A Seven-coordinate Manganese(II) Complex Formed with the Tripodal Tetradentate Ligand Tris(*N*-methylbenzimidazol-2-ylmethyl)amine

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Z. Naturforsch. **2010**, *65b,* 1097 – 1100; received May 6, 2010

A seven-coordinate manganese(II) complex with the tripodal tetradentate ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb), with composition [Mn(Mentb)(α-methacrylate)(DMF)]-(ClO_4) · (DMF), was synthesized and characterized by elemental analysis, electrical conductivity, and IR and UV/Vis spectral measurements. The crystal structure of the complex has been determined by single-crystal X-ray diffraction. The Mn^{II} cation is bonded to a Mentb ligand, an α-methacrylate ligand and a DMF molecule through four N atoms and three O atoms, resulting in a seven-coordinate geometry. Cyclovoltammograms of the complex indicate a quasireversible Mn^{3+}/Mn^{2+} couple. The X-band EPR spectrum of the complex exhibits a six-line manganese hyperfine pattern with $g = 2$, $A = 91$, and confirms that the material is high-spin Mn(II).

Key words: Manganese(II) Complex, Crystal Structure, Cylovoltammetry, EPR, Tris(*N*-methylbenzimidazol-2-ylmethyl)amine

Introduction

Benzimidazoles have a wide variety of pharmacological applications including fungicides or anti-helminthics [1]. Tripodal ligands have also long been used in both coordination and bioinorganic chemistry; typical examples include tri(pyridylalkyl)amine and triazacyclononane [2 – 4]. The tetradentate tripodal ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) may mimic the histidine imidazole in coordination chemistry. 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 as forms of assembly of this ligand with metal ions of low coordination number [5 – 9]. In this work, we have prepared and investigated the properties and crystal structure of a seven-coordinate manganese(II) complex with the Mentb ligand.

Experimental Section

Materials and physical measurements

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

C, H and N contents were determined using a Carlo Erba 1106 elemental analyzer, metal contents by EDTA titration. 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 on a LabTech UV BlueStar plus spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A-type conductivity bridge using a 10^{-3} mol L^{-1} solution in DMF at r. t. Electrochemical measurements were performed on an LK2005A electrochemical analyzer under nitrogen atmosphere 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-electrode measurements. The electroactive component was at 1.0×10^{-3} mol L^{-1} concentration with tetrabutylammonium perchlorate (TBAP) (0.1 mol L^{-1}) used as the supporting electrolyte in DMF solution. The EPR spectra were recorded on a Bruker 200D spectrometer with the X-band.

Tris(N-methylbenzimidazol-2-ylmethyl)amine and its complex

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

To a stirred solution of Mentb (0.5 mmol) in hot methanol (20 mL) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) followed

0932–0776 / 10 / 0900–1097 $ 06.00

Table 1. Crystal data and structure refinement for [Mn(Mentb)(α-methacrylate)(DMF)] (ClO_4) · (DMF).

Formula	$C_{37}H_{46}MnN_9O_8Cl$
Molecular weight	835.22
Color, habit	light-yellow, block
Crystal size, mm^3	0.38 × 0.34 × 0.30
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	12.139(5)
b, Å	12.354(5)
c, Å	15.146(6)
α, deg	89.168(4)
β, deg	71.098(4)
γ, deg	76.936(5)
V, Å^3	2088.9(2)
Z	2
T, K	296(2)
$D_{\mathrm{calcd.}}$, g cm^{-3}	1.32
μ(MoK_α), mm^{-1}	0.4
F(000), e	874
θ range, deg	1.70 to 25.5
hkl range	±14, $-14 \rightarrow 13$, ±18
Refinement	full-matrix least-squares on F^2
Data / restraints / ref. param.	7680 / 18 / 513
Finial $R1$ / $wR2$ [$I \geq 2\ \sigma(I)$]^a	0.0578 / 0.1753^a
$R1$ / $wR2$ indices (all data)^a	0.0848 / 0.1887
Goodness-of-fit on F^2 ^{b}	1.079
Largest diff. peak / hole, e Å^{-3}	0.62 / −0.47

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.1190P)^2]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; ^{b} GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{\mathrm{obs}} - n_{\mathrm{param}})]^{1/2}$.

by a solution of sodium (α-methacrylate) (0.5 mmol) in methanol (5 mL), whereupon a colorless microcrystalline precipitate was produced and collected by filtration. After drying in air the colorless product was redissolved in DMF/methanol (1 : 1) and filtered. Light-yellow block-shaped crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of diethyl ether into the filtrate for 4 weeks at r. t.; yield 0.34 g (82 %). – Analysis for $C_{37}H_{46}MnN_9O_8Cl$ (835.22): calcd. C 53.21, H 5.55, N 15.09, Mn 6.58; found C 53.04, H 5.39, N 15.13, Mn 6.54 %. – Λ_M (DMF, 297 K): 69.8 s · cm^2 · mol^{-1}.

X-Ray structure determination

All data were collected using a Bruker Smart CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 296 K. Data reduction and cell refinement were performed using the programs SMART and SAINT [11]. An empirical absorption correction was carried out using SADABS [11]. The structure was solved by Direct Methods using SHELXTL [12]. The non-H atoms in the structure were subjected to anisotropic refinement (SHELXTL [12]). Hydrogen atoms 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.

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

Mn–N(1)	2.309(3)	Mn–O(1)	2.280(3)
Mn–N(3)	2.299(3)	Mn–O(2)	2.311(3)
Mn–N(5)	2.233(3)	Mn–O(3)	2.404(3)
Mn–N(7)	2.538(3)		
N(5)–Mn–O(1)	92.2(1)	N(5)–Mn–O(3)	80.8(1)
N(5)–Mn–N(3)	115.3(1)	O(1)–Mn–O(3)	86.4(1)
O(1)–Mn–N(3)	145.5(1)	N(3)–Mn–O(3)	78.5(1)
N(5)–Mn–N(1)	105.0(1)	N(1)–Mn–O(3)	173.5(1)
O(1)–Mn–N(1)	90.5(1)	O(2)–Mn–O(3)	82.6(1)
N(3)–Mn–N(1)	101.1(1)	N(5)–Mn–N(7)	69.5(1)
N(5)–Mn–O(2)	145.7(1)	O(1)–Mn–N(7)	145.8(1)
O(1)–Mn–O(2)	56.9(1)	N(3)–Mn–N(7)	67.5(1)
N(3)–Mn–O(2)	90.3(1)	N(1)–Mn–N(7)	68.2(1)
N(1)–Mn–O(2)	91.0(1)	O(2)–Mn–N(7)	144.6(1)
O(3)–Mn–N(7)	117.1(1)		

CCDC 776039 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.

Results 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(Mentb)(α-methacrylate)(DMF)](ClO_4) · (DMF). A comparsion of the molar conductance value (in DMF) shows a 1 : 1 electrolyte similar to previously reported data [13].

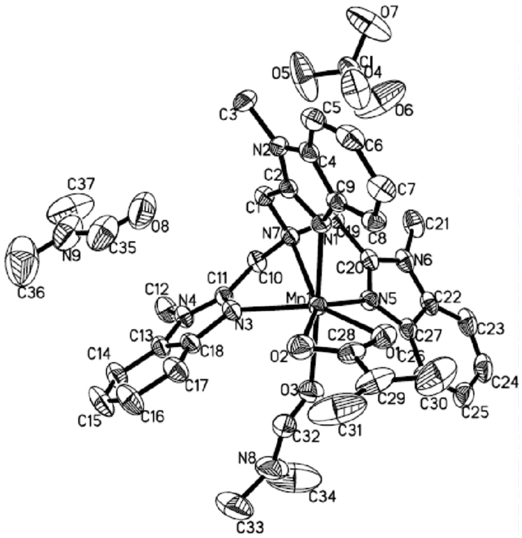

Fig. 1. Molecular structure and atom numbering of [Mn(Mentb)(α-methacrylate)(DMF)] (ClO_4) · (DMF). (Hydrogen atoms omitted for clarity).

Table 3. IR spectral data for the Mn complex and their relative assignments[a].

Compound	ν_{as}(COO)	ν_s(COO)	$\Delta\nu$	ν(C=C)	ν(C=N)	ν(C=N–C=C)	$\nu(ClO_4^-)$
NaL	1552s	1420s	132	1648m	–	–	–
Mentb	–	–	–	–	1515m	1475s	–
Mn complex	1543s	1412s	131	1640m	1494m	1456s	1095bs

[a] L = α-methacrylate; ν in cm^{-1}; b = broad; s = strong; m = medium.

The molecular structure of the manganese(II) complex is shown in Fig. 1, selected bond lengths and angles are given in Table 2. The asymmetric unit consists of a $[Mn(Mentb)(\alpha\text{-methacrylate})(DMF)]^+$ cation, a perchlorate anion, and one molecule of DMF. The ligand forms a tripodal pyramidal geometry with the manganese ion, and the remaining open axial site of the complex is occupied by a chelating α-methacrylate anion and a monodentate DMF. The complex has a seven-coordinate manganese(II) geometry with a N_4O_3 donor set. The bond length between the manganese ion and the apical nitrogen atom N(7)–Mn(1) is 2.538(3) Å, which is about 0.258 Å longer than the bond lengths between the manganese ion and the basal nitrogen atoms (2.233 – 2.309 Å, average = 2.280 Å). This significant elongation has been observed in other manganese complexes with tripodal tetradentate ligands with a benzimidazolylmethyl group [14]. The average bond angle (N_A–Mn–N_B) of the axial nitrogen atoms (N_A), the manganese ion, and the basal nitrogen atoms (N_B) is 68.4°, and the manganese ion is 0.838(3) Å above the trigonal basal plane. The oxygen atom of the monodentate DMF is coordinated in a *trans* position of the basal N(1) atom (N(1)–Mn(1)–O(3) = 173.5(1)°). The oxygen atoms of the chelating α-methacrylate group are coordinated to the approximate *trans* positions of the remaining two basal nitrogen atoms (O(1)–Mn(1)–N(3) = 145.5(1)°, O(2)–Mn(1)–N(5) = 145.7(1)°). In the manganese complex, all additional ligands are accommodated at the opened axial site without significant change in the trigonal pyramidal part of the complex (N(3)–Mn(1)–N(5) = 115.3(1)°). The steric crowding of the ligands is avoided because the manganese(II) ion is slightly above the trigonal basal plane. The space-filling model of the complex shows that up to three donor atoms 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. All the bond lengths related to the manganese atom are comparable to the values observed in other complexes [15].

IR and UV/Vis spectra

The IR spectral data of the manganese complex along with their relative assignments are given in Table 3. In the free ligand Mentb, a strong band is found at *ca.* 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) [16, 17]. These bands are shifted to lower frequencies by *ca.* 19∼21 cm^{-1} in the complex, which implies direct coordination of the three imine nitrogen atoms to manganese(II). This is the preferred nitrogen atom for coordination as found for other metal complexes with benzimidazoles [18]. Information regarding the possible bonding modes of the perchlorate may also be obtained from the IR spectra. The strong, fairly broad absorption bands at 1095 and 625 cm^{-1} indicate that ionic perchlorate groups (T_d) are present [19]. Since the carboxylate group can coordinate to the metal ion in a bidentate or a monodentate fashion, 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 currently employed to determine the coordination mode [19, 20]. The data in Table 3 suggest that the α-methacrylate group in the complex behaves as a bidentate ligand. This conclusion is confirmed by the result of the crystal structure analysis. The band present at 1640 cm^{-1} may originate from the C=C bond vibration of the α-methacrylate group. Medium bands near 1279 cm^{-1} probably correspond to ν(N–Ar).

DMSO solutions of the ligand 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 (10 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.

Cyclovoltammogram and EPR spectrum

The electrochemical properties of the manganese complex were studied by cyclovoltammetry (CV) in DMF. The voltammogram shows only a single reduction peak (E_{pc}) at 0.213 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 0.342 V. The separation between the cathodic and anodic peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) of 129 mV indicates a quasi-reversible redox process assignable to the Mn(III)-Mn(II) couple and $E_{1/2}$ [$(E_{pa} + E_{pc})/2$] to be equal to 0.278 V. The free Mentb ligand was proven not to be electroactive over the range −1.2 to +1.2 V. According to previous reports [21 – 23], to be an effective mimic of superoxide dismutase (SOD), 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 0.278 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 = 91 G and is of the same order as that found for other mononuclear Mn(II) complexes [14, 15]. This spectrum confirms that the material is high-spin Mn(II). The signal features are assignable to the allowed transitions ($\Delta m_s = \pm 1$, $\Delta m_I = \pm 0$).

Acknowledgements

The authors acknowledge financial support and grant from 'Qing Lan' Talent Engineering Funds and Students' Science and Technology Innovation Funds (grant no. DXS2010-040) by Lanzhou Jiaotong University. The grant from 'Long Yuan Qing Nian' of Gansu Province is also acknowledged. This work was also supported by the open foundation of the Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Northwest University.

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