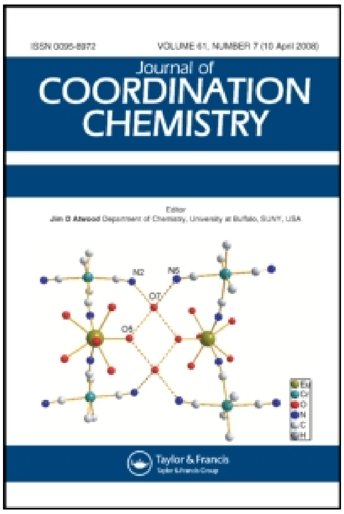

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A MANGANESE(III) COMPLEX WITH SALICYLATE AND IMIDAZOLE LIGANDS

Xiang Shi Tan[a]; Dao Feng Xiang[a]; Wen Xia Tang[a]; Guang Wei Wang[b]; Peiju Zheng[b]
[a] State Key Laboratory for Coordination Chemistry. Coordination Chemistry Institute. Nanjing University, Nanjing, P. R. China [b] Research Centre for Analysis and Measurement Fudan University., Shanghai, P. R. China

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A MANGANESE(III) COMPLEX WITH SALICYLATE AND IMIDAZOLE LIGANDS

XIANG SHI TAN[a], DAO FENG XIANG[a], WEN XIA TANG[a*],
GUANG WEI WANG[b] and PEIJU ZHENG[b]

[a]*State Key Laboratory for Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P. R. China;* [b]*Research Centre for Analysis and Measurement, Fudan University, Shanghai 200433, P. R. China*

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A new manganese(III) complex $[HimH][Mn(sal)_2(imH)_2]\cdot CH_3OH$ (sal = salicylate, $C_7H_4O_3^{2-}$; imH = imidazole, $C_3H_4N_2$; $[HimH]^+$ = imidazole cation ($C_3H_5N_2$) has been prepared and characterized by X-ray analysis and magnetic measurements. The compound crystallizes in the monoclinic space group $P2_1$ with $a = 9.931(2)$, $b = 10.237(1)$, $c = 12.926(7)$ Å, $\beta = 102.740°$ and $Z = 2$. The structure has been refined to $R = 0.030$ and $R_w = 0.031$. The Mn(III) ion has elongated octahedral coordination with mutually *trans* imidazoles occupying axial sites. The equatorial plane is defined by four O atoms of two salicylates. Each $[HimH]^+$ cation (imidazolium) is associated with two complex anions through hydrogen bonds as an imidazolium bridge. The variable temperature magnetic susceptibility for the complex in the temperature range 77-300 K has been interpreted in terms of a single-ion zero-field splitting model with a molecular field term correction. The values obtained for D, g, and zJ′ are -6.93 cm^{-1}, 2.00 and -0.90 cm^{-1}.

Keywords: manganese, complexes, crystal structure, magnetism

INTRODUCTION

The chemistry of manganese in various oxidation states is currently receiving much attention owing to its importance in many biological systems, such as superoxide dismutation [1], and peroxide disproportionation [2]. Most important is the realization that manganese plays an essential and specific role in the water-

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[*] Author for correspondence.

TABLE I Crystal Data for the Title Complex.

Formula	$C_{24}H_{25}MnN_6O_7$
Formula weight	564.4
crystal system	monoclinic
Space group	$P2_1$
Temperature (K)	295
a (Å)	9.931(2)
b (Å)	10.237(1)
c(Å)	12.926(7)
β(°)	102.74(3)
V(Å^3)	1281.8(1)
Z	2
F(000)	584
Cryst dimension (mm)	0.15 × 0.13 × 0.40
d_{calc}, d_{obs} (g cm^{-3})	1.46, 1.47
Radiation (MoKα, Å)	0.71073
μ (cm^{-1})	5.46
Scan type	ω-2Θ
Scan range (°)	$0 < 2\Theta \leq 52$
No. of total data	2785
No. of unique data	2669
No. of obs. data [$I > 3\sigma(I)$]	2428
No. of variables	343
R	0.030
R_w	0.031
Max. shift $(\Delta/\sigma)_{max}$ in final cycle	0.04
Largest peaks in final diff. map (e/Å^3)	0.24

$R = \Sigma \,|F_O - F_c|/\Sigma F_O$; $R_w = [\Sigma w(F_O - F_c)^2/\Sigma w F_O^2]^{1/2}$.

oxidizing complex of photosystem II (PSII) [3]. We now report the preparation, crystal structure and magnetic properties of the title manganese(III) complex with imidazole and salicylate ligands whose functions act as convenient models for the side groups of the amino acids histidine, tyrosine, and aspartic and glutamic acid. The structure is also interesting for its novel hydrogen-bonding character.

EXPERIMENTAL

N-n-Bu_4MnO_4 [4] was prepared as described previously. Other reagents and solvents were reagent grade and used as received.

Synthesis of [HimH][Mn(sal)$_2$(imH)$_2$] · CH_3OH

To a stirring solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (5.0 mmol), NaHsal (10.0 mmol) and imidazole (10.0 mmol) in CH_3OH (60 cm^3) a purple solution of N-n-Bu_4MnO_4

TABLE II Fractional atomic coordinates for the title complex.

atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Mn	0.73356(4)	0.481	0.75136(4)	2.567(7)
O(10)	0.8100(2)	0.5738(3)	0.6544(2)	3.64(5)
O(20)	0.8686(2)	0.3426(2)	0.7622(2)	3.11(5)
O(30)	0.6573(2)	0.3847(2)	0.8486(2)	2.98(5)
O(40)	0.5931(2)	0.6141(2)	0.7388(2)	3.21(5)
O(50)	1.2586(5)	0.0554(6)	0.7554(7)	18.0(3)
O(107)	1.0535(3)	0.2378(3)	0.7448(2)	4.30(6)
O(207)	0.4111(3)	0.7194(3)	0.7596(2)	4.32(6)
N(10)	0.8714(3)	0.5901(3)	0.8865(3)	3.75(7)
N(11)	0.9522(4)	0.6682(4)	1.0453(3)	4.69(8)
N(20)	0.5949(3)	0.3667(4)	0.6144(2)	3.89(7)
N(21)	0.5400(6)	0.2571(5)	0.4666(3)	8.8(1)
N(31)	0.5941(4)	0.9240(4)	0.7602(3)	4.78(8)
N(32)	0.6865(4)	1.1125(4)	0.7894(3)	5.17(9)
C(10)	0.8613(4)	0.5881(4)	0.9852(3)	4.24(9)
C(11)	1.0260(5)	0.7249(5)	0.9818(4)	5.4(1)
C(12)	0.9758(4)	0.6768(5)	0.8832(4)	4.7(1)
C(20)	0.4795(5)	0.2933(5)	0.6140(4)	5.2(1)
C(21)	0.4446(5)	0.2252(6)	0.5234(5)	8.2(1)
C(22)	0.6265(6)	0.3423(6)	0.5225(4)	6.4(1)
C(31)	0.7180(5)	0.9135(5)	0.7307(4)	5.8(1)
C(32)	0.7757(5)	1.0362(5)	0.7493(4)	5.9(1)
C(34)	0.5792(5)	1.0428(5)	0.7939(4)	5.6(1)
C(50)	1.1839(8)	−0.0521(7)	0.7307(8)	15.4(3)
C(101)	0.9282(4)	0.5498(4)	0.6252(3)	3.04(7)
C(102)	0.9704(4)	0.6422(4)	0.5589(3)	4.23(9)
C(103)	1.0902(4)	0.6261(5)	0.5241(3)	4.8(1)
C(104)	1.1725(4)	0.5190(5)	0.5542(3)	4.8(1)
C(105)	1.1337(4)	0.4279(4)	0.6186(3)	3.88(8)
C(106)	1.0112(3)	0.4400(3)	0.6557(3)	2.89(7)
C(107)	0.9782(4)	0.3348(4)	0.7242(3)	2.98(7)
C(201)	0.5393(3)	0.4082(4)	0.8803(3)	2.83(7)
C(202)	0.5016(4)	0.3173(4)	0.9503(3)	3.69(8)
C(203)	0.3794(4)	0.3317(5)	0.9829(3)	4.52(9)
C(204)	0.2916(4)	0.4359(4)	0.9481(3)	4.42(9)
C(205)	0.3290(4)	0.5262(4)	0.8815(3)	3.88(8)
C(206)	0.4531(3)	0.5157(3)	0.8473(3)	2.71(7)
C(207)	0.4858(3)	0.6212(3)	0.7785(3)	2.87(7)

(2.5 mmol) in CH_3OH (20 cm^3) was added dropwise. The reacting solution turned black-brown gradually, and was filtered after stirring for 5 h to remove a brown microcrystalline material. The black mother liquor was left undisturbed for one week, when large green-black crystals, suitable for X-ray crystallographic studies, were collected by filtration, washed with MeOH and dried *in vacuo*. Yield: 57% based on available Mn. *Anal.* Calcd. for $C_{24}H_{25}MnN_6O_7$%: C,

TABLE III Selected bond distances (Å) and angles (°) for the title complex.

Distances			
Mn-O(10)	1.860(4)	Mn-O(20)	1.939(4)
Mn-O(30)	1.885(3)	Mn-O(40)	1.927(4)
Mn-N(10)	2.260(6)	Mn-N(20)	2.310(8)
Angles			
O(10)-Mn-O(2)	92.5(2)	O(10)-Mn-O(30)	178.8(3)
O(10)-Mn-O(40)	89.0(2)	O(10)-Mn-N(10)	90.2(2)
O(10)-Mn-N(20)	90.3(4)	O(20)-Mn-O(30)	86.5(2)
O(20)-Mn-O(40)	177.5(2)	O(20)-Mn-N(10)	90.8(2)
O(20)-Mn-N(20)	88.2(3)	O(30)-Mn-O(40)	92.2(2)
O(30)-Mn-N(10)	90.4(2)	O(30)-Mn-N(20)	89.2(4)
O(40)-Mn-N(10)	91.3(2)	O(40)-Mn-N(20)	89.7(3)
N(10)-Mn-N(20)	178.8(3)		

TABLE IV Hydrogen-bonding parameters for the title complex.

A···H-D	A···H, Å	H-D, Å	A···D, Å	<ADH°
O(107)···H(50)-O(50)	1.693(5)	1.110(6)	2.745(6)	156.0(3)
O(207)···H(41)-N(31)	1.821(5)	0.952(4)	2.772(9)	176.7(4)
O(30')···H(33)-N(32)	2.041(5)	0.887(4)	2.921(8)	171.1(4)
O(107')···H(13)-N(11)	1.865(5)	0.969(4)	2.818(8)	167.0(4)
O(207')···H(23)-N(21)	2.116(6)	0.991(5)	3.090(2)	167.3(5)

51.12; H, 4.29; N, 14.91; Mn, 9.75. Found: C, 50.63; H, 4.54; N, 14.67; Mn, 10.06.

X-ray Crystallography

A suitable single crystal was mounted on glass fibre and aligned on an Enraf-Nonius CAD-4 diffractometer for data collection. Cell parameters were determined on the basis of 25 reflections with $11 < \Theta < 14°$. Intensity data were obtained with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and ω-2Θ scan mode in the range $0 < 2\Theta \leq 52°$ at room temperature. During data collection, the intensity of three standard reflections monitored at every 3600s of X-ray exposure time showed no significant decay. After taking into account Lorentz and polarization effects, an empirical absorption correction based on a series of PSI scans was applied to the data. Relative transmission coefficients ranged from 0.920 to 1.000. The structure solution by direct methods (MULTAN-86) revealed the metal atom coordinates and subsequently difference

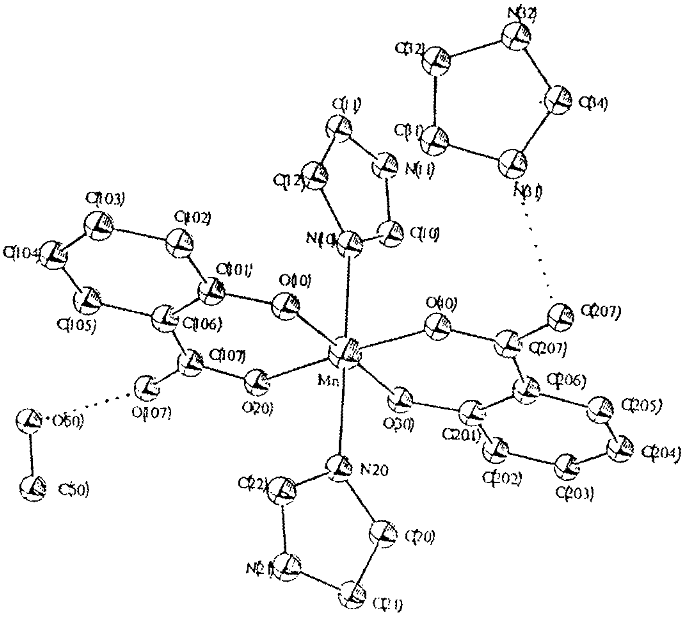

FIGURE 1 ORTEP plot and labelling scheme for the title complex. Hydrogen atoms are omitted for clarity, and the broken lines represent hydrogen bonds.

Fourier methods yielded positions of all remaining non-H atoms and most hydrogen atoms. All non-H atoms were refined anisotropically by unit-weighted full-matrix least-squares methods, while the hydrogen atoms, located in a difference Fourier map, were allowed to ride on related carbon atoms with fixed isotropic thermal parameters. Refinement converged at $R = 0.030$ and $R_w = 0.031$ for 2428 observed reflections from 2669 unique ones. A final difference Fourier map exhibited no significant peaks greater than 0.24(4) e/Å^3. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations were performed on a MICRO VAX II computer using SDP/VAX and ORTEP programs.

Physical Measurements

Magnetic measurements on powder samples were carried out using a CAHN-2000 Faraday magnetometer in the 77-300 K temperature range. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were made using Pascal's constants.

RESULTS AND DISCUSSION

Description of the Crystal Structure

Parameters for data collection and refinement are given in Table I. Fractional atomic coordinates and thermal parameters for the non-hydrogen atoms are listed in Table II. Selected bond distances and angles are listed in Table III. Important hydrogen-bonding parameters are listed in Table IV. The structure of the title complex is shown in Figure 1. It consists of imidazolium cations, mononuclear manganese(III) complex anions, $[Mn(sal)_2(imH)_2]^-$, and solvent, CH_3OH, molecules. The Mn(III) ion has elongated octahedral coordination with mutually *trans* imidazoles occupying axial sites. The equatorial plane is defined by four O atoms of two salicylates. The phenoxide atoms (O10 and O30) and the carboxylate oxygen atoms (O20 and O40) are *trans* about the Mn(III) ion. The angles at the Mn subtended by *cis* and *trans* ligand atoms are reasonably close to the theoretical values for an octahedron, being at the range 86.5(2)-92.5(2)° and 177.5(2)-178.8(3)°, respectively. The Mn-phenoxide (Op) and -carboxylate

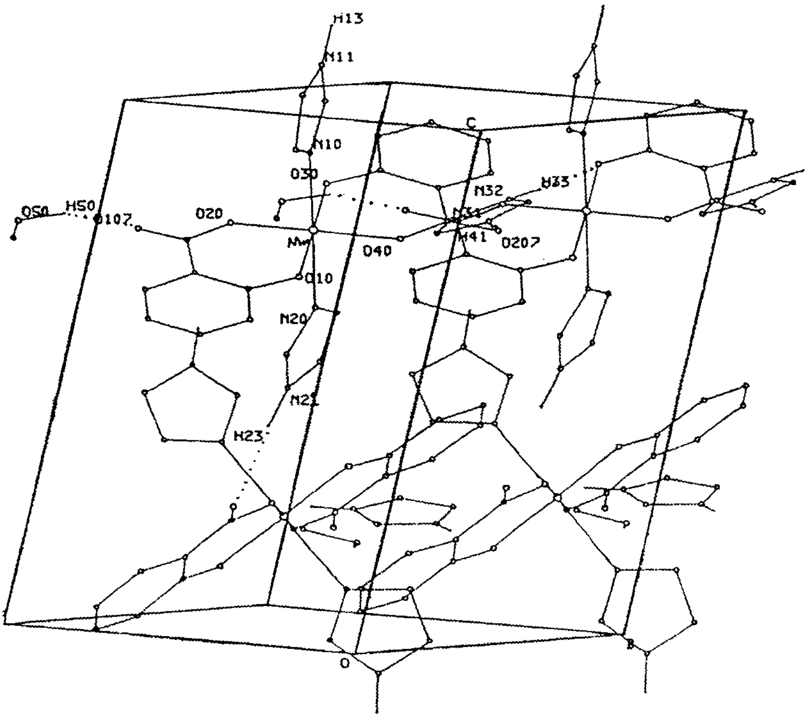

FIGURE 2 Packing diagram for the title complex showing the net-like structure with hydrogen-bonding bridges.

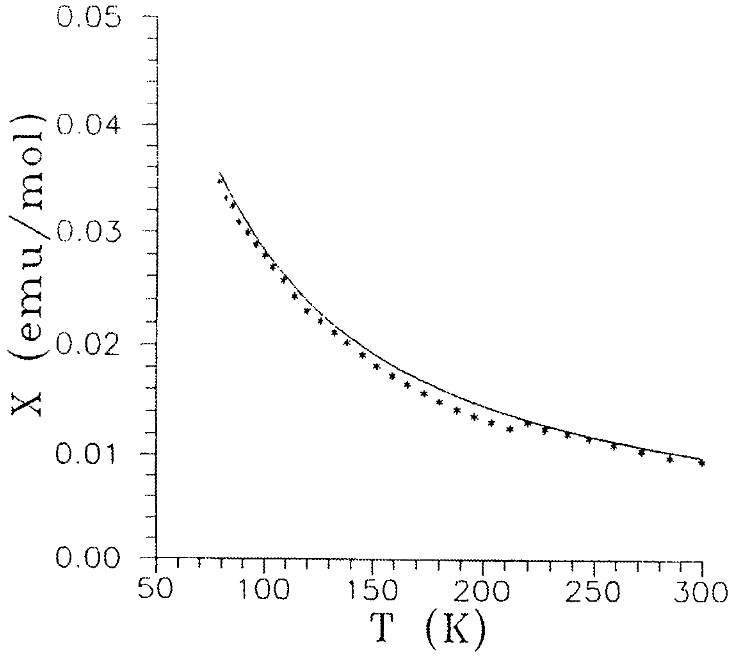

FIGURE 3 Temperature dependence of molecular susceptibility for the title complex.

oxygen (Oc) bond lengths (Mn-Op = 1.860(4), 1.885(3)Å; Mn-Oc = 1.939(4), 1.927(4)Å) are close to those in [Mn(sal)(bpy)$(H_2O)_2$]ClO_4·H_2O [5] and [$Mn_4$$(sal)_4$$(H_2O)_4$$(py)_8$]$_n$[salH]$_{2n}$·4n py [6]. The axial Mn-N bond lengths (Mn-N10 = 2.260(6)Å, Mn-N20 = 2.310(8)Å) are distinctly longer than those in the equatorial plane of [Mn(sal)(bpy)$(H_2O)_2$]ClO_4·H_2O (Mn-N = 2.041(4)Å), and similar to those in [$Mn_4$$(sal)_4$$(H_2O)_4$$(py)_8$]$_n$[salH]$_{2n}$·4n py ($Mn^{III}$-N distances are 2.319(5) and 2.345(7) Å, respectively). Such marked axial elongation is typical for the high spin d^4 system.

The MnO_4 fragment is perfectly planar with a maximum deviation of (0.022 Å for Mn) from the mean plane, and the planarity of salicylate and imH is also exceedingly good. Dihedral angles between the equatorial plane and the two imidazole planes N10-C10-N11-C11-C12 and N20-C20-C21-N21-C22 are 87.31 and 80.77°, respectively, while the dihedral angle for the two axial imH planes is 15.77°. The solvent CH_3OH molecule is associated with the uncoordinated carboxylate oxygen (O107) of salicylate by a hydrogen bond (O50-H50···O107). The imidazolium cations are cross-linked to two complex anions by N31-H31...O207 and N32-H33...O30′ hydrogen bonds. In addition, each mononuclear Mn(III) complex unit is associated with four neighbouring units by O···H-N hydrogen bonds, as shown in Figure 2, involving two axial imH groups linked to its two neighbors above and below by N11-H13···O107′ and N21-H23···O207′ and two uncoordinated carboxylate oxygens of salicylates joined by O107···H13′-N11′ and O207···H23′-N21′. The hydrogen-bonding parameters are listed in Table IV. Thus the compound is a supramolecular complex with hydrogen-bonding bridges; the minimal Mn···Mn separation is 8.755(1) Å.

Magnetic Properties

The temperature dependence of the molecular magnetic susceptibility in the form of χ_M *versus* T is shown in Figure 3. The magnetic moment of $[HimH][Mn(sal)_2(imH)_2]\cdot CH_3OH$ at 285 K is 4.80 B.M., which is close to the spin-only value of 4.89 B.M. expected for one uncoupled high-spin Mn(III) ion ($S = 2$). When the temperature is lowered, the magnetic moment of the title complex decreases slightly and reaches a value of 4.67 B.M. at 78 K. The magnetic behaviour may be due to zero-field splitting of the ground state and intermolecular magnetic interactions. The crystal structure of the title complex shows the Mn(III) centre to exist in a distorted octahedral arrangement as a result of the Jahn-Teller effect. Due to the axial distortion and spin-orbit coupling, the $S = 2$ state is split into three zero-field levels, Ms = 0, ±1, and ±2, the separation between Ms = 0 and ±1 and between Ms = 0 and ±2 being D and 4D, respectively. By use of spin-Hamiltonian formalism of the form (*1*) [7], in which any rhombic splitting was ignored and D is the ZFS parameter,Equation (1) the following equation for the principal magnetic susceptibility can be derived. [7, 8]Equation (1)Equation (1)Equation (1) To describe intermolecular interactions, a molecular field term [9] was added, and the expression for the magnetic susceptibility becomes that given in (*2*).

Using (*2*), the data were analyzed at 77-300 K, and the best fit parameters obtained are $g = 2.00$, $D = -6.93\ \mathrm{cm}^{-1}$, $zJ' = -0.90\ \mathrm{cm}^{-1}$, and $R = 5.64 \times 10^{-4}$, where $R = \Sigma(X_{cald} - X_{obs})^2/\Sigma(X_{obs})^2$.

$$H = DS_z^2 + g\beta H\cdot S \qquad (1)$$

$$X_{\parallel} = 2Ng^2\beta^2/KT\cdot(e^{-D/KT} + 4e^{-4D/KT})/(1 + 2e^{-D/KT} + 2e^{-4D/KT})$$

$$X_{\perp} = Ng^2\beta^2/3D\cdot(18 - 14e^{-D/KT} - 4e^{-4D/KT})/(1 + 2e^{-D/KT} + 2e^{-4D/KT})$$

$$X_M = (X_{\parallel} + 2X_{\perp})/3$$

$$X_M' = X_M/(1 - 2zJ'X_M/Ng^2\beta^2)$$

The D value found here is slightly larger than those in ref. 10, but similar to previous data in ref. 6. The zJ' value of $-0.83\ \mathrm{cm}^{-1}$ reflects the possibility of weak antiferromagnetic intermolecular exchange interactions through hydrogen bonds and magnetic dipole-dipole interactions.

SUPPLEMENTARY DATA

Full lists of H atom positions thermal parameters and observer and calculated structure factors are available from the author upon request.

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