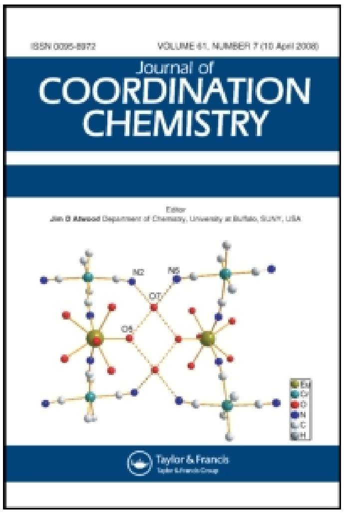

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Synthesis, crystal structure, and properties of a seven-coordinate manganese(II) complex formed with the tripodal tetradentate ligand *tris* (*N* -methylbenzimidazol-2-ylmethyl)amine and salicylate

Hui-Lu Wu[a b]; Fei Jia[a]; Xuan Meng[a]; Qian Chen[a]; Bin Liu[a]; Yu-Lin Lai[a]; Fan Kou[a]
[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, P.R. China [b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Material Science, Northwest University, Xi'an, Shaanxi 710069, P.R. China

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Synthesis, crystal structure, and properties of a seven-coordinate manganese(II) complex formed with the tripodal tetradentate ligand *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine and salicylate

HUI-LU WU*†‡, FEI JIA†, XUAN MENG†, QIAN CHEN†,
BIN LIU†, YU-LIN LAI† and FAN KOU†

†School of Chemical and Biological Engineering,
Lanzhou Jiaotong University, Lanzhou, Gansu 730070, P.R. China
‡Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Material Science, Northwest University, Xi'an, Shaanxi 710069, P.R. China

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A seven-coordinate manganese(II) complex with the tripod tetradentate ligand *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb), [Mn(Mentb)(salicylate)(DMF)](ClO_4) · (DMF), was synthesized and characterized by elemental, electrical conductivity, infrared, and UV-Vis spectral measurements. The crystal structure of the complex has been determined by single-crystal X-ray diffraction. Mn^{II} is bonded to a Mentb, a salicylate and dimethylformamide through four nitrogens and three oxygens, resulting in seven-coordination. Cyclic voltammograms of the complex indicate a quasi-reversible Mn^{3+}/Mn^{2+} couple. The X-band electron paramagnetic resonance spectrum exhibits a six-line manganese hyperfine pattern with $g = 2$, $A = 93$, confirming that the material is high-spin Mn(II).

Keywords: Manganese(II) complex; Crystal structure; Cyclic voltammetry; EPR; *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine

1. Introduction

Manganese plays an important role in many biological systems including photosystem II (water oxidation), catalase (disproportionation of the hydrogen peroxide), and superoxide dismutase (dismutation of the superoxide radical) [1–3]. While preparation and characterization of polynuclear manganese complexes relevant to the active center of photosystem II and catalase have been studied extensively [4, 5], relatively simple mononuclear centers have received very less attention. Therefore, synthesis and characterization of mononuclear manganese centers with biologically relevant donors

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*Corresponding author. Email: wuhuilu@163.com

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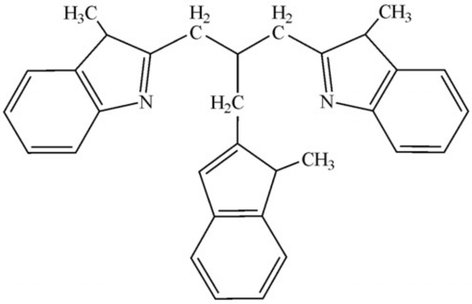

Figure 1. Structure of Mentb.

and their geometry is an important area of investigation. Benzimidazoles have a wide variety of pharmacological applications including fungicides or antihelminthics [6]. Tripodal ligands have also long been used in both coordination and bioinorganic chemistry; typical examples include the tripodal ligands, tripyridylalkylamine, and triazacyclononane [7–9]. The tetradentate tripodal ligand *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb; figure 1) may mimic the histidine imidazole in coordination chemistry [10]. Since the three arms of this type of ligand can each rotate freely around an N(apical)–C bond, multicomponent complexes or coordination polymeric networks may be expected from assembly of this ligand with metal ions of low coordination number [11–13]. In this study, we have prepared and investigated the properties and crystal structure of a seven-coordinate manganese(II) complex with Mentb.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals and solvents were reagent grade and used without purification.

C, H, and N contents were determined using a Carlo Erba 1106 elemental analyzer. Metal contents were determined by ethylenediaminetetraacetic acid (EDTA) titration. Infrared (IR) spectra were recorded in the range 4000–400 $\mathrm{cm^{-1}}$ with a Nicolet FT-IR AVATAR 360 spectrometer using KBr pellets. Electronic spectra were taken on a LabTech UV BlueStar plus spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using $10^{-3}\,\mathrm{mol\,L^{-1}}$ solution in dimethylformamide (DMF) at room temperature. Electrochemical measurements were performed on a LK2005A electrochemical analyzer under nitrogen at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel (SCE) reference electrode were used in the three-electode measurements. The electroactive component was at $1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ concentration with tetrabutylammonium perchlorate (TBAP; $0.1\,\mathrm{mol\,dm^{-3}}$) used as the supporting electrolyte in DMF solution. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker 200D spectrometer with the X-band.

2.2. Tris*(N-methylbenzimidazol-2-ylmethyl)amine and Mn complexes*

2.2.1. *Tris*(N-methylbenzimidazol-2-ylmethyl)amine (Mentb). This compound was synthesized by a literature method [10] (yield: 4.6 g (51%); m.p.: 215–217°C).

2.2.2. [Mn(Mentb)(salicylate)(DMF)](ClO_4) • (DMF). To a stirred solution of Mentb (0.0899 g, 0.2 mmol) in hot methanol (10 mL), $Mn(ClO_4)_2 \cdot 6H_2O$ (0.0724 g, 0.2 mmol) was added, followed by a solution of Na(salicylate) (0.032 g, 0.2 mmol) in methanol (5 mL), whereupon a white microcrystalline precipitate was produced and collected by filtration. After drying in air, the white product was redissolved in DMF/methanol (1 : 1) and filtered. Light yellow block crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of diethyl ether into the filtrate for 4 weeks at room temperature, yield 0.12 g (67%). Calcd for $C_{40}H_{46}MnN_9O_9Cl$ (887.25) (%): C 54.15, H 5.23, N 14.21, and Mn 6.19; Anal. Found (%): C 54.09, H 5.59, N 14.13, and Mn 6.33; Λ_M (DMF, 297 K): 65.7 $s\,cm^2\,mol^{-1}$.

2.3. *X-ray structure determination*

All data were collected using a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) at 296 K. Data reduction and cell refinement were performed using SMART and SAINT programs [14]. Absorption corrections were carried out by the empirical method. The structure was solved by direct methods (Bruker SHELXTL) using all unique data [15]. The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogens were located geometrically and treated with the riding model. The crystal data and experimental parameters relevant to the structure determination are listed in table 1.

3. Results and discussion

The manganese complex is soluble in DMF and dimethyl sulfoxide (DMSO), but insoluble in water and organic solvents, such as methanol, ethanol, benzene, petroleum ether, trichloromethane etc. Elemental analyses show that the composition is [Mn(Mentb)(salicylate)(DMF)](ClO_4) · (DMF). Molar conductances show 1 : 1 electrolyte similar to those previously reported [16].

3.1. *Crystal structure of [Mn(Mentb)(salicylate)(DMF)](ClO_4) • (DMF)*

The molecular structure of the manganese(II) complex is shown in figure 2; selected bond lengths and angles are shown in table 2. The asymmetric unit consists of a $[Mn(Mentb)(salicylate)(DMF)]^+$ cation, a perchlorate anion and one DMF. The tripodal ligand forms a tripodal pyramidal geometry with manganese, and the remaining open axial site is occupied by a chelating bidentate salicylate anion and monodentate DMF. The complex has a seven-coordinate manganese(II) with a N_4O_3 donor set. The bond length between manganese ion and the apical nitrogen N(7)–Mn(1)

Table 1. Crystallographic data and structure refinement for [Mn(Mentb)(salicylate)(DMF)](ClO_4) · (DMF).

Empirical formula	$C_{40}H_{46}MnN_9O_9Cl$
Molecular weight ($g\,mol^{-1}$)	887.25
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.3689(13)
b	12.4809(13)
c	15.3759(16)
α	69.9250(10)
β	87.9260(10)
γ	74.7040(10)
Volume ($Å^3$), Z	2146.6(4), 2
Calculated density ($g\,cm^{-3}$)	1.373
Absorption coefficient (mm^{-1})	0.434
$F(0\,0\,0)$	926
Crystal size (mm^3)	0.38 × 0.36 × 0.32
θ range for data collection (°)	1.71–25.5
Limiting indices	$-13 \le h \le 14$; $-15 \le k \le 15$; $-18 \le l \le 18$
Refinement method	Full-matrix least-squares on F^2
Data/parameters	7890/551
Goodness-of-fit on F^2	1.069
Final R indices $[I \ge 2\sigma(I)]$[a]	$R_1 = 0.0610$, $wR_2 = 0.1868$[a]
R indices (all data)[a]	$R_1 = 0.0758$, $wR_2 = 0.1999$
Largest difference peak and hole ($e\,Å^{-3}$)	1.885 and −0.549

[a] $w = 1/[\sigma^2 F_o^2 + (0.1346\,P)^2 + 0.5398\,P]$, where $P = (F_o^2 + 2\,F_c^2)/3$.

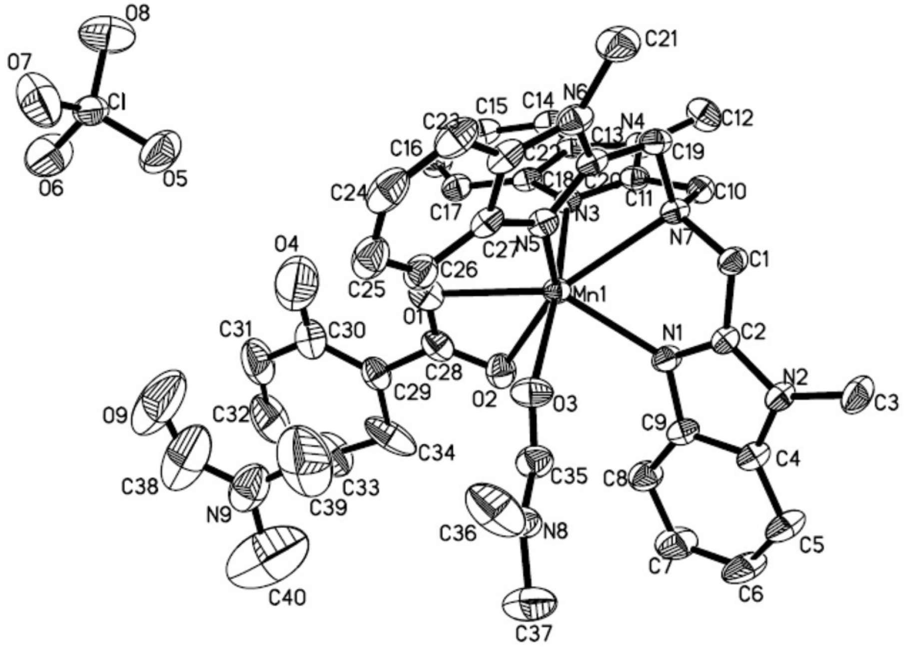

Figure 2. Molecular structure and atom numbering of [Mn(Mentb)(salicylate)(DMF)](ClO_4) · (DMF) (solvate molecules and hydrogens omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (°).

Mn–N(1)	2.308(3)	Mn–O(1)	2.354(3)
Mn–N(3)	2.299(2)	Mn–O(2)	2.285(3)
Mn–N(5)	2.227(2)	Mn–O(3)	2.340(2)
Mn–N(7)	2.503(2)		
N(5)–Mn–O(1)	92.87(9)	N(5)–Mn–O(3)	79.00(9)
N(5)–Mn–N(3)	103.81(9)	O(1)–Mn–O(3)	84.73(9)
O(1)–Mn–N(3)	89.28(9)	N(3)–Mn–O(3)	173.52(9)
N(5)–Mn–N(1)	92.87(9)	N(1)–Mn–O(3)	81.87(10)
O(1)–Mn–N(1)	142.32(9)	O(2)–Mn–O(3)	81.19(9)
N(3)–Mn–N(1)	101.55(9)	N(5)–Mn–N(7)	70.44(9)
N(5)–Mn–O(2)	144.55(9)	O(1)–Mn–N(7)	147.88(9)
O(1)–Mn–O(2)	56.12(9)	N(3)–Mn–N(7)	69.48(8)
N(3)–Mn–O(2)	93.43(9)	N(1)–Mn–N(7)	67.98(9)
N(1)–Mn–O(2)	87.01(9)	O(2)–Mn–N(7)	145.00(9)
O(3)–Mn–N(7)	117.00(9)		

is 2.503(2) Å, which is about 0.225 Å longer than the bond lengths between manganese and the basal nitrogen (2.227–2.308 Å, average = 2.278 Å). Significant elongation has been observed in other manganese complexes of tripodal tetradentate ligands with benzimidazolylmethyl group [17]. The average bond angle (N_A–Mn–N_B) of the axial nitrogens (N_A), the manganese ion, and the basal nitrogens (N_B) is 69.3°, and the manganese is 0.804(9) Å above the trigonal basal plane. A chelating bidentate salicylate and a monodentate DMF are coordinated at the opened site. The oxygen of DMF is coordinated *trans* to basal N(1) (N(3)–Mn(1)–O(3) = 173.52(9)°). The oxygen of the chelating bidentate salicylate is coordinated *trans* to the remaining two basal nitrogens (O(1)–Mn(1)–N(1) = 142.32(9)°, O(2)–Mn(1)–N(5) = 144.55(9)°). All additional ligands are accommodated at the open axial site without significant change in the trigonal pyramidal part of the complex (N(1)–Mn(1)–N(5) = 118.59(9)°). The steric crowding of ligands is avoided because manganese(II) is slightly above the trigonal basal plane. The space-filling model of the complex shows that up to three donors can be accommodated in the open site without significant disturbance of the trigonal pyramidal part of the structure. The high-spin d^5 manganese(II) ion has no crystal field stabilization energy; so it could have various geometries depending on the coordinated ligand [18, 19]. All bond lengths related to the manganese are comparable to values observed in other complexes [20].

Weak supramolecular CH···O, OH···O hydrogen bonding interactions play important roles in the crystal packing in the complex. Selected hydrogen bonds are listed in table 3.

3.2. *IR and UV-Vis spectra*

IR spectra of the manganese complex along with their relative assignments are given in table 4. In free Mentb, a strong band is at 1475 cm^{-1} along with a weak band at 1515 cm^{-1}. By analogy with the assigned bands of imidazole, the former can be attributed to ν(C=N–C=C), while the latter can be attributed to ν(C=N) [21, 22]. These bands were shifted to the lower frequency *ca* 18–28 cm^{-1} in the complexes, which implies direct coordination of the three imine nitrogens to manganese(II). This is the

Table 3. Selected hydrogen bonding distances (Å) and angles (°).

D–H···A	D–H	D···A	H···A	∠D–H···A
O7–H1W···O4	0.84	3.55(2)	2.71	179.9
O7–H2W···O2	0.84	3.05(2)	2.21	179.4
C(36)–H(36A)···O(3)	0.96	2.784(5)	2.38	104.5
C(8)–H(8)···O(2)	0.93	3.259(5)	2.57	131.0
O(4)–H(4)···O(1)	0.82	2.533(6)	1.79	150.2
C(14)–H(14)···O(2)#1	0.93	3.412(4)	2.59	148.4
C(10)–H(10A)···O(9)#2	0.97	3.185(7)	2.27	156.5
C(5)–H(5)···O(6)#3	0.93	3.396(6)	2.52	157.1
C(1)–H(1B)···(7)#4	0.97	3.321(5)	2.53	138.9

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+2$, $-z+1$; #2 x, $y+1$, z; #3 $x+1$, $y+1$, z; #4 $-x+1$, $-y+1$, $-z+2$.

Table 4. IR spectral data for the Mn complex and their relative assignments (cm^{-1}).

Compound	ν_{as}(COO)	ν_s(COO)	$\Delta\nu$	ν(Ar–O)	ν(C=N)	ν(C=N–C=C)	$\nu(ClO_4^-)$
NaL	1523 s	1374 s	149	1247 m	–	–	–
Mentb	–	–	–	–	1515 m	1475 s	–
Mn complex	1583 s	1442 s	141	1254 m	1487 m	1457 s	1089 bs

L, salicylate; b, broad; s, strong, and m, medium.

preferred nitrogen for coordination as found for other metal complexes with benzimidazoles [23]. Information regarding possible bonding modes of perchlorate may also be obtained from IR spectra. The strong, fairly broad absorptions at 1089 and 625 cm^{-1} indicate that ionic perchlorates (T_d) are present [24]. Since the carboxylate group can coordinate to the metal bidentate or monodentate, the "Δ criterion," which is based on the difference between the ν_{as}(O–C–O) and ν_s(O–C–O) values, compared to the corresponding value in sodium carboxylate, is employed to determine the coordination [25–27]. The data in table 4 suggest that salicylate in the complex is bidentate, confirmed by the crystal structure analysis. Medium bands near 1254 cm^{-1} probably correspond to ν(O–Ar).

DMSO solutions of Mentb and its manganese(II) complex show, as expected, almost identical UV spectra. The UV bands of Mentb (290 nm) are only marginally blue-shifted (7 nm) in the complex, which is a clear evidence of C=N coordination to manganese(II). The absorption band is assigned to $\pi \rightarrow \pi^*$ (imidazole) transitions.

3.3. *Cyclic voltammogram and EPR spectrum*

Electrochemical properties of the manganese complex have been studied by cyclic voltammetry (CV) in DMF. The voltammogram shows only a single reduction peak (E_{pc}) at 0.232 V during the cathodic potential scan. During the return anodic potential scan, just after the reduction peak, an anodic peak (E_{pa}) is observed at 0.378 V. The separation between the cathodic and anodic peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) of 146 mV indicates a quasi-reversible redox process assignable to Mn(III)–Mn(II) couple and $E_{1/2}$ [$(E_{pa} + E_{pc})/2$] is equal to 0.305 V. The free Mentb ligand was not electroactive over the range -1.2 to $+1.2$ V. According to previous reports [28, 29], to be an effective mimic of superoxide dismutase, a transition metal complex must have a reduction potential below 0.65 V $[E^\circ(^1O_2 - O_2^-)]$ and above -0.33 V $[E^\circ(O_2 - O_2^-)]$ such that catalysis can take place without toxic singlet oxygen being formed. Thus, the redox potential 0.305 V of the complex shows that it has SOD activity.

The X-band EPR spectrum of a single crystal was measured at 285 K. The spectrum exhibits the typical six-line hyperfine signal centered at $g = 2$, which is associated with the $I = 5/2$ nuclear spin of ^{55}Mn. The experimental hyperfine coupling constant $A = 93$ G is of the same order as that found for other mononuclear Mn(II) complexes [30, 31]. This spectrum confirms that the material is high spin Mn(II). The signal features are assignable to allowed transitions ($\Delta m_s = \pm 1$, $\Delta m_l = \pm 0$).

4. Conclusions

We have synthesized a seven-coordinate manganese(II) complex with the tripod tetradentate ligand Mentb. The complex has been characterized by element analysis, IR, UV spectra, and single-crystal X-ray diffraction. Cyclic voltammograms of the complex indicate a quasi-reversible Mn^{3+}/Mn^{2+} couple. The X-band EPR spectrum confirms that the material is high-spin Mn(II).

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 776040. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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