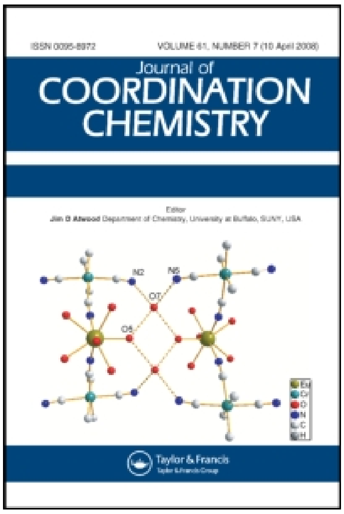

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SYNTHESIS AND CRYSTAL STRUCTURE OF A MANGANESE(III) COMPLEX WITH THE TETRADENTATE SCHIFF BASE *N,N'*-ETHYLENE*BIS*(SALICYLIDENEIMINATO)

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SYNTHESIS AND CRYSTAL STRUCTURE OF A MANGANESE(III) COMPLEX WITH THE TETRADENTATE SCHIFF BASE *N,N′*-ETHYLENE*BIS*(SALICYLIDENEIMINATO)

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The complex [Mn(salen)NCS] (H_2salen = *N,N′*-ethylene*bis*(salicylideneiminato)) has been synthesized by the reaction of [Mn(salen)]$ClO_4 \cdot 2H_2O$ with KSCN. It crystallizes in space group *Pbca*, $a = 12.453(1)$, $b = 13.756(2)$, $c = 18.777(1)$Å, $V = 3216.6(16)$Å^3, $Z = 8$. X-ray structure analysis revealed a dimeric structure, in which two Mn (III) ions are bridged by two phenoxo oxygen atoms, O(2) and O(2A), of the salen ligand in an out-of-plane fashion with an Mn-O(2A) distance of 2.742(2)Å. Each manganese atom has distorted octahedral coordination geometry. The thiocyanate ion coordinates to Mn(III) with the N-atom with Mn-N(3) equal to 2.160(2)Å.

Keywords: tetradentate Schiff base ligand; Mn(III); crystal structure; *N,N′*-ethylene *bis*(salicylideneiminato)

INTRODUCTION

Manganese polynuclear complexes have aroused considerable interest in recent years, since they can mimic the biologically active centres of manganese-containing enzymes and may serve as precursors of molecular-based magnets.[1] Although a large number of Mn(III) complexes of a tetradentate Schiff base has been synthesized[2–6], few of them have defined molecular geometry.[7–15] In this work, [Mn(salen)NCS] has been prepared by a method different from Kennedy[11] and its X-ray crystal structure investigated.

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EXPERIMENTAL

Chemicals

All chemicals were obtained from commercial sources and used without further purification. $Mn(CH_3COO)_3 \cdot 2H_2O$ were prepared according to a literature method.[16] **CAUTION**: Although no problems were encountered during the preparation of the perchlorate salts described below, suitable care and precautions should be taken when handling such potentially hazardous compounds.

Preparation of Complexes

[Mn(salen)]ClO₄ · 2H₂O

A methanol solution (10 cm^3) of manganese(III) acetate dihydrate (1 mmol) was added to a methanol suspension (10 cm^3) of H_2salen (1 mmol). The mixture was stirred at room temperature for six hours and filtered. To the filtrate was added a methanol solution (6 cm^3) of sodium perchlorate (3 mmol). The solution was left to stand for several days and the black precipitates collected. These were recrystallized from a methanol/water (3:1) mixture. *Anal.* Calcd. for $C_{16}H_{18}ClMnN_2O_8$(%): C, 42.07; H, 3.97; N, 6.13 Found: C, 41.73; H, 4.42; N, 6.71.

[Mn(salen)NCS]

A methanol solution (10 cm^3) of KSCN (1 mmol) was added to methanol solution (20 cm^3) of $[Mn(salen)]ClO_4 \cdot 2H_2O$ (1 mmol). The mixture was allowed to stand for several days to give black prisms of the title complex. *Anal.* Calcd. for $C_{17}H_{14}MnN_3O_2S$(%): C, 53.71; H, 3.89; N, 11.84. Found: C, 53.84; H, 3.72; N, 11.08.

Physical Measurements

Elemental analyses were performed at the Analysis and Measurement Centre of Nanjing University. IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Nicolet 170 SX FTIR spectrophotometer.

X-ray Structure Determination

A single crystal of approximate dimensions $0.25 \times 0.40 \times 0.40$ mm^3 was used for data collection and cell parameter determination on a MSC/ Rigaku RAXIS IIC imaging plate system diffractometer, with a rotating anode graphite-monochromatized Mo-Kα X-ray source (λ = 0.71073Å)[17] at room temperature (21°C). Intensity data were collected in a scan mode which takes oscillation IP photos, 36 frames in total (Φ = 0–180°, $\Delta\Phi$ = 0.5°) with 10 min per frame scan rate. The collection range was $-15 \leq h 15$, $0 \leq k \leq 17$, $-23 \leq l \leq 23$. The intensity of one standard reflection was essentially constant throughout the experiment. Of the 3400 indenpendent data measured, 2625 had $F_0 \geq 10\sigma(|F_0|)$ and these were employed in the refinement procedure, which included 218 parameters. Data were corrected for absorption using the DIFABS program.[18]

The structure was solved using the heavy atom method and full- matrix least-squares methods with the SHELXS 86 system.[19] In the final cycles of refinment, all non-H atoms were treated anisotropically; H-atom positions were generated geometrically (C–H = 0.96 Å). Anomalous dispersion corrections were incorporated.[20] The refinement converged to final R = 0.031, R_w = 0.040 and S = 2.17 [$S = (\Sigma w(|F_0|-|F_c|)^2/(n-p))^{1/2}$, where n = number of obervations, p = number of refined parameters]. In the final refinment cycle, the maximum and minimum electron densities in the difference map were +0.24 and –0.29e Å^{-3}, respectively. All calculations were performed on a PC 486 computer with the SHELXTL PLUS system package.[21] Data collection and refinement parameters are summarized in Table I, atomic coordinates for non-hydrogen atoms are given in Table II and selected bond lengths and angles for the title complex are listed in Table III.

TABLE I Crystallographic and refinement data

Crystal data		
Formula	$C_{17}H_{14}N_2O_2SMn$	
Formula weight	379.3	
Crystal size	0.25 × 0.40 × 0.40 mm^3	
Crystal system	orthorhombic	
Space group	Pbca (No. 61)	
Unit cell parameters	a = 12.453(1)Å	V = 3216.6(16)Å
	b = 13.756(2)Å	Z = 8
	c = 18.777(1)Å	
D_{calc}(g cm^{-1})	1.567	
Radiation	graphite-monochromatized Mo-Kα, λ = 0.71073Å	
μ (mm^{-1})	0.164	
Data collection		
Scan mode and rate	take oscillation IP photos; 36 frames in total, ϕ = 0–180°, $\Delta\phi$ = 0.5°, 10 min frame	
Collection range	$-15 \leq h \leq 15$, $0 \leq k \leq 17$, $-23 \leq l \leq 23$	
Total reflection collected	11201	
Unique data measured	3400 (R_{int} = 4.19%)	
F(000)	1552	
Structure determination and refinement		
Obs. data with $|F_o| \geq 10\sigma|F_o|$)	2625	
No. of variables	218	

TABLE I *(Continued)*

Weighting scheme	$w = [\sigma^2 \lvert F_o \rvert + 0.0001 \lvert F_o \rvert^2]^{-1}$
$R = [\Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$	0.031
$R_w = [\Sigma w^2 (\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert]^{1/2}$	0.040
$S = [\Sigma w (\lvert F_o \rvert - \lvert F_c \rvert)^2 / (n-p)]^{1/2}$	2.17
Residual extreme in final difference map	+0.24 to –0.29 eÅ^{-3}

TABLE II Atomic coordinates (× 10^5 for Mn, S; × 10^4 for others) and equivalent isotropic temperature factors* (Å^2 × 10^4 for Mn, S; × 10^3 for others) for [Mn(salen)NCS]

Atom	*x/a*	*y/b*	*z/c*	*ueq*
Mn(1)	13902(3)	99301(2)	2115(2)	309(1)
N(3)	2797(2)	10638(2)	640(1)	47(1)
C(17)	3574(2)	10755(2)	973(1)	37(1)
S(1)	46587(6)	109625(5)	14260(4)	523(2)
C(1)	2757(2)	7369(2)	–1195(1)	44(1)
C(2)	2900(2)	7477(2)	–1914(1)	51(1)
C(3)	2682(2)	8367(2)	–2230(1)	48(1)
C(4)	2332(2)	9150(2)	1831(1)	42(1)
C(5)	2176(2)	9057(2)	–1095(1)	34(1)
C(6)	2397(2)	8152(2)	–769(1)	35(1)
C(7)	2262(2)	7984(2)	–25	36(1)
N(1)	1919(1)	8615(1)	432(1)	32(1)
C(8)	1875(2)	8392(2)	1200(1)	42(1)
C(9)	863(2)	8855(2)	1496(1)	42(1)
N(2)	794(2)	8943(1)	1195(1)	33(1)
O(1)	1791(1)	9817(1)	–741(1)	38(1)
O(2)	507(1)	11023(1)	37(1)	38(1)
C(10)	422(2)	10570(2)	1547(1)	35(1)
C(11)	82(2)	12312(2)	1727(1)	40(1)
C(12)	–41(2)	13245(2)	1479(1)	47(1)
C(13)	18(2)	13432(2)	750(1)	43(1)
C(14)	209(2)	12677(2)	277(1)	35(1)
C(15)	361(2)	11731(2)	520(1)	31(1)
C(16)	309(2)	11538(2)	1260(1)	32(1)

* U_{eq} defined as one third of the trace of the orthogonalized U tensor.

TABLE III Selected bond distances (Å) and bond angles (°)

Mn(1)—N(3)	2.160(2)	C(5)—O(1)	1.329(3)
Mn(1)—N(2)	1.993(2)	C(7)—N(1)	1.294(3)
Mn(1)—O(2)	1.892(2)	C(8)—C(9)	1.517(4)
Mn(1)—N(1)	1.969(2)	N(2)—C(10)	1.285(3)
Mn(1)—O(1)	1.863(2)	N(1)—C(8)	1.475(3)
Mn(1)—O(2A)	2.742(2)	C(9)—N(2)	1.475(3)
C(17)—S(1)	1.622(2)	O(2)—C(15)	1.342(3)
N(3)—Mn(1)N(1)	93.7(1)	N(3)—Mn(1)—O(1)	100.2(1)
N(1)—Mn(1)—N(2)	82.8(1)	N(2)—Mn(1)—O(1)	169.6(1)
N(1)—Mn(1)—O(1)	92.0(1)	N(1)—Mn(1)—O(2)	164.0(1)
N(3)—Mn(1)—O(2)	100.3(1)	O(1)—Mn(1)—O(2)	93.2(1)
N(2)—Mn(1)—O(2)	89.5(1)	N(2)—Mn(1)—O(2A)	79.0(1)
N(1)—Mn(1)—O(2A)	83.4(1)	O(2)—Mn(1)—(2A)	81.4(1)

TABLE III (*Continued*)

O(1)—Mn(1)—O(2A)	91.6(1)	N(3)—C(17)—S(1)	177.7(2)
Mn(1)—N(3)—C(17)	159.6(2)	Mn(1)—N(1)—C(7)	126.0(2)
Mn(1)—N(1)—C(8)	112.6(1)	C(7)—N(1)—C(8)	121.4(2)
N(1)—C(8)—C(9)	107.5(2)	C(8)—C(9)—N(2)	107.1(2)
Mn(1)—N(2)—C(9)	112.9(1)	Mn(1)—N(2)—C(10)	124.3(2)
C(9)—N(2)—C(10)	122.8(2)	Mn(1)—O(1)—C(5)	130.1(1)
Mn(1)—O(2)—C(15)	122.5(1)		

RESULTS AND DISCUSSION

Synthesis

In this paper, we used $Mn(CH_3COO)_3 \cdot 2H_2O$ as starting material and treated it with H_2salen in a 1:1 ratio in methanol. After adding $NaClO_4$, black prisms of $Mn(salen)ClO_4 \cdot 2H_2O$ formed. Interestingly, Garcia-Deibe *et al.*[15] also obtained same complex by visible light irradiation of a Manganese(III) complex of an unsymmetrical tetradentate Schiff base ligand, and showed it to be a dimer structure by X-ray analysis. Previously, Kennedy prepared Mn(salen)NCS by the method in which equimolar amounts of $Mn(acac)_2$ NCS and H_2salen were refluxed in 20 cm^3 of a 1:3 DMF/ethanol solution for 30 mins.[11] We obtained the same complex easily by reaction of $[Mn(salen)]ClO_4 \cdot 2H_2O$ with KSCN at room temperature and formed single crystals suitable for X-ray analysis. To our knowledge, no crystal structure of an Mn(III) complex containing a tetradentate Schiff base and NCS has been reported so far.

Description of the Structure

The crystal structure consists of binuclear [Mn(salen)NCS] units containing a crystallographic centre of symmetry. The molecular structure with the atom numbering scheme is shown in Figure 1. As seen in Figure 2, two crystallographically unique units related by a centre of inversion form a binuclear structure in which two manganese(III) ions are bridged by two phenoxo oxygen atoms O(2) and O(2A) of the salen ligand in an out-of-plane fashion. The manganese(III) ion has distorted octahedral geometry, in which the equatorial coordination plane is composed of the N_2O_2 donor atoms of the tetradentate ligand. Two axial positions are occupied by an NCS^- anion and a phenoxo oxygen atom of a neighboring tetradentate ligand. In the equatorial coordination plane, the bond distances Mn—O(1) (1.863(2)Å), Mn—O(2) (1.892(2)Å), Mn—N(1) (1.969(2)Å) and Mn—N(2) (1.993(2)Å) are consistent with those in $[Mn(salen)(H_2O)]_2(ClO_4)_2\ H_2O$[15], which has a similar dimeric structure.

Values are close to those in Mn(salen)(CH_3COO)[8] and [Mn(salen)(TCNQ)$_{0.5}$] [Mn(salen)(TCNQ)$_{0.5}$(CH_3OH)] .[14] Thiocyanate is coordinated to Mn(III) via the N(3) atom. Mn—N(3) (2.160(2)Å) is longer than Mn-N in the equatorial plane. The other axial bond distance Mn—O(2A) (2.742(2)Å) is longer. This effect should be due to the Jahn-Teller effect in the high-spin d^4 system. The Mn(1)—N(3)—C(17) and N(3)—C(17)—S(1) angles are 159.6(2) and 177.7(2)°, respectively, showing that the four atoms Mn(1), N(3), C(17) and S(1) are not colinear.

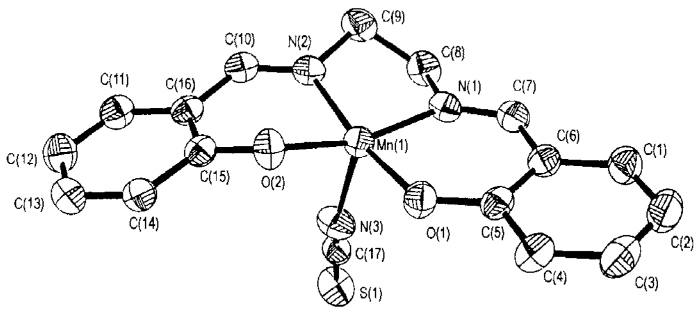

FIGURE 1 The molecular structure of the crystallographic unique unit.

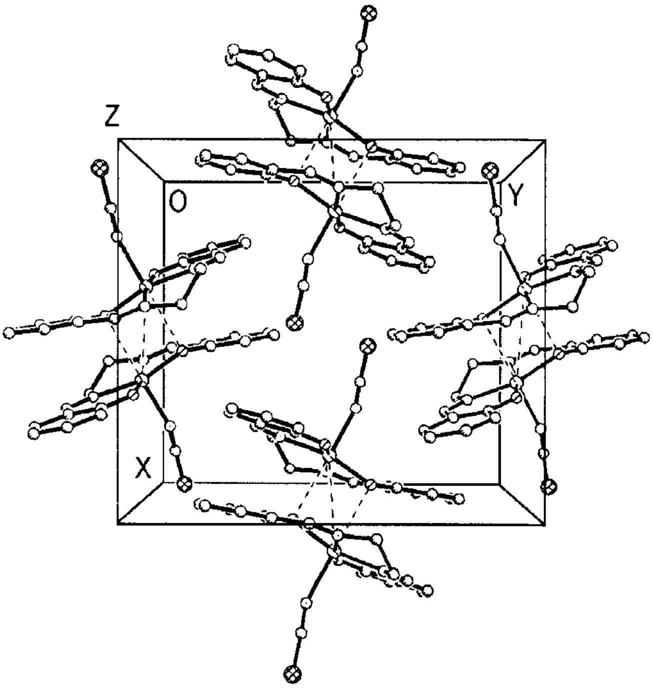

FIGURE 2 Packing diagram viewed down the *c* axis.

Infrared spectra of the complex display a strong absorption in 2045 cm^{-1}. This is characteristic of the C=N stretch for an *N*-coordinated thiocyanate ion. It is consistent with the X-ray analysis. IR spectra also show a strong absorption band around 1623 cm^{-1} which is assigned to a C=N stretching mode in the Schiff base. By comparison with the free H_2salen ligand (1635 cm^{-1}), this absorbtion band is slightly red-shifted.

SUPPLEMENTARY DATA

Additional material consisting of H-atom coordinates, thermal parameters, observed and calculated structure factors and a complete list of bond distances and angles are available from the authors on request.

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