A Manganese(II) 4-Hydroxycinnamate Complex with the Tripod Ligand Tris(2-benzimidazolylmethyl)amine

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A six-coordinate manganese (II) complex with the tripod ligand tris(2-benzimidazolylmethyl)amine (ntb), with composition [Mn(ntb) (4-hydroxycinnamate)](4-hydroxycinnamate) · $(DMF)_{0.5} \cdot (H_2O)_3$, was synthesized and characterized by elemental and thermal analyses, electrical conductivity, IR, and UV/vis spectral measurements. The crystal structure of the complex has been determined by the single-crystal X-ray diffraction. The Mn (II) cation is bonded to an ntb ligand and a 4-hydroxycinnamate ligand through four N atoms and two O atoms, giving a distorted octahedral coordination geometry. Cyclic voltammograms of the complex indicate a quasi-reversible Mn^{3+}/Mn^{2+} couple. The X-band EPR spectrum of the complex exhibits a six-line manganese hyperfine splitting pattern with $g = 2$, $A = 95$, and confirms that the material is high-spin Mn(II).

Key words: Crystal Structure, Cylic Voltammetry, EPR, Manganese(II) Complex, Tris(2-benzimidazylmethyl)amine

Introduction

Model systems that mimic the active sites of metalloenzymes are important not only for the understanding of enzyme mechanisms, but also for the development of small molecular weight biomimetic catalysts. The imidazole part of histine plays an important role in the coordination of transition metals at the active sites of numerous proteins. For example, superoxide dismutases (SOD) [1 – 2], which are contained in microbes, plants and animals, protects cells against oxygen toxicity [3 – 4], because these enzymes catalyze the conversion of superoxide (O_2^-) to hydrogen peroxide and dioxygen *via* redox-active metals. The tetradentate tripodal ligand tris(2-benzimidazolylmethyl)amine (ntb) (Fig. 1) may mimic the histidine imidazole in coordination aspects. Reports on the synthesis and spectroscopic characterization of manganese(II) complexes with ntb have appeared in the literature [5 – 9]. Herein we report the synthesis, crystal structure and properties of a novel manganese(II) complex with the tripodal tris(2-benzimidazolylmethyl)amine and 4-hydroxycinnamate ligands.

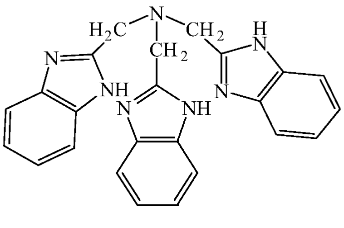

Fig. 1. Structure of ntb.

Experimental Section

Materials and physical measurements

All chemicals, of AR/GR quality, were used without further purification.

C, H and N contents were determined using a Carlo Erba 1106 elemental analyzer. Metal contents were determined by EDTA titration. Thermal analyses were carried out under an N_2 flow at a heating rate of 10 °C min^{-1} on a ZRY-2P thermal analyzer. The IR spectra were recorded in the 4000 – 400 cm^{-1} region with a Nicolet FI-IR AVATAR 360 spectrometer using KBr pellets. Electronic spectra were taken with a UV/vis spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using a 10^{-3} mol dm^{-3} solution in DMF at r. t. Electrochemical measurements were performed with a LK98APLUS electrochemical analyzer under nitrogen atmosphere at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated

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Table 1. Crystal data and structure refinement for [Mn(ntb) (4-hydroxycinnamate)] (4-hydroxy-cinnamate) · $(DMF)_{0.5}$ · $(H_2O)_3$.

Formula	$C_{43.50}H_{44.50}MnN_{7.50}O_{9.50}$
Molecular weight, g mol^{-1}	879.31
Crystal size, mm^3	0.33 × 0.30 × 0.27
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	11.9360(12)
b, Å	14.4348(16)
c, Å	14.7519(15)
α, deg	83.052(2)
β, deg	89.970(2)
γ, deg	66.287(2)
Vol, Å^3	2306.7(4)
Z	2
T, K	293 (2)
D_{calcd}, g · cm^{-3}	1.266
Absorption coefficient, mm^{-1}	0.374
F(000), e	918
θ Range for data collection, deg	1.55 to 28.37
hkl Ranges	$-15 \le h \le 15$; $-19 \le k \le 17$; $-19 \le l \le 17$
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11406 / 11 / 614
Goodness-of-fit on F^2	0.933
$R1/wR2$ [I $\ge 2\sigma$(I)]^a	0.068/0.194
$R1/wR2$ (all data)^a	0.163/0.261
Large diff. peak and hole, e Å^{-3}	1.23/−0.37

^{a} $w = 1/[\sigma^2 F_o{}^2 + (0.1402\ P)^2 + 0.0000\ P]$, where $P = (F_o{}^2 + 2\ F_c{}^2)/3$.

calomel (SCE) reference electrode were used in the three-electrode measurements. The electroactive component was at a 1.0×10^{-3} mol dm^{-3} concentration with tetrabutylammonium perchlorate (TBAP) (0.1 mol dm^{-3}) used as the supporting electrolyte in DMF solution. The EPR spectra were recorded with a Bruker 200D spectrometer with the X-band.

Preparation of tris(2-benzimidazolylmethyl)amine and its manganese complex tris(2-benzimidazolylmethyl)amine (ntb)

This compound was synthesized by the literature method [10]. Yield: 19.5 g (60 %); m. p.: 274 – 275 °C (271 °C [10]). The infrared and ^{1}H NMR spectra were consistent with the literature [10].

[Mn(ntb) (4-hydroxycinnamate)](4-hydroxycinnamate) · $(DMF)_{0.5}$ · $(H_2O)_3$

To a stirred solution of ntb (407.5 mg, 1 mmol) in hot MeOH (20 mL) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (361.8 mg, 1 mmol), followed by a solution of sodium-4-hydroxycinnamate (372.4 mg, 2 mmol). A light yellow crystalline product formed rapidly. The precipitate was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF to give a light yellow solution which was allowed to evaporate at r. t. After four weeks a mass of light yellow crystals appeared, yield 0.62 g (70 %). – $C_{43.50}H_{44.50}MnN_{7.50}O_{9.50}$ (879.31): calcd. C 59.42, H 5.10, N 11.95, Mn 6.25; found: C 59.74, H 5.31, N 11.73, Mn 6.20. – Λ_M (DMF, 297 K): 63.7 s · cm^2 · mol^{-1}.

X-Ray structure determination

Intensity data were collected using a Bruker Smart CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.071073 nm) at 293 K. Data reduction and cell refinement were performed using the programs SMART and SAINT [11]. The absorption corrections were carried out by the empirical method. The structure was solved by Direct Methods (SHELXTL) using all unique data [12]. The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogen atoms were placed geometrically and treated with the riding model. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1.

CCDC 627350 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Result and Discussion

The manganese complex is soluble in DMF and DMSO, but insoluble in water and organic solvents, such as methanol, ethanol, benzene, petroleum ether, trichloromethane *etc*. The elemental analyses show that the composition is [Mn(ntb)(4-hydroxycinnamate)] (4-hydroxycinnamate) · $(DMF)_{0.5}$ · $(H_2O)_3$. A comparison of the molar conductance value shows a 1 : 1 electrolyte similar to previously reported data [13].

Thermogravimetric analysis (TGA) of the manganese(II) complex shows that it undergoes endothermic dehydration. The initial mass loss within the temperature range 80 – 124 °C is attributed to elimination of the hydrate H_2O molecules. Differential thermal analysis (DTA) also indicates that the dehydration process appears as an endothermic peak. The mass losses in the range 160 – 181 °C are due to the loss of the DMF molecules. The decomposition of the complex starts at 273 °C and is complete at *ca*. 610 °C, yielding MnO_2 as the final product.

The molecular structure of the manganese(II) complex is shown in Fig. 2, selected bond lengths and an-

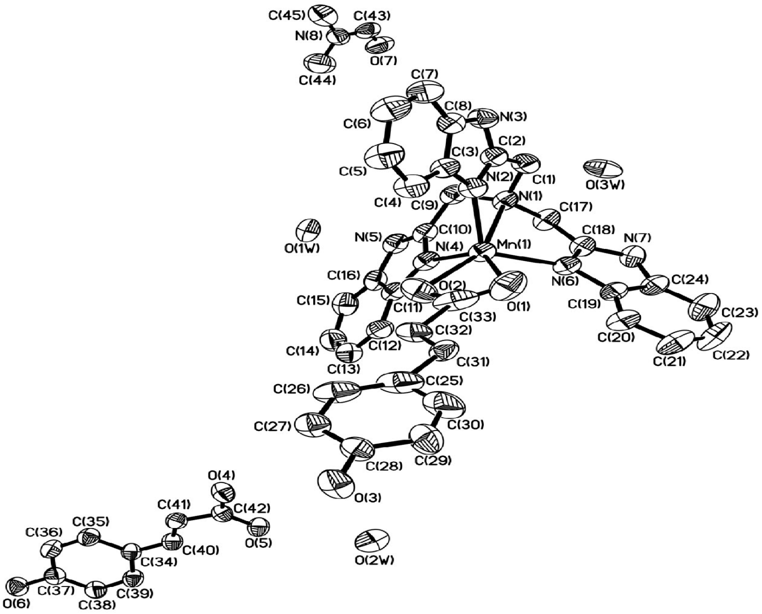

Fig. 2. Molecular structure and atom numbering of [Mn(ntb) (4-hydroxycinnamate)] (4-hydroxycinnamate) · (DMF)$_{0.5}$ · (H$_2$O)$_3$ with hydrogen atoms omitted for clarity.

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

Mn(1)–O(1)	2.323(4)	Mn(1)–O(2)	2.228(3)
Mn(1)–N(2)	2.194(4)	O(1)–C(33)	1.237(8)
Mn(1)–N(4)	2.206(4)	O(2)–C(33)	1.250(7)
Mn(1)–N(6)	2.188(3)	C(31)–C(32)	1.324(1)
Mn(1)–N(1)	2.543(3)	C(32)–C(33)	1.599(1)
N(6)–Mn(1)–N(2)	114.3(1)	N(6)–Mn(1)–N(1)	71.94(1)
N(6)–Mn(1)–N(4)	104.6(1)	N(2)–Mn(1)–N(1)	71.08(1)
N(2)–Mn(1)–N(4)	111.6(1)	N(4)–Mn(1)–N(1)	70.86(1)
N(6)–Mn(1)–O(2)	131.5(1)	O(2)–Mn(1)–N(1)	153.0(1)
N(2)–Mn(1)–O(2)	103.1(1)	O(1)–Mn(1)–N(1)	148.9(1)
N(4)–Mn(1)–O(2)	88.03(1)	C(33)–O(1)–Mn(1)	90.6(3)
N(6)–Mn(1)–O(1)	89.39(1)	C(33)–O(2)–Mn(1)	94.7(4)
N(2)–Mn(1)–O(1)	95.85(1)	C(32)–C(31)–C(25)	112.0(1)
N(4)–Mn(1)–O(1)	139.4(1)	O(1)–C(33)–O(2)	118.7(4)
O(2)–Mn(1)–O(1)	56.04(1)	C(31)–C(32)–C(33)	113.7(1)

gles are summarized in Table 2. The asymmetric unit consists of a [Mn(ntb)(4-hydroxycinnamate)]$^+$ cation, a 4-hydroxycinnamate anion, 0.5 molecule of DMF and 3 molecules of water of crystallization. The tripodal ntb ligand forms a pyramidal geometry with manganese, and the remaining open axial site is occupied by a chelating bidentate 4-hydroxycinnamate anion. The manganese(II) ion is six-coordinate with a $\mathrm{N_4O_2}$ ligand donor set and a pseudo-octahedral structure. The bond length between the manganese ion and the apical nitrogen atom N(1)–Mn(1) is 2.543(3) Å, which is about 0.347 Å longer than the bond lengths between the manganese ion and the basal nitrogen atoms (2.188 – 2.206 Å, average = 2.196 Å). This significant elongation has been observed in other manganese complexes of tripodal tetradentate ligands with benzimidazolylmethyl groups [7]. The average bond angle ($\mathrm{N_A}$–Mn–$\mathrm{N_B}$) of the axial nitrogen atoms ($\mathrm{N_A}$ = N1), the manganese ion, and the basal nitrogen atoms ($\mathrm{N_B}$ = N2, N4, N6) is 71.3°, and the manganese ion is 0.704 Å above the basal plane N2–N4–N6. The 4-hydroxycinnamate ligand is accommodated at the open axial site without any significant change in the pseudo-octahedral geometry of the complex (average $\mathrm{N_B}$–Mn(1)–$\mathrm{N_B}$ = 110.2°). In the dichloro complex Mn$^{\mathrm{II}}$(ntb)Cl$_2$, a sixth ligand, the chloride anion, opens one site of the trigonal basal plane to form a square basal plane ($\mathrm{N_B}$–Mn–$\mathrm{N_B}$ = 143.1°) [8]. When a sixth ligand is coordinated to the metal complex of a tripodal tetradentate ligand, the geometry of the three benzimidazole nitrogen atoms may be retained with the complex changing its geometry from trigonal bipyramidal to partial trigonal pyramidal; alternatively, the geometry of the three benzimidazole nitrogen atoms may change from trigonal basal to square basal to accommodate the new ligand with the complex changing its geometry from trigonal bipyramidal to octahedral. 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. All the bond lengths related to the manganese atom are comparable to the values observed in other complexes [14, 15].

IR and UV/visible spectra

In the free ligand ntb, a strong band is found at *ca.* 1440 cm^{-1} along with a weak band at 1460 cm^{-1}. By analogy with the assigned bands of imidazole, the former is attributed to ν(C=N–C=C), while the latter is ν(C=N) [10, 16 – 18]. These bands are shifted to higher frequencies by 10 cm^{-1} for the complex, which implies direct coordination of all four imine nitrogen atoms to Mn(II) as found for other metal complexes with benzimidazoles [19]. The ν_{as} (COO) vibration is assigned to the strong band at 1527 cm^{-1} whereas ν_s(COO) is attributed to the 1395 cm^{-1} peak, which suggest the presence of coordinated 4-hydroxycinnamate [20 – 22]. The bands at 1701 and 1445 cm^{-1} are attributed to ν(C=O) and ν(C–O) indicative of free 4-hydroxycinnamate. The bands present at 1640 cm^{-1} may originate from the C=C bond vibration of the α,β-unsaturated carboxylate groups. Medium bands near 1281 cm^{-1} probably correspond to ν(N–Ar). A broad band in the 3000 – 3300 cm^{-1} region may be ascribed to hydrogen-bonded ν(O–H) and ν(N–H), and may also include ν(C–H).

DMSO solutions of the ligand ntb and its manganese(II) complex show, as expected, almost identical UV spectra. The UV bands of ntb (284, 277 nm) are only marginally blue-shifted (7 nm) in the complex, which is clear evidence of C=N coordination to manganese(II). The two absorption bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (imidazole) transitions.

Cyclic voltammogram and EPR spectrum

The 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 0.343 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 0.487 V. The separation between the cathodic and anodic peak potentials ΔE_p (ΔE_p = $E_{pa} - E_{pc}$) of 144 mV indicates a quasi-reversible redox process assignable to the Mn(III)-Mn(II) couple and $E_{1/2}$ = $(E_{pa} + E_{pc})/2$ is equal to 0.415 V [5, 8]. The free ntb ligand was proven to be not electroactive over the range -1.2 to $+1.2$ V. According to previous reports [7, 23 – 27], to be an effective mimic of superoxide dismutase, a transition metal complex must have a reduction potential below 0.65 V [$E°(^1O_2 - O_2{}^-)$] and above -0.33 V [$E°(O_2 - O_2{}^-)$] such that catalysis can take place without toxic singlet oxygen being formed. Thus the redox potential of 0.415 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 is equal to A = 95 G and is of the same order as that found for other mononuclear Mn(II) complexes [7 – 9]. This spectrum confirms that the material is high-spin Mn(II). The signal features are assignable to allowed transitions ($\Delta m_s = \pm 1$, $\Delta m_l = \pm 0$).

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