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Synthesis and characterization of a bis-μ,η^1-carboxylate-bridged dinuclear manganese(II) complex containing a tetradentate tripodal ligand, *N*-(benzimidazol-2-ylmethyl)iminodiacetic acid

Dohyun Moon [a], Junghyun Kim [a], Minhak Oh [a], Byoung Jin Suh [b], Myoung Soo Lah [a],*

[a] *Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do 426-791, Republic of Korea*
[b] *Department of Physics, Catholic University of Korea, Puchon, Kyunggi-do 420-473, Republic of Korea*

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Abstract

The dinuclear Mn(II) complex, $[Mn_2(Hbida)_2(H_2O)_2]$, was prepared using a tetradentate tripodal ligand, *N*-(benzimidazol-2-ylmethyl)iminodiacetic acid (H_3bida) which has two carboxylate and one benzimidazole groups. The manganese ions are doubly bridged using μ,η^1-bridging monodentate carboxylate oxygen atoms. The Mn–Mn bond distance of 3.446 Å in the complex is comparable to that observed in the active site of the native *manganese arginase* enzyme (3.30 Å). The geometry of the complex with four carboxylates in two different types of binding modes, non-bridging monodentate and μ,η^1-type bridging monodentate, mimics the active site structure of *manganese arginase*. The magnetic properties of the complex show a coupling constant of $J = -0.471(1)\ \mathrm{cm}^{-1}$, which is consistent with weakly coupled antiferromagnetic Mn^{II} ($S = 5/2$) centers. The cyclic voltammograms of the Mn(II) complex in DMF show irreversible oxidation occurring around 570 mV (versus Ag/AgCl).

Keywords: Dinuclear manganese complex; Carboxylate bridge; Tetradentate tripodal ligand; Arginase

1. Introduction

Many of the studies on the synthesis and characterization of multinuclear manganese complexes have been directed towards the development of synthetic models [1–3] for diverse manganese enzymes, such as manganese arginase [4], manganese catalase [5] and the oxygen-evolving complex (OEC) of photosystem II [6]. These synthetic complexes have been prepared using multidentate ligands having various donor groups, among which a carboxylate donor group is important because of its role in forming the active site of metalloenzymes [7]. Various binding modes of carboxylates have been observed at the active sites of manganese metalloenzymes [4–7b,7d] (Scheme 1). The active site of manganese arginase that catalyzes the hydrolysis of L-arginine to L-ornithine and urea contains a dinuclear manganese center associated with four carboxylate groups, with all of which are in different binding modes [4f]. The manganese(II) ions in the arginase are bridged by a *syn–syn*-μ-carboxylate group, a μ,η^1-carboxylate group, and a water molecule, which leads to a Mn–Mn bond distance of 3.3 Å [4f]. Each manganese coordination sphere is completed by a histidine and either a monodentate carboxylate or a chelating bidentate carboxylate group, giving either a penta-coordinate square pyramidal or a hexa-coordinate distorted octahedral manganese center, respectively. The bridging water molecule is involved in a hydrogen bond interaction with the monodentate carboxylate oxygen atom and is supposed to participate in the hydrolysis of L-arginine through a metal-activated hydroxide mechanism [4d]. Even though numerous model complexes for either the manganese catalase [2] or the OEC [3] have been proposed and characterized,

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* Corresponding author. Tel.: +82 31 400 5496; fax: +82 31 436 8100.
E-mail address: mslah@hanyang.ac.kr (M.S. Lah).

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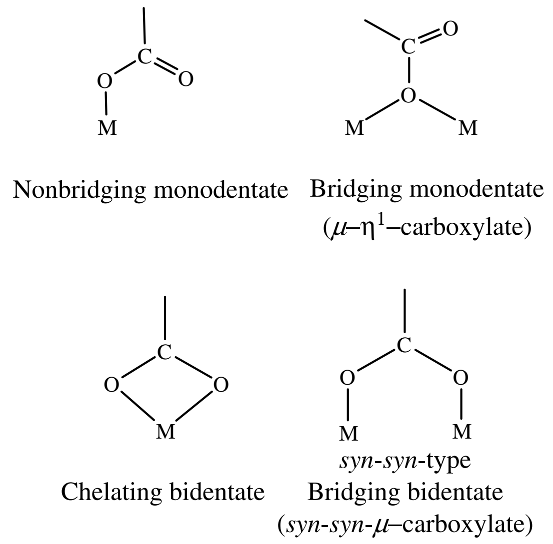


Scheme 1. The carboxylate binding modes observed in various manganese metalloproteins.

only a few manganese model complexes for the arginase have been reported so far [1].

Here we report on the preparation and characterization of a dinuclear manganese(II) complex, which has two important structural features of the active site of the manganese arginase: the bridging μ,η^1-carboxylate group and intramolecular hydrogen bonding between the ligated water molecule and a non-bridging monodentate carboxylate. The complex was prepared using a manganese(II) acetate tetrahydrate and a tripodal tetradentate ligand, *N*-(benzimidazol-2-ylmethyl)iminodiacetic acid (H_3bida) that contains two carboxylate and one benzimidazole groups.

2. Experimental

2.1. Materials

The following commercially available chemicals were purchased and used without further purification: Mn(II) acetate tetrahydrate from Yakuri; methanol from Junsei; and pyridine from Aldrich Chemicals. *N*-(benzimidazol-2-ylmethyl)iminodiacetic acid (H_3bida) was prepared according to a literature procedure [8].

2.2. Physical measurements

Elemental analysis was performed at the Organic Chemistry Research Center in Sogang University (Korea) using a TE Flash EA 1112 series elemental analyzer. Infrared spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} employing a Varian FTS 1000 FT-IR spectrometer.

2.3. Synthesis

[$Mn_2(Hbida)_2(H_2O)_2$] (**1**) 0.132 g (0.502 mmol) of H_3bida was dissolved in 10 mL of methanol and 10 mL of pyridine. Then 0.123 g (0.502 mmol) of Mn(II) acetate tetrahydrate was added to the solution. The solution was stirred until the solution became clear, and then it was allowed to stand for a period of 7 days. Pale yellow crystals were separated from the solution, washed with methanol and water, and vacuum dried. (0.088 g, 53% yield). *Anal.* Calc. for [$Mn_2(Hbida)_2(H_2O)_2$] ($Mn_2C_{24}H_{26}N_6O_{10}$) (*fw* = 668.38): C, 43.13; H, 3.92; N, 12.57. Found: C, 43.10; H, 3.99; N, 12.61%. IR (cm^{-1}): 3391.7(br), 3208.4(br), 3115.6(w), 3063.3(w), 2922.2(w), 1638.5(w), 1626.3(m), 1612.2(s), 1592.0(m), 1490.4(m), 1467.2(w), 1453.7(s), 1435.8(w), 1402.7(s), 1367.0(s), 1328.4(s), 1316.4(w), 1277.2(s), 1264.1(m), 1129.4(s), 1116.7(m), 1039.3(s), 1003.6(s), 977.0(s), 932.5(s), 911.0(m), 899.1(s), 844.7(w), 768.8(m), 754.1(s), 622.1(m), 428.9(m).

2.4. Electrochemistry

Electrochemical measurements were performed using a BAS CV-50W under an argon atmosphere in a conventional three-electrode cell consisting of an Ag/AgCl (3 M KCl) reference electrode, Pt wire counter electrode, and a glassy carbon working electrode. The glassy carbon electrode was freshly polished using alumina before each scan. The cyclic voltammogram of complex **1** was recorded using a DMF solution of the complex (~1 mmol/dm^3) with 0.1 mol/dm^3 of tetrabutylammonium tetrafluoroborate ($[CH_3(CH_2)_3]_4NBF_4$) as the supporting electrolyte.

2.5. Magnetic measurements

Magnetization measurements were carried out on powdered sample using a SQUID magnetometer (Quantum Design MPMS-7XL). Field-cooled magnetization data were collected in an applied magnetic field of $H = 500$ Oe in the temperature range $2\ K < T < 300\ K$. All the data shown were corrected for the diamagnetic background.

2.6. X-ray crystallography

A crystal was coated with paratone oil to prevent loss of crystallinity on exposure to air. The data collection was performed at −100 °C using Mo Kα radiation ($\lambda = 0.71073$ Å) employing a Bruker SMART CCD equipped with a graphite crystal, incident-beam monochromator. The SMART and SAINT software packages [9] were used for data collection and integration, respectively. The collected data were corrected for absorbance using SADABS [10] based upon Laue symmetry using equivalent reflections. Structures were solved by direct methods, and refined using full-matrix least-squares calculations employing the SHELXTL-PLUS software package [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except those attached to the lattice solvents, were found by difference Fourier peaks, and refined isotropically. Two pyridine sites were found as lattice solvents: one was located at a general position and the other was on a crys-

Table 1
Crystal structure and refinement data for $[Mn_2(Hbida)_2(H_2O)_2]\cdot 3py$ (**1**)

Empirical formula	$Mn_2C_{39}H_{41}N_9O_{10}$
Formula weight (g/mol)	905.69
Temperature (K)	173(2)
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	14.001(4)
b (Å)	14.797(4)
c (Å)	9.974(3)
β (°)	107.674(5)
Volume ($Å^3$)	1968.9(10)
Z, D_{calc} (mg/m^3)	2, 1.528
Absorption coefficient (mm^{-1})	0.713
Reflections collected/unique [R_{int}]	11679/4651 [0.0748]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0685$, $wR_2 = 0.1490$
R indices (all data)	$R_1 = 0.1500$, $wR_2 = 0.1818$
Maximum/minimum residual density ($e\,Å^{-3}$)	0.533/−0.526

tallographic inversion center. The position of the largest electron density in the pyridine site of the general position was assigned as pyridyl nitrogen because there were no other indications, such as the involvement of a hydrogen bonding interaction, for any atoms around the site. All the atoms of the other pyridine site with the inversion symmetry were treated using the PART instruction to refine each position as 5/6 carbon and 1/6 nitrogen atom site, because the pyridyl nitrogen had to be disordered and it was not possible to distinguish it from other carbon atoms. Hydrogen atoms of the pyridine molecule on the inversion center were not included in the final least-squares refinement. Crystal and intensity data are given in Table 1.

3. Results and discussion

3.1. Preparation and characterization

$[Mn_2(Hbida)_2(H_2O)_2]$ (**1**) was prepared using manganese(II) acetate tetrahydrate as a metal source and $Hbida^{2-}$ as a dianionic tripodal tetradentate ligand in the presence of pyridine as base (Scheme 2). Two different sets of carboxylate peaks in the IR spectrum of complex **1** suggest the presence of two different binding modes of the carboxylate groups. The bands occurring at 1612 cm^{-1} and 1403 cm^{-1} were assigned to an asymmetric and symmetric stretching vibrational mode of the bridging monodentate carboxylate group, respectively, and the bands occurring at 1592 cm^{-1} and 1454 cm^{-1} were assigned to an asymmetric and symmetric stretching vibrational mode of the non-bridging monodentate carboxylate group [12]. The $\Delta(\mu_{as} - \mu_s)$ splittings of 209 and 138 cm^{-1} for the carboxylate groups are similar to those of manganese complexes that have both a bridging monodentate carboxylate group and a non-bridging monodentate carboxylate group [13a,13c,14]. The two different carboxylate binding modes in complex **1** were identified from the single crystal structural analysis of the compound.

3.2. Molecular structure

An ORTEP drawing [15] of $[Mn_2(Hbida)_2(H_2O)_2]\cdot 3py$ (**1**) is shown in Fig. 1. Each hexa-coordinate manganese(II) center in the dinuclear complex with an inversion symmetry has an N_2O_4 donor environment, where the nitrogen (N1) atom is from the benzimidazolyl group and the other nitrogen (N3) atom is from the tertiary amine nitrogen of the ligand, one oxygen (O5) atom is from a water molecule,

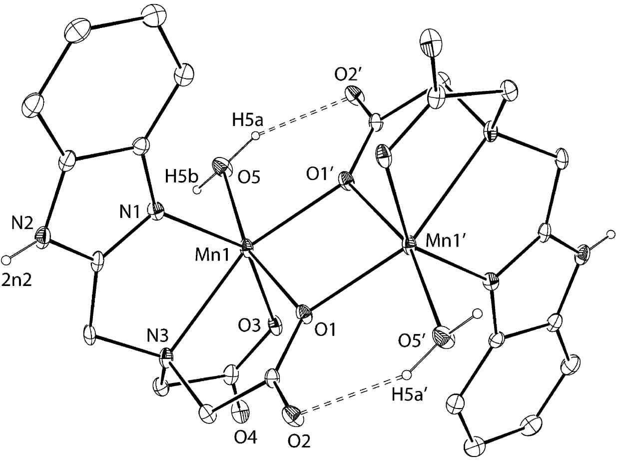
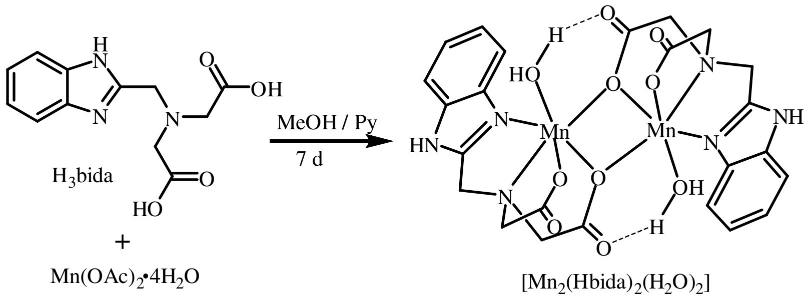


Fig. 1. An ORTEP drawing of $[Mn_2(Hbida)_2(H_2O)_2]\cdot 3py$ (**1**) at 30% probability thermal ellipsoids. Only the hydrogen atoms involved hydrogen bonding are shown, and the lattice solvent molecules have been omitted for clarity.



Scheme 2. Reaction scheme for $[Mn_2(Hbida)_2(H_2O)_2]$ (**1**).

and the remaining three oxygen atoms (O1, O1′, and O3) are from the carboxylate groups. The distorted octahedral coordination geometry of the manganese center is not unusual for a high-spin six-coordinate Mn(II) ion [16] (Table 2). The Mn–O bond distances (2.140(4)–2.184(3) Å) are in the range of the usual Mn^{II}–O bond distances. The distance between the manganese and the nitrogen atoms of the tertiary amine, 2.399(4) Å, is long for a Mn^{II}–N bond distance. This type of weak coordination has also been reported in the other Mn^{II} complexes having similar tertiary nitrogen atoms [13,17]. The two carboxylate groups in Hbida^{2-} are in different binding modes: one in the non-bridging monodentate binding mode and the other in the bridging monodentate, μ,η^1-binding mode. This bridging mode leads to a dinuclear metal complex with a bis-μ,η^1-bridging Mn$_2$O$_2$ core. The Mn–Mn distance in this dinuclear complex (3.446(8) Å) is shorter than that of any known bis-μ,η^1-bridging dinuclear manganese model complex (3.489–4.091 Å range) [13,17,18], and nearly equal to that of the manganese arginase core (3.3 Å) [4f]. The sixth coordination site of the manganese(II) center is occupied by a water molecule, which is involved in intramolecular hydrogen bonding as the water molecule in the active site of the arginase. While the water molecule in the active site of the arginase enzyme bridges the two manganese(II) ions and participates in intramolecular hydrogen bonding with a non-coordinating oxygen atom of a monodentate terminal carboxylate, in complex **1**, the non-bridging terminal water molecule participates in intramolecular hydrogen bonding with a non-coordinating oxygen atom of a μ,η^1-bridging monodentate carboxylate. In addition to this intramolecular hydrogen bonding, the coordinate water molecule simultaneously participates in intermolecular hydrogen bonding with the carboxylate oxygen atom of the neighboring dinuclear complex (Table 3). A similar simultaneous intra- and intermolecular hydrogen bonding pattern has already been reported in a hepta-coordinated bis-μ,η^1-bridging dinuclear manganese complex prepared using a tripodal tetradentate ligand with two imidazole and one carboxylate groups [17a]. It is reported that the reaction of H$_3$bida with other transition metal ions such as V(IV), Ni(II), Co(II), and Zn(II) ions has led to only mononuclear six-coordinate complexes, where none of the carboxylates of the ligand are involved in any bridging modes [19]. While the reaction with Cu(II) ion in the presence of an additional chelating bidentate ligand has also led to a mononuclear complex [19b], but in the absence of the additional chelating bidentate ligand one-dimension coordination polymer has been obtained, where one carboxylate group is involved in a *syn–anti*-type bridging mode [19c]. Even though numerous carboxylate-bridged manganese complexes have been reported, most of these are of the *syn-syn*-type carboxylate-bridged complexes [20], and only a few μ,η^1-bridged manganese complexes have been reported in the literature [13,17]. All known μ,η^1-bridged manganese complexes have only one type of carboxylate group [13b,17]. μ,η^1-Bridged manganese complexes with more than one type of carboxylate group are: [Mn$^{II}_2$(2,6-dimethoxybenzoate)$_4$(Me$_2$Phen)$_2$(H$_2$O)$_2$] · 2EtOH [13a] and Mn$^{II}_2$(2,6-dimethoxybenzoate)$_4$(bpy)$_2$(H$_2$O)$_2$ [13c]. These complexes contain four carboxylate groups of two different types, where one is a non-bridging monodentate carboxylate group and the other is a μ,η^1-bridging monodentate group. Complex **1** is another example of a bis-μ,η^1-bridging dinuclear manganese complex with two different types of carboxylate groups prepared using a tripodal tetradentate ligand with two carboxylates and an benzimidazole group that provides a N$_2$O$_2$ coordination environment.

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

Mn(1)–O(1)	2.184(3)	Mn(1)–O(1)^a	2.161(3)
Mn(1)–O(3)	2.149(3)	Mn(1)–O(5)	2.140(4)
Mn(1)–N(1)	2.210(4)	Mn(1)–N(3)	2.399(4)
Mn(1)–Mn(1)^a	3.446(8)		
O(1)–Mn(1)–O(1)^a	75.0(1)	O(1)–Mn(1)–O(3)	94.3(1)
O(1)–Mn(1)–O(5)	162.5(2)	O(1)–Mn(1)–N(1)	88.5(1)
O(1)–Mn(1)–N(3)	75.7(1)	O(3)–Mn(1)–O(1)^a	109.2(1)
O(5)–Mn(1)–O(1)^a	87.4(2)	O(1)^a–Mn(1)–N(1)	104.4(1)
O(1)^a–Mn(1)–N(3)	150.8(1)	O(3)–Mn(1)–O(5)	90.9(2)
O(3)–Mn(1)–N(1)	145.8(1)	O(3)–Mn(1)–N(3)	73.3(1)
O(5)–Mn(1)–N(1)	96.5(2)	O(5)–Mn(1)–N(3)	121.8(2)
N(1)–Mn(1)–N(3)	74.5(1)	Mn(1)–O(1)–Mn(1)^a	105.0(1)

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1$, $-y+1$, $-z+2$.

Table 3
Hydrogen bonds for **1** (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(5)–H(5a)···O(2)^a	0.89(8)	1.97(8)	2.768(6)	148(6)
O(5)–H(5b)···O(4)^b	0.83(7)	1.84(7)	2.661(6)	166(7)
N(2)–H(2n2)···O(3)^c	0.78(7)	2.30(7)	3.027(6)	155(8)
N(2)–H(2n2)···O(4)^c	0.78(7)	2.30(7)	2.976(6)	145(8)

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1$, $-y+1$, $-z+2$, ^{b} $-x+1$, $-y+1$, $-z+1$, ^{c} $-x+1$, $y-1/2$, $-z+3/2$.

3.3. Magnetic properties

The magnetic susceptibility of complex **1** was measured in the temperature range 2–300 K. The effective magnetic moment ($\mu_{\rm eff}$) decreases slightly with decreasing temperature from 8.16 $\mu_{\rm B}$ at 300 K to 7.88 $\mu_{\rm B}$ at 30 K. Below 30 K, $\mu_{\rm eff}$ decreases rapidly, and reaches a value of 4.57 $\mu_{\rm B}$ at 2 K (Fig. 2). This behavior is typical of a weakly coupled antiferromagnetic system. We analyzed the $\chi_{\rm mol}$ data by fitting it to the Eq. (1) derived from the isotopic Heisenberg exchange Hamiltonian $H = -2JS_1 \cdot S_2$ (where $S_1 = S_2 = 5/2$ for Mn^{II} high-spin d^5 ion systems) [21]. N is the Avogadro's number, $\mu_{\rm B}$ is Bohr magneton, g is the Landé g-value, J is the exchange integral, and k is the Boltzmann's constant. A good fit curve was obtained for $J = -0.471(1)$ cm^{-1} and $g = 1.940$. This weakly antiferromagnetically coupled value of J for complex **1** is similar

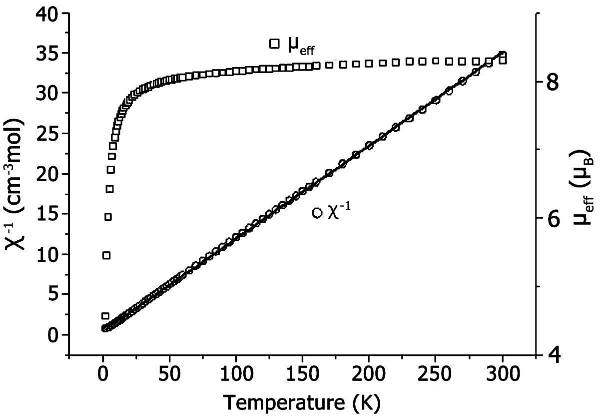


Fig. 2. The effective magnetic moment, μ_{eff}, of **1** and the Curie–Weiss plot ($1/\chi_{mol}$ vs. T).

to that of the other bis-μ,η^1-carboxylate bridged manganese complexes [13b,14a,17]

$$\chi_{\text{mol}} = \frac{2Ng^2\mu_B^2}{kT} \times \left[\frac{e^{J/kT}+5e^{3J/kT}+14e^{6J/kT}+30e^{10J/kT}+55e^{15J/kT}}{1+3e^{J/kT}+5e^{3J/kT}+7e^{6J/kT}+9e^{10J/kT}+11e^{15J/kT}}\right] \quad (1)$$

3.4. Electrochemical properties

The cyclic voltammogram of complex **1** in a DMF solution showed an irreversible oxidation wave around 570 mV (versus Ag/AgCl) as shown in Fig. 3. This irreversible redox feature of complex **1** is also similar to those in the other manganese(II) complexes with bis-μ,η^1-bridged carboxylate groups [13b,17b].

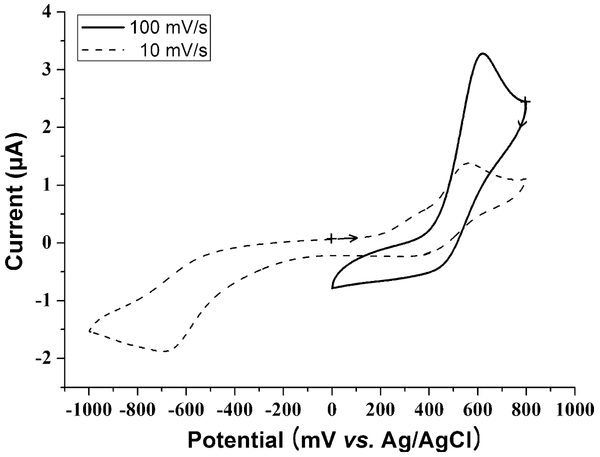


Fig. 3. Cyclovoltammogram of $[Mn_2(Hbida)_2(H_2O)_2]$ (**1**) in DMF with 0.1 mol/dm^3 of $[CH_3(CH_2)_3]_4NBF_4$ as supporting electrolyte. The scan presented with dashed lines was performed from 0 mV with initial anodic sweep at 10 mV/s scan rate, followed by cathodic sweep till −1000 mV, and then reversed back to 0 mV. The scan presented with solid line was performed from 800 mV with initial cathodic sweep at 100 mV/s scan rate, and then reversed at 0 mV.

4. Conclusions

We have characterized a hexa-coordinate dinuclear manganese(II) complex prepared using a tripodal tetradentate ligand, *N*-(benzimidazol-2-ylmethyl)iminodiacetic acid, having one benzimidazole and two carboxylate podal units. The coordination environment of complex **1** resembles that of the first coordination sphere of the native manganese *arginase*. Complex **1** mimics important structural features of the *manganese arginase* active site, such as the Mn–Mn distance, the hydrogen bonding pattern, the presence of four carboxylate groups with the same μ,η^1-bridging monodentate and non-bridging monodentate carboxylate groups. The Mn–Mn distance of 3.446 Å in complex **1** is closer to the value observed in the native *manganese arginase* core (Mn–Mn distance, 3.3 Å) than in any other dinuclear manganese complexes with the same μ,η^1-bridging monodentate carboxylate group. A similar intramolecular hydrogen bonding structure was also observed between the coordinated water molecule and the oxygen atom of the carboxylate group that is not involved in the coordination, as in the active site of the arginase. The magnetic properties and the redox behavior of complex **1** are similar to those reported in other bis-μ,η^1-bridging manganese(II) complexes [13,17].

Supplementary materials

CCDC 642507 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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