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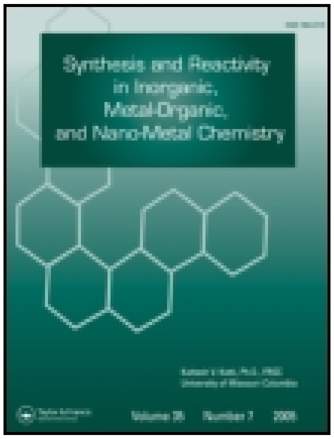

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Synthesis and Crystal Structure of A Novel Polymeric Manganese(IV) Complex Derived From the Schiff Base 2-Ethoxy-6-[(2-hydroxyethylimino)methyl]phenol

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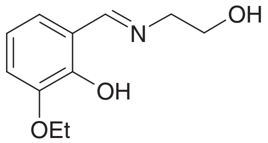
A novel polymeric manganese(IV) complex, $[Mn(L)(HL)(N_3)]_n \cdot nCH_3OH$, has been synthesized from the Schiff base 2-ethoxy-6-[(2-hydroxyethylimino)methyl]phenol (H_2L) with manganese chloride and sodium azide in methanol. The complex was characterized by elemental analysis, IR spectrum, and single-crystal X-ray diffraction. The Mn atom in the complex is coordinated by two phenolic oxygen, two imino nitrogen, and one hydroxyl oxygen atoms from two Schiff base ligands, and by one azido N atom, giving an octahedral coordination.

Keywords crystal structure, manganese, polymeric complex, Schiff base, synthesis

INTRODUCTION

Schiff bases derived from salicylaldehde and similar derivatives have attracted much interest in recent years, especially for their application in coordination chemistry.[1–3] The Schiff bases derived from salicylaldehyde with 2-aminoethanol and similar derivatives have been widely used to prepare complexes with metal ions.[4–6] However, the transition metal complexes with the Schiff base derived from 3-ethoxysalicylaldehyde and 2-aminoethanol, 2-ethoxy-6-[(2-hydroxyethylimino) methyl]phenol (H_2L; Scheme 1), have never been reported. In this article, the synthesis and crystal structure of a novel manganese(IV) complex, $[Mn(L)(HL)(N_3)]_n \cdot nCH_3OH$, are reported.



SCH. 1. H_2L.

EXPERIMENTAL

Materials and Measurements

3-Ethoxysalicylaldehyde and 2-aminoethanol were purchased from Aldrich with AR grade (China). Other chemicals were obtained commercial, and were used as received. The analyses of carbon, hydrogen, and nitrogen were performed with a Perkin-Elmer 240C elemental analyzer (USA). Infrared spectra were recorded in KBr pellets with a Perkin-Elmer 597 infrared diffraction grating spectrophotometer (USA) in the range 4000–400 cm^{-1}.

Caution: Sodium azide is potentially explosive, and only a small quantity should be used and handled with great care.

Synthesis of 2-Ethoxy-6-[(2-hydroxyethylimino)methyl] phenol (H_2L)

To a warm methanol solution (20 mL) of 3-ethoxysalicylaldehyde (1.0 mmol, 166 mg), 2-aminoethanol (1.0 mmol, 61 mg) in methanol (10 mL) was added dropwise. The yellow solution was maintained under reflux for 1 h, and the methanol was evaporated to give a yellow solid product. It was washed with methanol, and dried *in vacuo*. Anal. Calcd. for $C_{11}H_{15}NO_3$ (%): C, 63.1; H, 7.2; N, 6.7. Found (%): C, 62.9; H, 7.3; N, 6.8.

Synthesis of the Complex $[Mn(L)(HL)(N_3)]_n \cdot nCH_3OH$

To a warm methanol solution (10 mL) of H_2L (0.1 mmol, 20.9 mg) and NaN_3 (0.1 mmol, 6.5 mg), $MnCl_2 \cdot 4H_2O$ (0.1 mmol, 19.8 mg) dissolved in methanol (10 mL) was added dropwise. The resulting solution was refluxed for 30 min. The brown crystals were filtered off, washed with methanol, and dried *in vacuo*. Yield, 37.0 mg, 68%. Anal. Calcd. for

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TABLE 1
Crystallographical and experimental data for the complex

Empirical formula	$C_{23}H_{31}MnN_5O_7$
Formula weight	544.5
Crystal shape/color	Block/brown
Temperature/K	298(2)
Wavelength/Å	0.71073
Crystal size/mm	0.20 × 0.20 × 0.18
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.453(3)
b/Å	11.674(3)
c/Å	17.814(3)
β/°	103.275(2)
V/Å^3	2520.6(9)
Z	4
D_c/g cm^{-3}	1.435
μ/mm^{-1} (Mo-Kα)	0.576
F(000)	1140
θ ranges/°	2.10–25.50
$h/k/l$	−15,15/−8,14/−17,21
Independent reflections	4436
Observed reflections [$I \geq 2\sigma(I)$]	2705
$T_{\min}$ and $T_{\max}$	0.8935 and 0.9034
Data/restraints/parameters	4436/19/330
Goodness-of-fit on F^2	01.035
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0832$
	$wR_2 = 0.2036$
R indices (all data)	$R_1 = 0.1345$
	$wR_2 = 0.2385$

$C_{23}H_{31}MnN_5O_7$ (%): C, 50.7; H, 5.7; N, 12.9. Found (%): C, 50.5; H, 5.9; N, 12.8.

Crystal Structure Determination

A well-shaped brown crystal of the complex suitable for X-ray crystallographic analysis was selected following examination under a microscope. Diffraction data were collected on a Bruker APEXII CCD diffractometer (Germany) using Mo$K\alpha$ radiation. The collected data were reduced using the SAINT program (Bruker, Germany),[7] and were corrected for Lorentz and polarization effects and for absorption using the SADABS program (Bruker, Germany).[8] The structure was solved by direct method and the structure solution and refinement were based on F^2 with the SHELXTL program (Bruker, Germany).[9] All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions and given isotropic U values 1.2 or 1.5 times those of the atoms to which they are bonded. The crystal data and data collection parameters of the complex are listed in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bonds are listed in Table 3.

TABLE 2
Selected bond lengths (Å) and angles (°) for the complex

	Bond lengths		
Mn1-O1	1.857 (4)	Mn1-O3A	2.360 (4)
Mn1-O4	1.854 (4)	Mn1-N1	2.045 (4)
Mn1-N2	2.041 (5)	Mn1-N3	2.367 (6)
	Bond angles		
O4-Mn1-O1	175.00 (18)	O4-Mn1-N2	90.96 (19)
O1-Mn1-N2	89.56 (19)	O4-Mn1-N1	89.17 (17)
O1-Mn1-N1	90.21 (17)	N2-Mn1-N1	178.8 (2)
O4-Mn1-O3A	86.21 (17)	O1-Mn1-O3A	88.81 (16)
N2-Mn1-O3A	90.9 (2)	N1-Mn1-O3A	87.91 (16)
O4-Mn1-N3	92.92 (19)	O1-Mn1-N3	92.05 (19)
N2-Mn1-N3	89.8 (2)	N1-Mn1-N3	91.38 (19)
O3A-Mn1-N3	178.88 (17)		

Symmetry code for A: 3/2 – x, 1/2 + y, 3/2 – z.

RESULTS AND DISCUSSION

The condensation of 3-ethoxysalicylaldehyde with 2-aminoethanol gave the yellow Schiff base. The Schiff base was identified by its IR spectrum, where replacement of the carbonyl by the imine group results in lowering of the energy of the ν(C=O) stretch. The Schiff base prepared in this way was formed in quantitative yield and was of high purity. The manganese(IV) complex was prepared by the reaction of the Schiff base, sodium azide, and manganese chloride in methanol. The Mn atom with +2 oxidate number in manganese chloride was oxidized to +4 in the complex by oxygen. The azide ligand is a versatile bridging groups in the construction of polymeric structures,[10–12] however, in the present complex, it acts as simple terminal ligand. The results of the elemental analyses are in accord with the composition suggested for the Schiff base and the complex. The Schiff base and the complex are soluble in acetonitrile, methanol, and ethanol. It should be noticed that the single crystals of the complex can only be formed from methanol system.

IR Spectra

The broad absorption bands centered at 3417 and 3372 cm^{-1} in the free Schiff base and at 3408 cm^{-1} in complex are assigned to the OH group vibrations. For the Schiff base, the strong band at 1623 cm^{-1} is assigned to the azomethine group vibration.[13] The band is shifted to lower wave number (1609 cm^{-1}) in the complex. This change shows that the imine nitrogen atom

TABLE 3
Hydrogen-bond geometry (Å, °) for the complex

D–H···A	D–H	H···A	D···A	D–H···A
O7–H7···N3$^{\#1}$	0.82	2.09	2.840 (10)	152
O6–H6···N5$^{\#2}$	0.82	2.43	2.869 (12)	115

Symmetry codes: #1: x, 1 + y, z; #2: 1/2 – x, 1/2 + y, 3/2 – z.

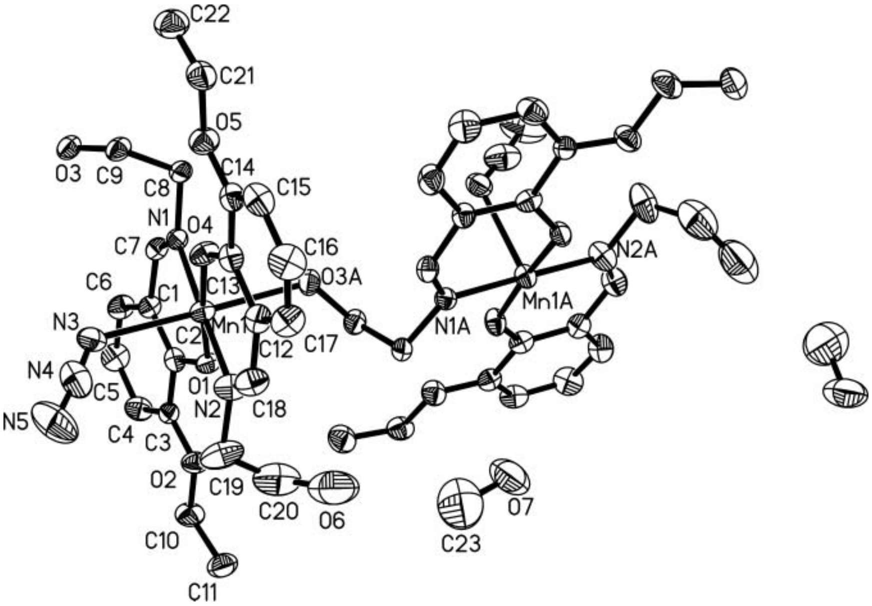

FIG. 1. Molecular structure of the complex at 30% probability displacement.

coordinated to the manganese atom. The middle absorption band at 1222 cm^{-1} is attributed to the phenolic stretch. The band is observed at lower wave number by 23 cm^{-1} relative to the free Schiff base, suggesting involvement of the oxygen atom of the Ph–O group in the coordination.[14] The complex shows characteristic intense IR band for coordinated azide groups at 2053 cm^{-1}. The weak bands in the range 535–405 cm^{-1} are assigned to the stretching vibrations of the Mn–O and Mn–N bonds.

Structure Description of the Complex

The view of the molecular structure of the complex is depicted in Figure 1. The compound contains a hydroxyl oxygen-bridged polymeric manganese(IV) complex and methanol molecules of crystallization. One Schiff base ligand is monoanionic form, and the other is dianionic form. The Mn atom in the complex is six-coordinated in an octahedral geometry, with two phenolic O and two imino N atoms from two Schiff base ligands defined the equatorial plane, and with one hydroxyl O atom of a Schiff base ligand, and one azido N atom occupying the two axial positions. The MnN_3O_3 coordination forms a slightly distorted octahedral geometry, with the three *trans* angles subtended at the Mn atom in the range 175.0(2)–178.9(2)°, and with the remaining angles subtended at the Mn atom in the range 86.2(2)–92.9(2)°. All the bond lengths and angles related to the Mn atom in the complex are comparable to the

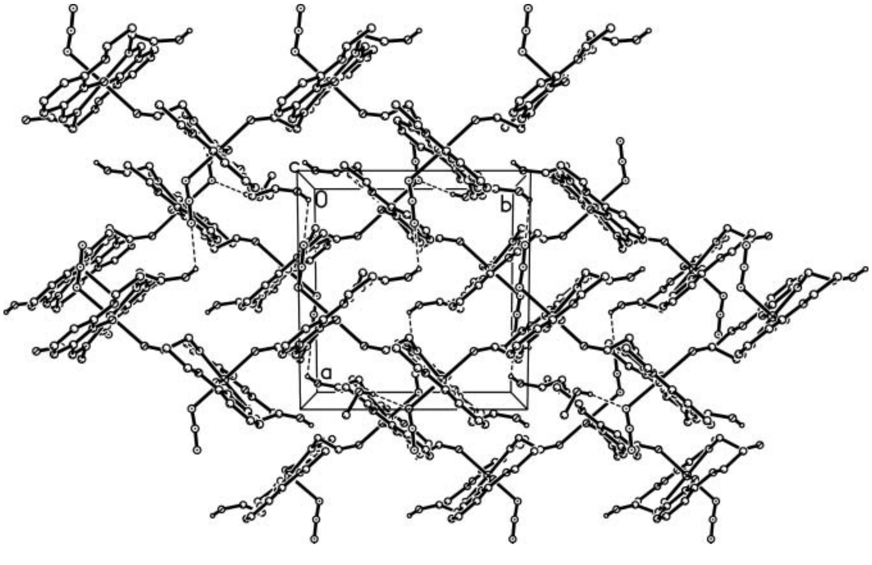

FIG. 2. Molecular packing arrangement of the complex, viewed along the *c*-axis.

values observed in the manganese(IV) complexes with Schiff bases.[5,15–17]

In the crystal structure of the complex, molecules are linked through intermolecular O−H···N hydrogen bonds, forming a three-dimensional network, as shown in Figure 2.

CONCLUSIONS

A novel manganese(IV) complex derived from the Schiff base 2-ethoxy-6-[(2-hydroxyethylimino)methyl]phenol has been synthesized and characterized by elemental analysis, IR spectra, and single-crystal X-ray crystallography. The Schiff base ligand coordinates to the Mn atom through the phenolic O, imino N, and/or hydroxyl O atoms.

SUPPLEMENTARY MATERIALS

Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Centre (CCDC 848870).

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