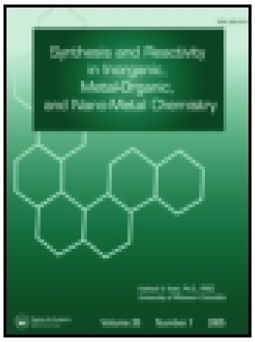

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Yan Lei & Qiwen Yang

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Synthesis, X-ray Structural Characterization, and Catalytic Property of an End-to-end Azido-bridged Polymeric Manganese(III) Complex Derived from *N,N'*-bis(5-Fluorosalicylidene)-1,2-diaminoethane

Yan Lei[1,2,*], Qiwen Yang[2,3]

[1]Key Laboratory of Water Environment Evolution and Pollution Control in Three Gorges Reservior, Chongqing Three Gorges University, Chongqing 404000, P. R. China

[2]School of City Construction and Environmental Engineering, Chongqing University, Chongqing 400030, P. R. China

[3]China Huaxi Engineering Design & Construction Co., ltd, Sichuan 610000, P. R. China

[*]Corresponding author. E-mail: leiyan222@126.com

Abstract

A new end-to-end azido-bridged polymeric manganese(III) complex $[MnL(\mu_{1,3}-N_3)]_n$ with the Schiff base ligand *N,N'*-bis(5-fluorosalicylidene)-1,2-diaminoethane (H_2L), has been synthesized and structurally characterized by physico-chemical methods and single crystal X-ray determination. Crystal of the complex crystallizes in orthorhombic space group $Pca2_1$, with a = 10.8211(5), b = 13.4644(6), c = 11.1811(5) Å, V = 1629.08(13) Å^3, Z = 4, R_1 = 0.0255, wR_2 = 0.0653, GOOF = 1.053. X-ray analysis indicates that the complex is an end-to-end azido-bridged polymeric manganese species. The Mn atom is coordinated in an octahedral coordination by two phenolate O and two imine N atoms from the Schiff base ligand, and two azido N atoms. The catalytic property for epoxidation of styrene by the complex was evaluated.

Keywords

Manganese complex, Schiff base ligand, azide ligand, crystal structure, catalytic property

INTRODUCTION

Schiff-base compounds represent one of the most attractive series of ligands in coordination chemistry. The ligands bearing typical C=N groups and suitable O, N, or S donor atoms are capable of binding various transition and rare earth metal atoms to form complexes with versatile structures and properties [1-3]. To date, most Schiff base complexes have been reported to have interesting catalytic properties, such as asymmetric epoxidation, oxidation of sulfides, and various type of polymerization [4-8]. Among the Schiff base complexes, those with Mn centers are of particular interest for their epoxidation of olefins [9-11]. Herein we report the synthesis, X-ray crystal structure, and catalytic property of a new manganese complex, $[MnL(\mu_{1,3}-N_3)]_n$, where L is the deprotonated form of *N,N'*-bis(5-fluorosalicylidene)-1,2-diaminoethane (see Scheme 1).

EXPERIMENTAL

Materials

Manganese perchlorate, 3-fluorosalicylaldehyde, and *N,N'*-diaminoethane were purchased from Aldrich. All other reagents with AR grade were used as received without further purification.

Physical measurements

Infrared spectra (4000-400 cm^{-1}) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. Microanalyses (C, H, N) of the complex were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

X-ray crystallography

Crystallographic data of the complex were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Absorption corrections were applied by using the multi-scan program [12]. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against F^2 (SHELXL-97) [12]. All non-hydrogen atoms were refined anisotropically. The crystallographic data and experimental details for the structure analysis are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Preparation of H_2L

Hot methanol solutions of 5-fluorosalicylaldehyde and *N*,*N'*-diaminoethane (2:1, v/v) were stirred under reflux for 1 h, and cooled to room temperature. The yellow precipitate was collected by filtration and dried in vacuo. Yield: 91%. Anal. calcd. for $C_{16}H_{14}F_2N_2O_2$ (%): C, 63.2; H, 4.6; N, 12.5. Found (%): C, 63.0; H, 4.7; N, 12.3.

Preparation of the manganese complex

To a stirred solution of H_2L (0.30 g, 1 mmol) and sodium azide (0.065 g, 1 mmol) in 20 mL methanol was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1 mmol). The resulting mixture was refluxed for 1 h. The deep brown reaction solution was filtered and the solvent removed under reduced pressure, yielding brown solid of the complex. Yield: 55%. Well-shaped single crystals suitable for X-ray diffraction were obtained by recrystallization of the solid from methanol. Anal. calcd. for $C_{16}H_{12}F_2MnN_5O_2$ (%): C, 48.1; H, 3.0; N, 17.5. Found (%): C, 48.2; H, 3.1; N, 17.7.

Styrene epoxidation

The epoxidation reaction was carried out at room temperature in acetonitrile under N_2 atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the complex (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH_2PO_4 and NaOH. The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. For each complex the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.1 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

RESULTS AND DISCUSSION

Synthesis

The Schiff base was readily prepared by condensation reaction of 5-fluorosalicylaldehyde with

N,N'-diaminoethane in methanol. The stoichiometric reaction of the Schiff base and sodium azide with manganese perchlorate in refluxing methanol yield the corresponding manganese complex (see Scheme 2). The reaction progress is accompanied by an immediate color change of the solution from yellow to deep brown. We have attempted to prepare and cultivate diffraction quality crystals of the complexes from various solvents; yet, only methanol and ethanol are suitable. The molar conductivity (Λ_{M} = 23 Ω^{-1} cm^{2} mol^{-1}) is consistent with the values expected for non-electrolyte [13].

Description of the structure of the complex

Single-crystal X-ray analysis reveals that the compound is an end-to-end azido-bridged polymeric manganese complex. The ORTEP plot of the complex is shown in Figure 1. The manganese atom is in a distorted octahedral geometry, which is coordinated by the N_2O_2 donor atoms from a Schiff base ligand in the equatorial plane and two N donor atoms from two azide ligands in the axial positions. The distortion of the octahedral coordination of the structure can be observed from the bond angles (Table 2) related to the Mn atoms. The *cis*- and *trans*- angles related to the Mn atom are in the range of 86.81(9)–94.45(7)° and 173.28(7)–173.52(8)°, respectively. The bond lengths of Mn–O and Mn–N (Table 2) are close to those in other Mn-salen complexes [14,15]. As expected, the bond lengths in the axial positions are elongated due to a Jahn-Teller distortion effect. The space packing of the complex along the *c* axis is shown in Figure 2, in which azide ligands link the manganese complex subunits into one-dimensional chains.

Spectral characterization

The IR spectrum of the complex is shown in Figure 3. The absorption at 1633 cm^{-1} is assigned to the azomethine group, ν(C=N) [16]. This band undergoes a negative shift of 15 cm^{-1} when compared to that of the free Schiff base. The presence of a single band for ν(C=N) in the spectrum of the complex indicates participation of both the azomethine nitrogen atoms in coordination bond formation with the metal ion. The phenolic ν(C-O) appears at 1286 cm^{-1}. The typical absorption for the azide ligand is observed at 2030 cm^{-1}.

The UV-Vis spectrum of the complex in acetonitrile is shown in Figure 4. The band at 340 nm is attributed to the azomethine chromophore π-π* transition. The band at higher energy (280 nm) is associated with the benzene π-π* transition [17]. The band observed at 415 nm may be due to the $d \rightarrow d$ transitions.

Catalytic epoxidation results

The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide and reaction time to obtain maximum yield using both the oxidants are given in Table 3. The data reveals that the complex as a catalyst converts styrene most efficiently in the presence of both oxidants. Nevertheless, the catalyst is selective towards the formation of styrene epoxides despite of the formation of by-products which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxides derivative, alcohols *etc.* From the data it is also clear that the complex exhibits excellent efficiency for styrene epoxide yield. When the reactions are carried out with PhIO and NaOCl, styrene conversions were about 82% and 73%, respectively. It is evident that between PhIO and NaOCl, the former acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity. The epoxide yields for the complex are 75% using PhIO as an oxidant and 60% using NaOCl as an oxidant.

CONCLUSION

An end-to-end azido-bridged polymeric manganese complex with a Schiff base ligand has been prepared and structurally characterized in this paper. Structural analysis shows that the Mn atom is in an octahedral coordination. The Schiff base ligand coordinates to the Mn atom through the phenolate oxygen and imino nitrogen atoms. The complex show effective catalytic epoxidation on styrene.

ACKNOWLEDGEMENTS

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Table 1 Crystallographic data for the single crystal of the complex

Empirical formula	$C_{16}H_{12}F_2MnN_5O_2$
Formula weight	399.25
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	$Pca2_1$
a (Å)	10.8211(5)
b (Å)	13.4644(6)
c (Å)	11.1811(5)
V (Å^3)	1629.08(13)
Z	4
F(000)	808
Data/restraints/parameters	2328/1/236
Goodness-of-fit on F^2	1.053
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0255$, $wR_2 = 0.0653$
R indices (all data)	$R_1 = 0.0291$, $wR_2 = 0.0681$

Table 2 Selected bond distances (Å) and bond angles (º) for the complex

(1)			
Bond distance			
Mn1-O1	1.8914(16)	Mn1-O2	1.8809(16)
Mn1-N1	1.986(2)	Mn1-N2	1.9913(18)
Mn1-N3	2.333(2)	Mn1-N5A	2.290(2)
Bond angle			
O2-Mn1-O1	94.45(7)	O2-Mn1-N1	173.52(8)
O1-Mn1-N1	91.93(8)	O2-Mn1-N2	91.58(7)
O1-Mn1-N2	173.28(7)	N1-Mn1-N2	82.11(8)
O2-Mn1-N5A	92.04(8)	O1-Mn1-N5A	89.83(9)
N1-Mn1-N5A	86.81(9)	N2-Mn1-N5A	92.92(8)
O2-Mn1-N3	91.07(9)	O1-Mn1-N3	89.57(9)
N1-Mn1-N3	90.13(9)	N2-Mn1-N3	87.35(8)
N5A-Mn1-N3	176.86(9)		

Table 3 Catalytic epoxidation results

Time (hour)	Oxidant	Conversion (%)	Epoxide yield (%)	Selectivity (%)
2	PhIO	82	75	85
3	NaOCl	73	60	81

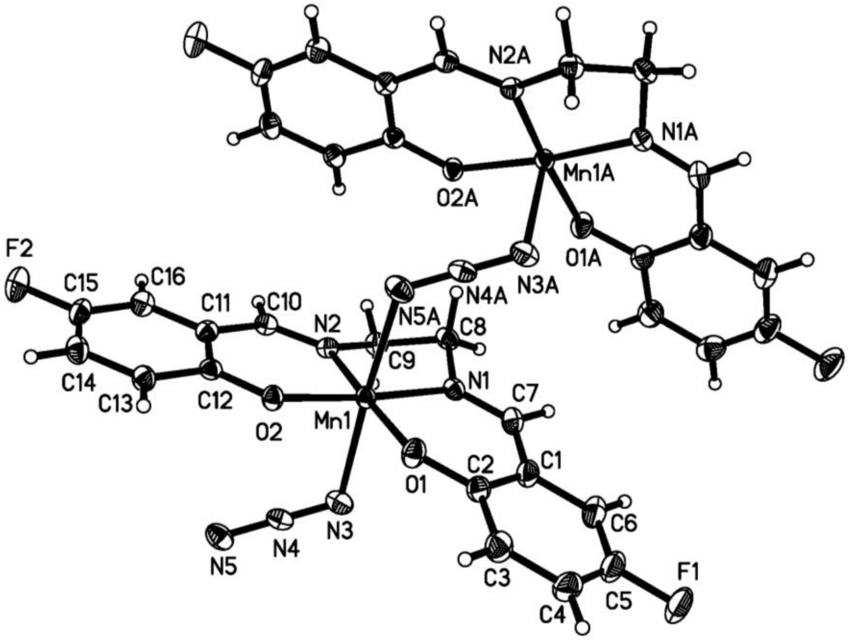


Figure 1. ORTEP diagram of the complex (30% thermal ellipsoid).

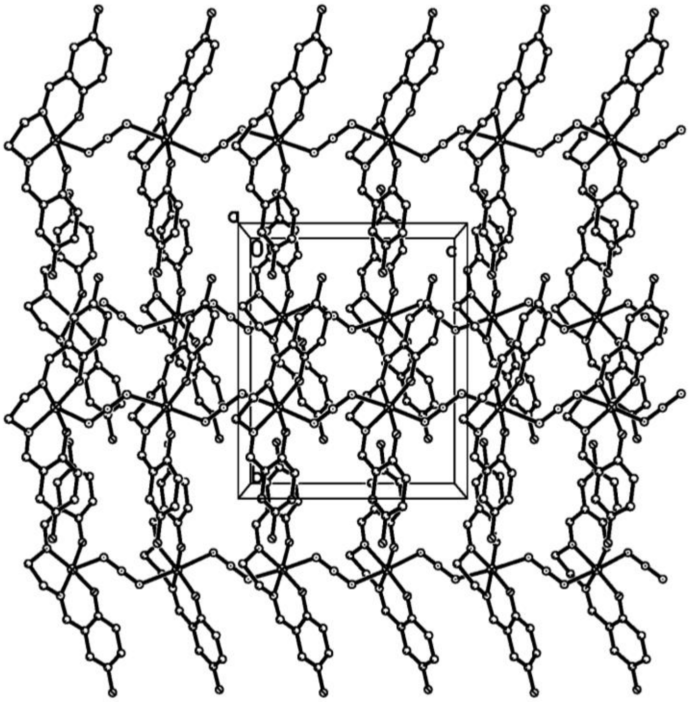


Figure 2. Molecular packing structure of the complex linked by azido bridges.

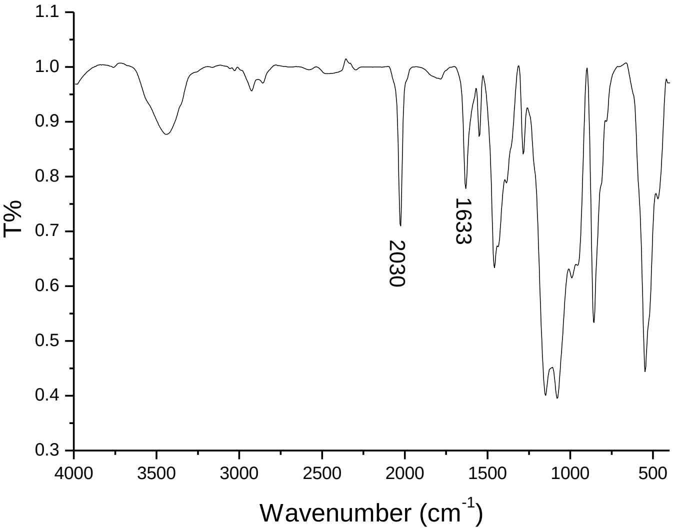


Figure 3. IR spectrum of the complex.

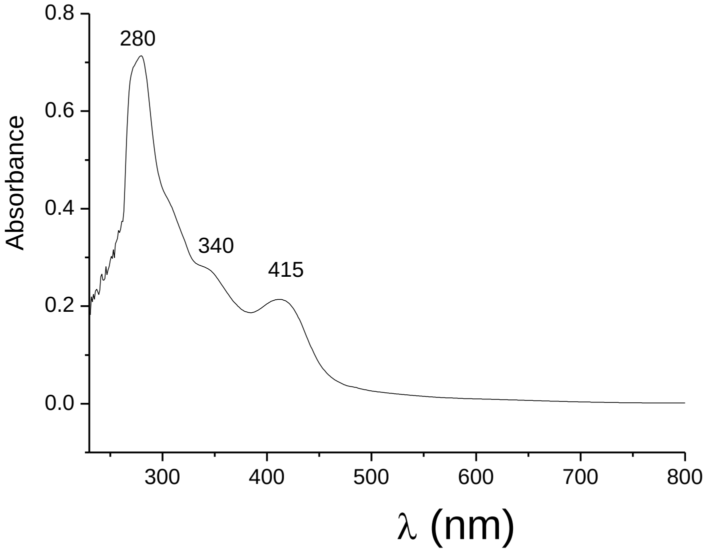
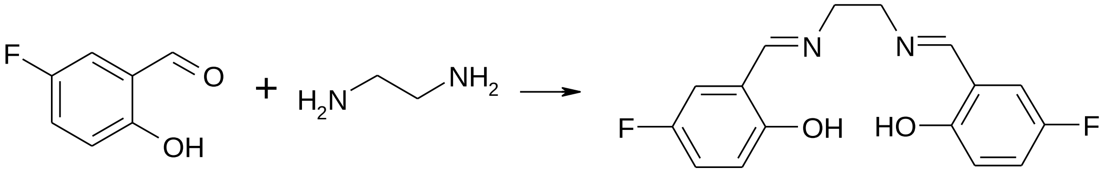
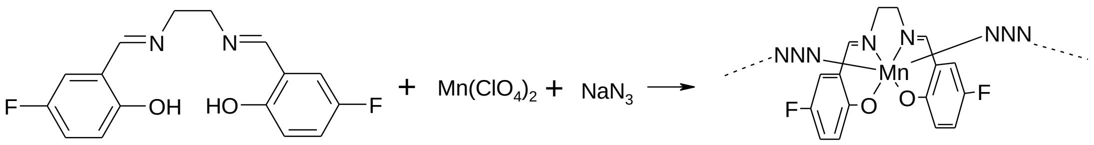


Figure 4. UV-Vis spectrum of the complex.



Scheme 1. The preparation of the Schiff base.



Scheme 2. The preparation of the complex.