyses were carried out using a PerkinElmer 2400 II elemental analyser. All the chemicals and solvents used for the syntheses were of reagent grade. 3,5-Dichlorosalicylaldehyde and 3-ethoxysalicylaldehyde (Fluka) were used as received. $Mn(ClO_4)_2 \cdot 6H_2O$ was prepared by the reaction of manganese carbonate with perchloric acid in distilled water. The Schiff base H_2L^1 was prepared according to the literature method [17].

Caution! Although no problems were encountered in this work, perchlorate salts are potentially explosive. They should be prepared in small quantities and handled with great care.

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Synthesis of H_2L^2. 3-Ethoxysalicylaldehyde (1.66 g, 10 mmol) and 2-amino-2-methylpropane-1,3-diol (1.05 g, 1 mmol) were stirred in 80 mL methanol, resulting in a yellow solution containing H_2L^2 and this was used for the preparation of the complex **II** without further purification.

Synthesis of I. A 10 mL methanolic solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1 mmol) was added to a stirred 16 mL methanolic solution of H_2L^1 (0.466 g, 2 mmol). The mixture was stirred for 1 h at ambient condition to give a brown solution. Brown block-shaped single crystals of **I** suitable for single crystal X-ray diffraction were obtained after a few days during evaporation. The yield was 0.312 g (59.2%).

IR spectrum (KBr; ν, cm^{-1}): 3454 w, 1625 s, 1520 m, 1438 s, 1413 w, 1383 w, 1310 s, 1210 m, 1178 m, 1161 m, 1058 w, 1038 w, 1016 w, 886 w, 867 m, 758 m, 593 m, 537 m, 493 w, 419 w.

For $C_{36}H_{29}N_4O_9Cl_8Mn_2$			
anal. calcd., %:	C, 40.98;	H, 2.77;	N, 5.31.
Found, %:	C, 40.72;	H, 2.83;	N, 5.39.

Synthesis of II. A 10 mL methanolic solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1 mmol) was added to a stirred 16 mL methanolic solution of H_2L^2 (0.506 g, 2 mmol). The mixture was stirred for 1 h at ambient condition to give an amount of precipation. The mixture was transferred to a Teflon-lined vessel, which was sealed and held at 150°C for 12 h. The vessel was allowed to slowly cool to room temperature. Brown block-shaped single crystals of **II** suitable for single crystal X-ray diffraction were obtained. The yield was 0.273 g (49.0%).

IR spectrum (KBr; ν, cm^{-1}): 3331 w, 1624 s, 1526 m, 1456 s, 1390 w, 1318 m, 1198 w, 1180 m, 1129 w, 1078 w, 991 w, 951 w, 907 w, 863 w, 823 m, 776 m, 707 m, 667 w, 594 w, 550 w, 460 w.

For $C_{26}H_{34}N_2O_8Mn$			
anal. calcd., %:	C, 56.01;	H, 6.12;	N, 5.02.
Found, %:	C, 55.89;	H, 6.26;	N, 4.90.

X-ray crystallography. Suitable single crystals of complexes **I** and **II** were selected and mounted in air onto thin glass fibers. Accurate unit cell parameters were determined by a least-squares fit of 2θ values, and intensity data sets were measured on a Bruker Smart 1000 CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. Both structures of the complexes were solved by direct methods using the SHELXL 97 program [18]. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. All hydrogen atoms were unambiguously located by difference maps and refined isotropically. The occupancy of the water molecule for **I** was estimated at 50% based on obtaining an equivalent isotropic displacement parameter of 0.0732 which is not unreasonable for a solvent molecule in a structure determined at room temperature. Crystallographic data and experimental details for structure analyses are summarized in Table 1. Selected bond lengths and angles of the complexes are listed in Table 2.

Supplementary materials for two compounds have been deposited with Cambridge Crystallographic Data Centre (nos. 859156 (**I**) and 859157 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases H_2L^1 and H_2L^2 were readily prepared by the reaction of equimolar quantities of 3,5-dichlorosalicylaldehyde with 2-aminoethanol and 3-ethoxysalicylaldehyde with 3-ethoxysalicylaldehyde, respectively, in methanol. The complex **I** was prepared by the reaction of H_2L^1 with manganese perchlorate in methanol at room temperature, while the complex **II** was prepared by the reaction of H_2L^2 with manganese perchlorate in methanol under solvothermal condition. During the search of literature, we found that most of the similar manganese(IV) complexes were prepared by the reaction of the Schiff bases with $KMnO_4$ [19, 20]. It is interesting that in the present paper, the Mn^{2+} in the metal salt was oxidized to Mn(IV) by air in the complexes.

Molecular structure of **I** contains a manganese(IV) complex molecule and half of one water molecule of crystallization, which is shown in Fig. 1. The molecular structure of **II** possesses a crystallogaphic inversion center symmetry, with the Mn(1) atom located at the inversion center, as shown in Fig. 2. In each of the complexes, two Schiff base ligands are bonded to the Mn atom in a tridentate fashion through the phenolate oxygen, imine nitrogen, and one hydroxy O atoms, resulting in an octahedral geometry. The largest deviations from octahedral geometry arise from the geometric constraints of this chelating ligand. The *trans* coordinate angles are in the range 159.6(3)°–173.8(3)° for **I** and 171.0(3)°–173.3(2)° for **II**, and the remaining coordinate bond angles are in the range 76.8(3)°–97.0(3)° for **I** and 83.8(2)°–95.9(2)° for **II**. The two Schiff bases in the complexes are approximately per-

Table 1. Crystallographic data and structure refinement parameters for **I** and **II**

Parameter	Value	
	I	**II**
M	1055.1	557.5
Shape and color	Block and brown	Block and brown
Temperature, K	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2	*C*2/*c*
a, Å	24.170(2)	13.931(4)
b, Å	32.021(3)	18.381(5)
c, Å	11.352(2)	12.444(5)
β, deg	90	121.980(3)
V, Å^3	8785.9(19)	2702.9(15)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.594	1.370
Absorption coefficient, mm^{-1}	1.117	0.539
F(000)	4240	1172
Crystal size, mm	0.18, 0.17, 0.16	0.33, 0.33, 0.29
θ Range for data collection, deg	2.54–26.99	2.22–27.00
Index ranges	$-26 \le h \le 30$, $-40 \le k \le 34$, $-14 \le l \le 14$	$-17 \le h \le 16$, $-22 \le k \le 23$, $-12 \le l \le 15$
Reflections collected/unique (R_{int})	10815/4656 (0.1026)	7156/2944 (0.0605)
Observed reflections	2711	1570
Data/restraints/parameters	4656/7/271	2944/0/171
Goodness-of-fit	0.976	1.025
Final R indices ($I \ge 2\sigma(I)$)	0.0818, 0.1855	0.0763, 0.2116
R indices (all data)	0.1339, 0.2214	0.1507, 0.2580
Largest diff. peak and hole, e Å^{-3}	0.876 and –0.762	1.214 and –0.448

Table 2. Coordinate bond lengths (Å) and angles (deg) for complexes **I** and **II***

Bond	d, Å	Bond	d, Å
		I	
Mn(1)–O(1)	1.896(6)	Mn(1)–O(2)	1.861(6)
Mn(1)–O(3)	2.052(6)	Mn(1)–O(4)	2.343(6)
Mn(1)–N(1)	2.012(6)	Mn(1)–N(2)	2.100(7)
		II	
Mn(1)–O(1)	1.874(4)	Mn(1)–O(4)	1.846(4)
Mn(1)–N(1)	1.963(5)		
Angle	ω, deg	Angle	ω, deg
		I	
O(2)Mn(1)O(1)	173.8(3)	O(2)Mn(1)N(1)	83.6(3)
O(1)Mn(1)N(1)	90.2(3)	O(2)Mn(1)O(3)	93.1(3)
O(1)Mn(1)O(3)	88.7(2)	N(1)Mn(1)O(3)	112.6(3)
O(2)Mn(1)N(2)	89.0(3)	O(1)Mn(1)N(2)	97.0(3)
N(1)Mn(1)N(2)	159.6(3)	O(3)Mn(1)N(2)	86.7(3)
O(2)Mn(1)O(4)	92.9(2)	O(1)Mn(1)O(4)	87.1(3)
N(1)Mn(1)O(4)	84.6(2)	O(3)Mn(1)O(4)	162.4(2)
N(2)Mn(1)O(4)	76.8(3)		
		II	
O(4)Mn(1)O(4*A*)	93.7(3)	O(4)Mn(1)O(1)	173.3(2)
O(4)Mn(1)O(1*A*)	89.9(2)	O(1)Mn(1)O(1*A*)	87.0(2)
O(4)Mn(1)N(1)	83.8(2)	O(4)Mn(1)N(1*A*)	90.1(2)
O(1)Mn(1)N(1)	90.6(2)	O(1)Mn(1)N(1*A*)	95.9(2)
N(1)Mn(1)N(1*A*)	171.0(3)		

* Symmetry code for A: $1 - x, y, 1/2 - z$.

pendicular to each other, with the dihedral angles between two benzene rings of 97.0(3)° for **I** and 71.7(3)° for **II**. The coordinate bond lengths in **I** and **II** are comparabel to each other, and within normal ranges for manganese(IV) complexes [19–21].

The infrared spectra of the complexes are very much consistent with the structural data presented by X-ray diffraction. The broad and weak peak at 3454 cm^{-1} for **I** is attributable to the O–H stretching vibrations of the water molecule. The band due to the phenolic OH groups in **II** appears at about 3331 cm^{-1}. Several weak peaks observed for the complexes in the range 3190–2850 cm^{-1} are assigned to the aromatic stretches. The complexes **I** and **II** display intense peaks at 1625 and 1624 cm^{-1}, respectively, which are assigned to the C=N stretches of the coordinated Schiff base ligands. The weak bands in the range 550–400 cm^{-1} are assigned to the Mn–N and Mn–O vibrations.

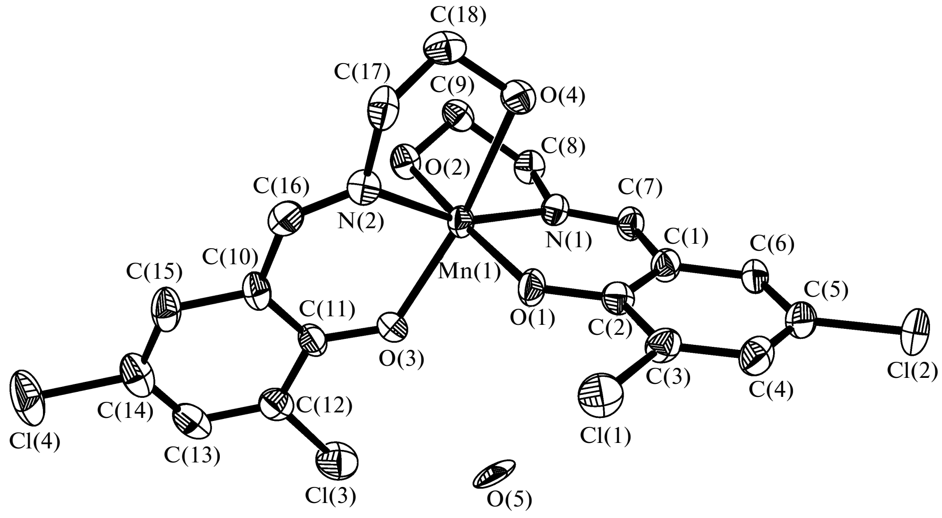

Fig. 1. The ORTEP view of **I** with atom numbering scheme. Hydrogen atoms are omitted for clarity.

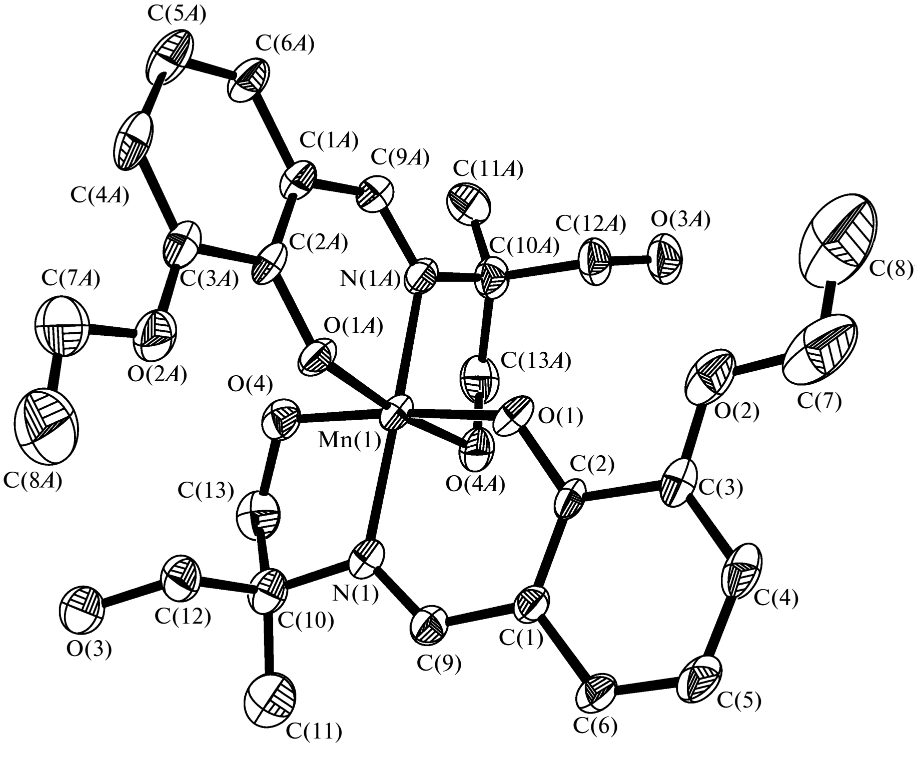

Fig. 2. The ORTEP view of **II** with atom numbering scheme. Hydrogen atoms are omitted for clarity. Atoms labeled with *A* are related to the symmetry position $1 - x, y, 1/2 - z$.

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