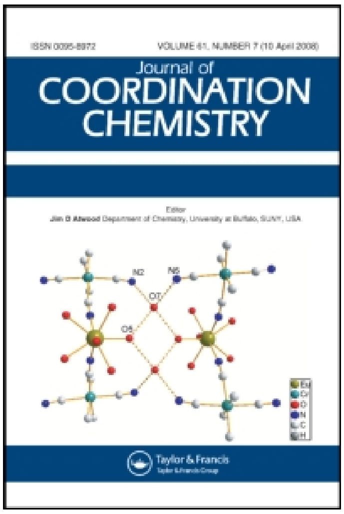

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Synthesis, crystal structure and properties of manganese(II) complexes with the tripod ligand tris(2-benzimidazylmethyl)amine and *α,β*-unsaturated carboxylates

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Synthesis, crystal structure and properties of manganese(II) complexes with the tripod ligand tris(2-benzimidazylmethyl)amine and α,β-unsaturated carboxylates

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Two new ternary complexes of manganese(II) with tris(2-benzimidazylmethyl)amine (ntb), and two different α,β-unsaturated carboxylates, $\{[Mn(ntb)(acrylate)](ClO_4)\}_2 \cdot (H_2O) \cdot 3(CH_3OH)$ (**1**) and $\{[Mn(ntb)(\alpha\text{-methacrylate})](ClO_4)\}_2 \cdot (H_2O) \cdot 2(CH_3OH)$ (**2**), have been synthesized and characterized by means of elemental analyses, thermal analyses, IR, UV and single crystal X-ray diffraction. In the two complexes, ntb functions as a tripodal tetradentate ligand, resulting in trigonal pyramidal geometry. In each complex, an additional ligand, acrylate anion, or α-methacrylate anion, is coordinated at the opened site trans to the apical nitrogen atom of the ntb ligand. The crystal structure of **1** shows two crystallographically independent but chemically identical $[Mn(ntb)(acrylate)]^+$ cations. In **2**, the crystal structure shows two crystallographically independent and chemically different $[Mn(ntb)(a\text{-methacrylate})]^+$ cations. Cyclic voltammograms of the manganese complexes indicate a quasireversible Mn^{3+}/Mn^{2+} couple. The X-band EPR spectrum of the complexes exhibits a six-line manganese hyperfine pattern with $g = 2$, $A = 97$ (**1**) and 93 G (**2**). The spectrum confirms that the material is high-spin Mn(II).

Keywords: Crystal structure; Manganese complexes; Spectroscopic characterization; Tris(2-benzimidazylmethyl)amine; α,β-Unsaturated carboxylate

1. Introduction

Histidine imidazole plays an important role in coordination of transition metals at the active sites of many proteins [1]. For example, superoxide dismutases (SOD), which are contained in microbes, plants and animals, protect cells against oxygen toxicity, because these enzymes catalyse the conversion of superoxide (O_2^-) to hydrogen peroxide and dioxygen via redox-active metals [2–6]. The tetradentate tripodal ligand, tris(2-benzimidazolylmethyl)amine (ntb), is similar to the histidine imidazole

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in coordination aspects [7]. 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 to form from this ligand with metal ions of low coordination number. We earlier studied the coordinating ability of the tripodal benzimidazole ligand ntb with metal ions like Cu(II), Ni(II), Co(II) and Zn(II) [8–11]. Reports on the synthesis and spectroscopic characterization of manganese(II) complexes with ntb have appeared in the literature [12–15]. No ternary complex of manganese(II) with ntb and α,β-unsaturated carboxylate were reported. To better understand the influence of the α,β-unsaturated carboxylate ligand on the structures and properties of the manganese(II) ntb complexes, we herein report the synthesis, crystal structures and properties of two novel manganese(II) ntb complexes $\{[Mn(ntb)(acrylate)](ClO_4)\}_2 \cdot (H_2O) \cdot 3(CH_3OH)$ (**1**) and $\{[Mn(ntb)(\alpha\text{-methacrylate})](ClO_4)\}_2 \cdot (H_2O) \cdot 2(CH_3OH)$ (**2**).

2. Experimental

2.1. *Reagents and physical measurements*

Tris(2-benzimidazolylmethyl)amine (ntb) was synthesized by the literature method [16]: yield 60%, m.p. 275°C. All other reagents and solvents were purchased from commercial sources and were analytical grade.

Microanalyses (C, H, N) were obtained using a Carlo Erba 1106 elemental analyser. Metal contents were determined by EDTA titration. The water content was determined by thermogravimetric analysis (t.g.a.). Thermal analyses were carried out under a N_2 flow at a heating rate of $10^\circ C\,min^{-1}$ on a ZRY-2P thermal analyser. The IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FT-IR AVATAR 360 spectrometer using KBr pellets. Electronic spectra were taken on a Specord 50 spectrophotometer using DMSO as solvent. Electrochemical measurements were performed on an LK98APLUS electrochemical analyser 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-electrode measurements. The electroactive component was at $1.0 \times 10^{-3}\,mol\,dm^{-3}$ concentration with tetrabutylammonium perchlorate (TBAP) ($0.1\,mol\,dm^{-3}$) used as the supporting electrolyte in DMF solution. The EPR spectra were recorded on a Bruker 200D spectrometer with the X-band.

2.2. *Preparation of the complex*

2.2.1. $\{[Mn(ntb)(acrylate)](ClO_4)\}_2 \cdot (H_2O) \cdot 3(CH_3OH)$ (1). To a stirred solution of ntb (407.5 mg, 1 mmol) in hot MeOH (40 cm^3) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (361.8 mg, 1 mmol), followed by a solution of Na(acrylate) (94 mg, 1 mmol) in MeOH (10 cm^3). The resulting clear solution was stirred for 8 h and then allowed to stand at room temperature. Light-yellow block crystals suitable for X-ray diffraction studies were obtained after two weeks. Yield: 0.484 g, 35%. Anal. Calcd for $Mn_2C_{54}H_{48}N_{14}O_{12}Cl_2 \cdot (H_2O) \cdot 3(CH_4O)$: C, 49.61; H, 4.53; N, 14.21; Mn, 7.96; H_2O, 1.3. Found: C, 49.44; H, 4.29; N, 13.98; Mn, 7.67; H_2O, 1.6%.

2.2.2. $\{[Mn(ntb)(\alpha\text{-methacrylate})](ClO_4)\}_2\cdot(H_2O)\cdot 2(CH_3OH)$ (2).

To a stirred solution of ntb (407.5 mg, 1 mmol) in hot MeOH (20 cm^3) was added $Mn(ClO_4)_2\cdot 6H_2O$ (361.8 mg, 1 mmol), followed by a solution of Na(α-methacrylate) (108 mg, 1 mmol) in MeOH (5 cm^3). The resulting clear solution was stirred for 8 h and then allowed to stand at room temperature. Light-yellow block crystals suitable for X-ray diffraction studies were obtained after one month. Yield: 0.564 g, 41%. Anal. Calcd for $Mn_2C_{56}H_{52}N_{14}O_{12}Cl_2\cdot(H_2O)\cdot 2(CH_4O)$: C, 50.63; H, 4.54; N, 14.25; Mn, 7.99; H_2O, 1.3. Found: C, 50.44; H, 4.65; N, 14.11; Mn, 8.31; H_2O, 1.9%.

2.3. *X-ray crystallography*

Crystals of **1** and **2** were mounted on a Bruker Smart APEX CCD diffractometer with the graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Data reduction and cell refinement were performed using SMART and SAINT programs [17]. Absorption corrections were carried out by the empirical method. The structure was solved by direct methods using SHELXTL [18, 19]. Non-H atoms in the structure were subjected to anisotropic refinement. Hydrogen atoms were located geometrically and treated with the riding model. Table 1 gives crystallographic data of the two complexes.

Table 1. Crystallographic data for complexes **1** and **2**.

Parameter	**1**	**2**
Empirical formula	$Mn_2C_{57}H_{62}N_{14}O_{16}Cl_2$	$Mn_2C_{58}H_{62}N_{14}O_{15}Cl_2$
Molecular weight	1379.99	1376.00
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.5408(18)	13.6619(17)
b (Å)	14.689(2)	14.6227(19)
c (Å)	17.993(2)	18.126(2)
α (°)	82.209(3)	83.870(3)
β (°)	85.553(3)	88.595(3)
γ (°)	63.517(3)	63.576(2)
V (Å^3)	3173.1(7)	3223.2(7)
Z	2	2
T (K)	293	293
D_{Calcd} (Mg m^{-3})	1.444	1.418
μ (mm^{-1})	0.560	0.550
$F(000)$	1428	1424
Crystal size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
θ range for data collection (°)	2.0–26.0	2.0–26.0
h, k, l range	−16 to 16, −18 to 17, −22 to 15	−16 to 15, −17 to 17, −22 to 13
R_{int}	0.023	0.047
Reflections measured	17,195	17,416
Observed reflections	8717	8619
Independent reflections	12,162	12,357
Parameters refined	823	831
S	1.01	1.09
R_1 [$I > 2\sigma(I)$]	0.0469	0.0547
wR_2	0.1342	0.1558
Max./Min. $\Delta\rho$ (e Å^{-3})	0.43 and −0.46	0.81 and −0.47

3. Results and discussion

3.1. *Crystal structure of 1*

An ORTEP plot with non-hydrogen atomic labelling is shown in figure 1. Selected bond distances and angles are listed in table 2. The asymmetric unit consists of two [Mn(ntb)(acrylate)]$^+$ cations, two perchlorate anions, three methanol molecules and one water of crystallization. The tripodal ligand ntb forms a trigonal pyramidal geometry with manganese, and the remaining open axial site of the complex is occupied by a chelating bidentate acrylate anion. The crystal structure shows two crystallographically independent but chemically identical [Mn(ntb)(acrylate)]$^+$ cations. Although Mn(1) and Mn(2) are six-coordinate with a N_4O_2 ligand donor set and trigonal pyramidal partial geometry, their bond distances and angles are different. The forming trigonal pyramidal partial geometry of Mn(1) is more distorted than Mn(2). The bond distances between the manganese ion and the apical nitrogen atom, i.e., Mn(1)–N(1), Mn(2)–N(8), are 2.520(3) and 2.497(3) Å, respectively, which are about 0.34 Å longer than the bond distances between the manganese ion and the trigonal basal nitrogen atoms (Mn(1): 2.159–2.200 Å, average 2.180 Å;

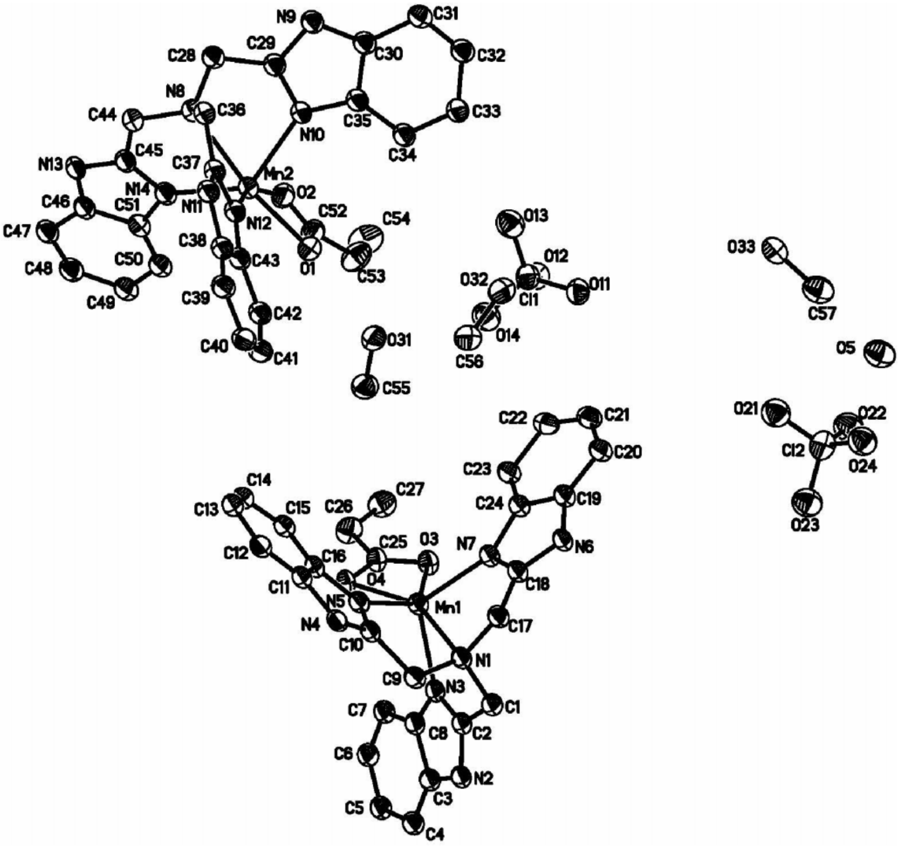

Figure 1. Molecular structure and atom numbering for complex **1**. H atoms are omitted for clarity.

Table 2. Selected bond distances (Å) and bond angles (°) for complex **1**.

Mn(1)–N(1)	2.520(3)	Mn(2)–N(8)	2.497(3)
Mn(1)–N(3)	2.200(3)	Mn(2)–N(10)	2.183(3)
Mn(1)–N(5)	2.181(3)	Mn(2)–N(12)	2.158(3)
Mn(1)–N(7)	2.159(3)	Mn(2)–N(14)	2.124(3)
Mn(1)–O(3)	2.289(2)	Mn(2)–O(1)	2.156(3)
Mn(1)–O(4)	2.211(2)	Mn(2)–O(1)	2.440(3)
O(3)–Mn(1)–O(4)	56.44(10)	O(1)–Mn(2)–O(2)	55.20(9)
O(3)–Mn(1)–N(1)	148.91(10)	O(1)–Mn(2)–N(8)	169.27(9)
O(3)–Mn(1)–N(3)	96.97(10)	O(1)–Mn(2)–N(10)	100.31(10)
O(3)–Mn(1)–N(5)	138.27(10)	O(1)–Mn(2)–N(12)	103.28(10)
O(3)–Mn(1)–N(7)	88.82(10)	O(1)–Mn(2)–N(14)	116.89(10)
O(4)–Mn(1)–N(1)	152.05(9)	O(2)–Mn(2)–N(8)	129.02(8)
O(4)–Mn(1)–N(3)	101.01(9)	O(2)–Mn(2)–N(10)	85.46(9)
O(4)–Mn(1)–N(5)	87.38(10)	O(2)–Mn(2)–N(12)	158.21(10)
O(4)–Mn(1)–N(7)	132.04(9)	O(2)–Mn(2)–N(14)	86.75(10)
N(1)–Mn(1)–N(3)	70.65(9)	N(8)–Mn(2)–N(10)	71.54(10)
N(1)–Mn(1)–N(5)	71.97(10)	N(8)–Mn(2)–N(12)	72.76(10)
N(1)–Mn(1)–N(7)	72.92(9)	N(8)–Mn(2)–N(14)	73.84(10)
N(3)–Mn(1)–N(5)	111.06(10)	N(10)–Mn(2)–N(12)	103.64(10)
N(3)–Mn(1)–N(7)	116.50(10)	N(10)–Mn(2)–N(14)	127.33(10)
N(5)–Mn(1)–N(7)	104.40(10)	N(12)–Mn(2)–N(14)	102.47(11)

Mn(2): 2.124–2.183 Å, average 2.155 Å). This significant elongation has been observed in manganese complexes of tripodal tetradentate ligands with benzimidazolylmethyl group [20, 21]. The average bond angle (N_A–Mn–N_B) of the axial nitrogen atom (N_A), the manganese ion, and the trigonal basal nitrogen atom (N_B) is 71.85° (N_A–Mn(1)–N_B) and 72.71° (N_A–Mn(2)–N_B), and the manganese ion is 0.449 and 0.453 Å above the trigonal basal plane, for Mn(1) and Mn(2), respectively. In complex **1**, the additional acrylate ligand is accommodated at the axial site without any significant change in the trigonal pyramidal partial geometry of the complex (average N_B–Mn(1)–$N_B = 110.65°$, N_B–Mn(2)–$N_B = 111.15°$), but in the dichloro complex Mn^{II}(tris(2-benzimidazolylmethyl)amine)Cl_2, a sixth ligand, the chloride anion, opens one site of the trigonal basal plane to form a square basal plane (N_B–Mn–$N_B = 143.1°$) [14]. When a sixth ligand is coordinated to the metal complex of a tripodal tetradentate ligand, the geometry of the three benzimidazole nitrogen atoms is unchanged and the complex changes its geometry from trigonal bipyramidal to trigonal pyramidal partial; or the geometry of the three benzimidazole nitrogen atoms changes from trigonal basal to square basal to accommodate the new ligand and the complex changes 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.

3.2. *Crystal structure of 2*

The manganese(II) coordination environment of complex **2** is depicted in figure 2. Selected bond distances and bond angles are given in table 3. The asymmetric unit consists of two $[Mn(ntb)(\alpha\text{-methacrylate})]^+$ cations, two perchlorate anions, two methanol molecules and one water of crystallization. The tripodal ligand ntb forms

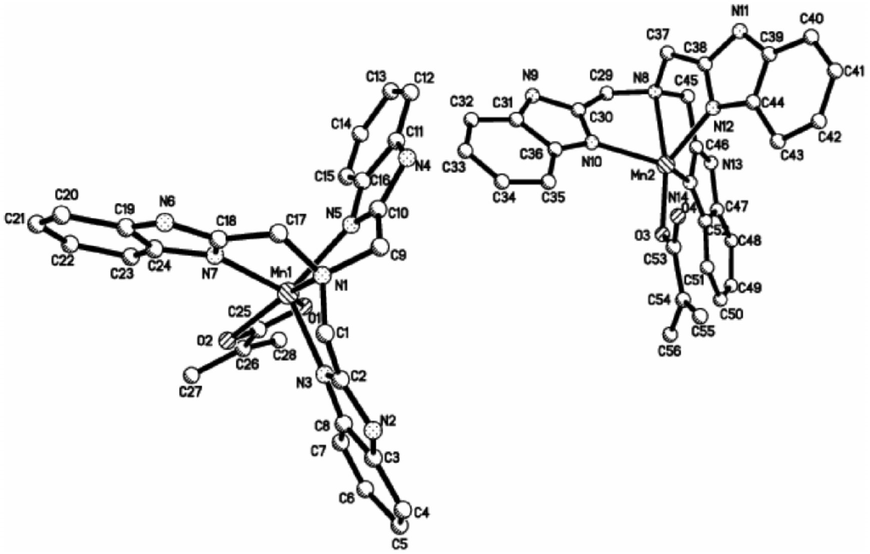

Figure 2. Coordination environment around Mn(1) and Mn(2) in **2**. H atoms are omitted for clarity.

Table 3. Selected bond distances (Å) and bond angles (°) for complex **2**.

Mn(1)–N(1)	2.553(3)	Mn(2)–N(8)	2.542(3)
Mn(1)–N(3)	2.172(3)	Mn(2)–N(10)	2.183(3)
Mn(1)–N(5)	2.177(3)	Mn(2)–N(12)	2.177(3)
Mn(1)–N(7)	2.160(3)	Mn(2)–N(14)	2.179(3)
Mn(1)–O(1)	2.251(3)	Mn(2)–O(3)	2.067(3)
Mn(1)–O(2)	2.319(3)	Mn(2) ··· O(4)	3.094(3)
O(1)–Mn(1)–O(2)	56.71(10)		
O(1)–Mn(1)–N(1)	152.56(10)	O(3)–Mn(2)–N(8)	169.27(9)
O(1)–Mn(1)–N(3)	99.20(11)	O(3)–Mn(2)–N(10)	100.31(10)
O(1)–Mn(1)–N(5)	88.53(11)	O(3)–Mn(2)–N(12)	103.28(10)
O(1)–Mn(1)–N(7)	132.07(10)	O(3)–Mn(2)–N(14)	116.89(10)
O(2)–Mn(1)–N(1)	146.50(9)		
O(2)–Mn(1)–N(3)	92.90(11)		
O(2)–Mn(1)–N(5)	141.11(11)		
O(2)–Mn(1)–N(7)	90.12(10)		
N(1)–Mn(1)–N(3)	71.26(10)	N(8)–Mn(2)–N(10)	71.19(10)
N(1)–Mn(1)–N(5)	72.13(11)	N(8)–Mn(2)–N(12)	72.27(10)
N(1)–Mn(1)–N(7)	72.97(10)	N(8)–Mn(2)–N(14)	73.40(10)
N(3)–Mn(1)–N(5)	111.03(11)	N(10)–Mn(2)–N(12)	110.40(11)
N(3)–Mn(1)–N(7)	117.70(11)	N(10)–Mn(2)–N(14)	115.34(11)
N(5)–Mn(1)–N(7)	104.00(11)	N(12)–Mn(2)–N(14)	107.65(11)

a trigonal pyramidal geometry with manganese ion in complex **2**, and the remaining opened axial site of the complex is occupied by a chelating bidentate acrylate anion or a monodentate one. The crystal structure shows two crystallographically independent and chemically different [Mn(ntb)(α-methacrylate)]$^+$ cations. The Mn(1) is six-coordinate with a N_4O_2 ligand donor set and trigonal pyramidal partial geometry.

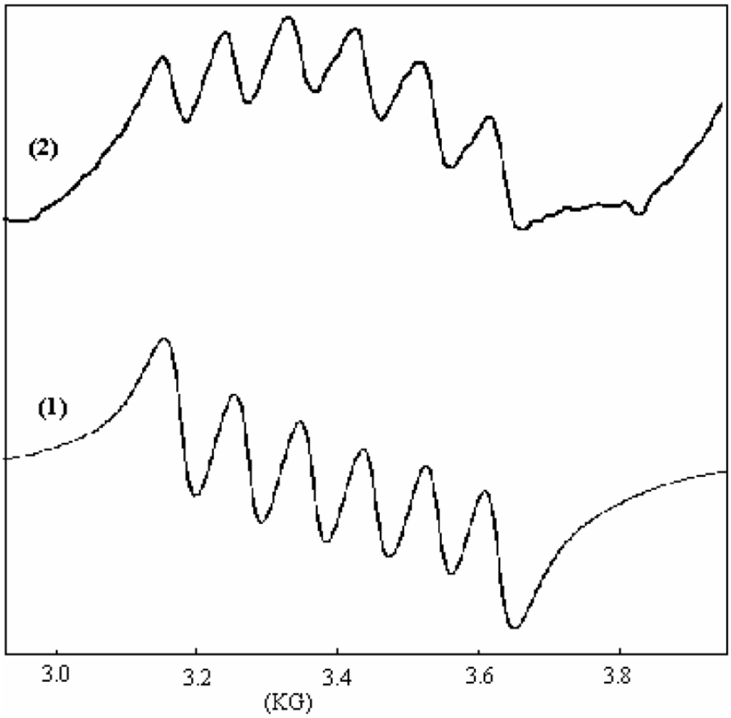

Figure 3. X-band EPR spectrum of the two Mn(II) complexes at 285 K in single crystal. Spectrometer conditions: microwave frequency, 9.65 GHz; microwave power, 10 mW; gain, 4.0×10^4; mid-range, 3181 G; scan range, 2000 G; time constant, 0.5 s; scan time, 200 s.

The Mn(2) is five-coordinate with a N_4O ligand donor set and distorted trigonal bipyramidal geometry of site symmetry C_3, which corresponds to the active-site geometry of native manganese superoxide dismutase. Elongation of the bond distance between the manganese ion and the apical nitrogen atom is also observed in **2**, with Mn(1)–N(1) = 2.553(3) Å and Mn(2)–N(7) = 2.542(3) Å, which are comparable to those of **1**. The average bond angles (N_A–Mn–N_B) of the axial nitrogen atom (N_A), the manganese ion, and the trigonal basal nitrogen atom (N_B) are 72.12° (N_A–Mn(1)–N_B) and 72.29° (N_A–Mn(2)–N_B); the manganese ion is 0.488 and 0.466 Å above the trigonal basal plane, for Mn(1) and Mn(2), respectively. In complex **2**, the additional α-methacrylate ligand is accommodated at the opened axial site without any significant change in the trigonal pyramidal part of the complex (average N_B–Mn(1)–N_B = 110.65°, N_B–Mn(2)–N_B = 111.15°). The axial ligating atoms of the Mn(2) are N(8) and O(3) with Mn(2)–N(8) 2.542(3) Å, Mn(2)–O(3) 2.067(3) Å and O(3)–Mn(2)–N(8) is 164.34(10)°. The distance between Mn(2) and O(4) is 3.094(3) Å, so O(4) is not coordinated.

3.3. *Infrared and electronic spectra*

In the free ligand ntb, a strong band is found at ca $1440\,\mathrm{cm}^{-1}$ along with a weak band at $1460\,\mathrm{cm}^{-1}$. 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) [7, 22, 23]. The shift to higher frequency by 10 cm^{-1} in the two complexes, implies direct coordination of all four imine nitrogen atoms to Mn(II). This is the preferred nitrogen atom for coordination as found for other metal complexes with benzimidazoles [24]. The strong, fairly broad absorptions at 1118 (**1**) and 1110 cm^{-1} (**2**) indicate that ionic perchlorate groups (T_d) are present [25, 26]. The ν_{as}(COO) is assigned to the strong bands at 1543 (**1**) and 1546 cm^{-1} (**2**) whereas the ν_s(COO) is attributed to the 1392 (**1**) and 1389 cm^{-1} (**2**) peaks, suggesting the presence of coordinated acrylate/α-methacrylate [27–29]. The bands present at 1638 (**1**) and 1641 cm^{-1} (**2**) may originate from the C=C bond vibration of the α,β-unsaturated carboxylate groups. Medium bands at 1276 (**1**) and 1277 cm^{-1} (**2**) probably correspond to ν(N–Ar). Both complexes exhibit a broad band in the 3000–3300 cm^{-1} region, which may be ascribed to hydrogen-bonded ν(O–H) and ν(N–H), and may also include ν(C–H).

A DMSO solution of free ntb and the two complexes show, as expected, identical UV spectra. The UV bands of ntb (284, 277 nm) are only marginally blue shifted (3–5 nm) in both complexes, which show clear evidence of C=N coordination to manganese(II). Two absorption bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (imidazole) transitions.

3.4. *Cyclic voltammograms and EPR spectra*

The electrochemical properties of the two manganese complexes have been studied by cyclic voltammetry (CV) in DMF. The voltammogram of the manganese(II) complexes shows only a single reduction peak (E_{pc}) at 0.341 (**1**) and 0.333 V (**2**) during the cathodic potential scan. During the return anodic potential scan, just after the reduction peak, an anodic peak (E_{pa}) is observed at 0.434 (**1**) and 0.480 V (**2**). The separation between the cathodic and anodic peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) of 93 (**1**) and 147 mV (**2**) indicate 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 0.387 (**1**) and 0.406 V (**2**) [12, 30, 31]. The neutral uncomplexed ligand ntb is not electroactive over the range −1.2 to +1.2 V. According to previous reports [32], 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 but toxic singlet oxygen cannot be formed, so the redox potentials 0.387 (**1**) and 0.406 V (**2**) showed that the two complexes have SOD activity.

The X-band EPR spectrum was measured in single crystal at 285 K. The spectrum (figure 3) 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 $A = 97$ (**1**) and 93 G (**2**) and is of the same order as that found for other mononuclear Mn(II) complexes [33–36]. This spectrum confirms high-spin Mn(II). The signal features are assignable to allowed transitions ($\Delta m_s = \pm 1$, $\Delta m_I = \pm 0$). The spectrum is typical of a Mn(II) complex.

3.5. *Thermochemical*

The crystal sample at first loses methanol at ca 73°C. The T.g.a. curves of the two manganese(II) complexes show that they undergo endothermic dehydration. Mass losses within the 75–120°C range are attributed to elimination of the hydration H_2O molecules; D.t.a. curves indicate that the dehydration process appear as endothermic peaks in the two complexes. The decomposition of the two complexes starts at 275 (**1**) and 282°C (**2**) and is completed at ca 610 (**1**) and 570°C (**2**), and the weight of the last residue is in agreement with that required for MnO_2.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 247575 and 247576 for complexes **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +/44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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