This article was downloaded by: On: 23 January 2011 Access details: Access Details: Free Access Publisher Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure, spectroscopic, and magnetic properties of a manganese(II) methoxyacetate complex  $[Mn(C_{\circ}O_{\circ}H_{10})(H_{2}O)]$  <*sub*>*n*</*sub*>

Barbara Hachuła<sup>a</sup>; Monika Pędras<sup>a</sup>; Maria Nowak<sup>b</sup>; Joachim Kusz<sup>b</sup>; Danuta Skrzypek<sup>b</sup>; Jerzy Borek<sup>a</sup>; Danuta Pentak<sup>a</sup>

<sup>a</sup> Institute of Chemistry, University of Silesia, 40-006 Katowice, Poland <sup>b</sup> Institute of Physics, University of Silesia, 40-007 Katowice, Poland

First published on: 08 October 2009

To cite this Article Hachuła, Barbara , Pędras, Monika , Nowak, Maria , Kusz, Joachim , Skrzypek, Danuta , Borek, Jerzy and Pentak, Danuta(2010) 'Synthesis, crystal structure, spectroscopic, and magnetic properties of a manganese(II) methoxyacetate complex [Mn(C  $O_0H_{10}$ )(H<sub>2</sub>O)]*sub>n</sub>*, Journal of Coordination Chemistry, 63: 1, 67 – 78, First published on: 08 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903315535 URL: http://dx.doi.org/10.1080/00958970903315535

# PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



# Synthesis, crystal structure, spectroscopic, and magnetic properties of a manganese(II) methoxyacetate complex $[Mn(C_6O_6H_{10})(H_2O)]_n$

BARBARA HACHUŁA\*†, MONIKA PĘDRAS†, MARIA NOWAK‡, JOACHIM KUSZ‡, DANUTA SKRZYPEK‡, JERZY BOREK† and DANUTA PENTAK†

<sup>†</sup>Institute of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland <sup>‡</sup>Institute of Physics, University of Silesia, 4 Uniwersytecka Street, 40-007 Katowice, Poland

(Received 30 January 2009; in final form 23 July 2009)

A metal-organic coordination polymer,  $[Mn(C_6O_6H_{10})(H_2O)]_n$  (1), has been synthesized and characterized by elemental analysis, FT-IR spectroscopy, and single-crystal X-ray diffraction. Thermogravimetric analysis and EPR spectrum of the compound have also been studied. Light pink crystals of the complex are monoclinic, space group  $P2_1/c$ , with a=7.9444(16)Å, b=9.0802(18)Å, c=13.142(3)Å,  $\beta=93.53(3)^\circ$ , V=946.2(3)Å<sup>3</sup>, Z=4, and  $R_1=0.0212$ . The compound is mononuclear and contains six-coordinate ions bound to bi- and tridentate methoxyacetate molecules and water. Each manganese ion is connected with the neighboring manganese *via* carboxylate bridges forming a polymeric chain of  $[Mn(C_6O_6H_{10})]_n$  and water. The 1-D manganese polymer chains are further hydrogen-bonded *via* the carboxyl groups and water to produce a 3-D extended network. The FT-IR spectrum from 4000 to 400 cm<sup>-1</sup> region confirms the bonding of water. Decomposition reaction takes place in the temperature range 25–900°C in nitrogen. The temperature dependence of magnetic susceptibility reveals weak antiferromagnetic coupling interaction  $(J=-0.74 \text{ cm}^{-1})$  between the Mn(II) sites.

*Keywords*: Manganese(II) complex; Methoxyacetic acid; X-ray crystal structure; Spectroscopic data; Magnetic properties

# 1. Introduction

Continuous efforts have been devoted to design and synthesize manganese(II) complexes because they are often present in active centers of enzymes, including, among others, aminopeptidase [1], peroxidase [2], superoxide dismutase [3], sialyl and fucosyl transferase [4–6], and different intergrins [7–9]. Biological role of Mn(II) ions seems to be connected with an interaction with carboxylate ligands which can form dinuclear, trinuclear, and higher nuclearity complexes exhibiting various oxidation states. Some complexes of simple mono- and dicarboxylic acid homologues with Mn(II) ion have been structurally established, e.g., manganese(II) acetate dihydrate [10], manganese(II) propionate dihydrate [11], manganese(II) malonate dihydrate [12], manganese(II)

<sup>\*</sup>Corresponding author. Email: barbara.hachula@us.edu.pl

glycolate dihydrate [13], manganese(II) L-lactate dihydrate [14], and other bridged metal carboxylates [15–20]. Here, we turn our attention to methoxycarboxylic acid as a prospective ligand for manganese(II).

Methoxyacetic acid (MAA) is the urinary metabolite of ethylene glycol dimethyl ether (EGAE) which is widely utilized in the production of coatings, paints, lacquers, jet printing inks, polish removers, and also as a solvent incorporated in the electrolyte of lithium cells [21]. EGAE itself is not an active hemolytic agent, but its metabolite (MAA) formed during metabolic activation in the liver and skin is a potent hemolysin [22–27]. MAA has three oxygens which are potential coordination sites. These carboxylic acid oxygens may be monodentate, bidentate or tridentate (bridging) as a monoanion. The presence of an additional functional group, as a potential coordination center in the carboxyl acid molecule, enables an increase in stability of its complexes with metal ions. The main purpose of this work is to study Mn(II) interaction with methoxyacetate anion, connected with the analysis of thermal, spectroscopic, and magnetic properties of a new Mn(II) complex.

# 2. Experimental

## 2.1. Physical measurements and materials

All reagents were obtained from commercial sources and used without purification. Elemental analyses of carbon and hydrogen were performed on a Perkin-Elmer 2400 Series II CHNS-O analyzer. The IR spectrum was recorded on an FT-IR Nicolet Magna 560 spectrometer from 4000 to  $400 \text{ cm}^{-1}$  using KBr pellets. The thermal stability of 1 was studied by thermogravimetric analysis (TGA) from 25°C to 900°C at a the heating rate of 10°C min<sup>-1</sup> in nitrogen using a Perkin-Elmer Pyris thermogravimetric analyzer. The X-band electron paramagnetic resonance spectra (9.7 GHz) were recorded with a Bruker EMX spectrometer at room temperature. DPPH was used as an internal field marker. For the EPR measurement, 0.1 mL of the sample solution was kept in closed quartz capillaries. The magnetic susceptibility measurement of a crystalline sample was carried out from 10 to 300 K at a magnetic field of 2 Tesla, using a Quantum Design MPMS SQUID magnetometer.

#### 2.2. Preparation of the complex

Manganese(II) carbonate (115 mg, 1 mmol) and methoxyacetic acid (180 mg, 2 mmol) were stirred in 4 mL of water until dissolved. The solution was filtered and the filtrate was left to stand undisturbed. After 2 days, light pink single crystals suitable for X-ray crystallographic analysis were collected and dried in air at room temperature (58.7 mg, 23.38% yield). Anal. Calcd for  $C_6H_{12}MnO_7$  (%): C, 28.70; H, 4.82. Found (%): C, 28.52; H, 4.91.

#### 2.3. X-ray crystallography

The intensity data for the compound were collected on an Oxford Diffraction kappa diffractometer with a Sapphire3 CCD detector using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å)



Figure 1. The coordination sphere of Mn(II) with atom-numbering scheme showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radius. Symmetry code: (a) 1 - x,  $-\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ ; (b) 1 - x,  $\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ .

at 100 K. Accurate cell parameters were determined and refined using the CrysAlis CCD program [28]. The structure was solved by direct methods using SHELXS-97 [29], and then the solution was refined by full matrix least-squares using SHELXL-97 [29]. Nonhydrogen atoms were refined with anisotropic displacement factors. All hydrogens were treated as "riding" on their parent carbon atoms [d(C-H) = 0.99 Å for methylene hydrogens, d(C-H) = 0.98 Å for methyl hydrogens, respectively] and had isotropic displacement parameters assigned, equal to 1.2 and 1.5 times, the value of the equivalent displacement parameter of the parent carbon atom. Hydrogens attached to oxygen were located from different Fourier maps and refined using riding model with  $U_{iso}(H)$  values of  $1.5U_{eq}(O)$  of their parent atoms. The figures (figures 1–3) were drawn using Ortep-3 [30] and Mercury programs [31]. Data collection and refinement parameters are listed in table 1. Selected bond lengths and angles are listed in table 2.

#### 3. Results and discussion

#### 3.1. Description of the structure

A single crystal X-ray diffraction analysis of **1** reveals that the asymmetric unit contains one manganese, three anionic methoxyacetate ligands and one water (figure 1). The local geometry around each Mn(II) is octahedral, involving two methoxy and three carboxylate oxygens from three different methoxyacetates, as well as one water. The angles around Mn are considerably distorted from ideal octahedral values of 90/180° (table 2). The main distortions are those of the chelate rings with narrow O–Mn–O angles: O2–Mn1–O1 = 71.13(3)°, O5–Mn1–O4 = 72.60(3)°, O7–Mn1–O4 = 168.31(2)°,



Figure 2. View of the crystal structure of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  along the *a*-axis showing the  $R_4^2(8)$  rings. The dashed lines indicate hydrogen-bonding interactions. For the sake of clarity, all H atoms bonded to C atoms were omitted.



Figure 3. View of the  $R_4^4(24)$  graph-set motif forming a closed ring through O-H···O hydrogen bonds between methoxyacetate and water.

O3–Mn1–O1 = 155.54(2)°, and O5–Mn1–O2 = 146.24(3)°. Similar distortions can be found in manganese(II) glycolate dihydrate [13], manganese(II) L-lactate dihydrate [14] or in tetra-aqua-*bis*(oxamato-O,O')manganese(II) [32]. The equatorial positions around Mn(II) are occupied by four oxygens, O1, O2, O5, and O3, from three methoxyacetates. The axial positions are occupied by O4 of the methoxyacetate ligand and O7 of water. Deviation of manganese(II) from the mean plane formed by the four equatorial atoms

CCDC deposit no.	716104	
Empirical formula	C <sub>6</sub> H <sub>12</sub> MnO <sub>7</sub>	
Formula weight	251.10	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Temperature (K)	100(1)	
Crystal size (mm <sup>3</sup> )	$0.42 \times 0.11 \times 0.11$	
Crystal form	Polyhedron	
Crystal color	Light pink	
Unit cell dimensions (Å, °)		
a	7.9444(16)	
b	9.0802(18)	
С	13.142(3)	
$\beta$ .	93.53(3)	
Volume ( $A^3$ ), Z	946.2(3), 4	
Calculated density $(g \text{ cm}^{-3})$	1.763	
Radiation type, wavelength $(\lambda)$	Μο-Κα, 0.71073	
Absorption coefficient (mm <sup>-1</sup> )	1.405	
F(000)	516	
$\theta$ range for data collection (°)	2.56-34.45	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0212, wR_1 = 0.0597$	
R indices (all data)	$R_2 = 0.0248, wR_2 = 0.0605$	
Reflections collected	11985	
Independent reflections	$3680 [R_{int} = 0.018]$	
Limiting indices	$-12 \le h \le 12, -14 \le k \le 7, -20 \le l \le 20$	
Refinement method	Full-matrix least-squares on $F^2$	
$R[F^2 > 2\delta(F^2)], wR(F^2), S$	0.0212, 0.0597, 0.996	
Data/restraints/parameters	3680/0/129	
Completeness to $\theta = 25.00$ (%)	99.1	
$(\Delta/\delta)_{\rm max}$	< 0.001	
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min}  ({\rm e  A^{-3}})$	0.533, -0.456	

Table 1. Crystal data and structure refinement details for 1.

Table 2. Selected bond lengths (Å) and angles ( $^{\circ}$ ) for 1.

Mn1–O1	2.2842(8)	O5-Mn1-O2	146.24(3)
Mn1–O2	2.1474(7)	O7–Mn1–O2	104.22(3)
Mn1–O3	2.1280(8)	O3–Mn1–O4	87.52(3)
Mn1–O4	2.2448(8)	O5–Mn1–O4	72.60(3)
Mn1–O5	2.1388(7)	O7–Mn1–O4	168.31(2)
Mn1–O7	2.1423(9)	O2–Mn1–O4	87.09(3)
C5-O6	1.2503(10)	O3-Mn1-O1	155.54(2)
O3-Mn1-O5	119.64(3)	O5-Mn1-O1	84.42(3)
O3-Mn1-O7	90.50(3)	O7–Mn1–O1	90.06(3)
O5-Mn1-O7	98.56(3)	O2–Mn1–O1	71.13(3)
O3-Mn1-O2	85.05(3)	O4-Mn1-O1	96.51(3)

is about 0.1624(3) Å and the maximum deviation of any equatorial atom (O2) from the mean plane is about 0.2861(4) Å. The distance between the Mn ··· Mn centers in the supramolecular network is 5.355 Å. The methoxyacetate exhibits a dual nature with one CH<sub>3</sub>OCH<sub>2</sub>COO<sup>-</sup>, a bidentate ligand *via* methoxy and carboxylate oxygens, while the remaining two are tridentate with one carboxylate oxygen and methoxy oxygen coordinating to one Mn ion, whereas another carboxylic oxygen links an adjacent Mn. The result of these connections is the formation of 1-D infinite chains of [Mn(C<sub>6</sub>O<sub>6</sub>H<sub>10</sub>)]<sub>n</sub>, running approximately along the *b*-axis, separated by water molecules (figure 1). The Mn–O distances are in the range of 2.128–2.284 Å, where the longest occurs between Mn1 and O1 of methoxy while the shortest corresponds to Mn1–O3 (table 2). All Mn–O distances are similar to those commonly found in six-coordinate manganese(II) complexes (*ca* 2.1–2.2 Å [33]). The C3–O1 (1.4292(11) Å) and C6–O4 (1.4306(11) Å) bond lengths are very close to the value specified by Allen *et al.* [34] for the methoxy substituent (1.424 Å). The carboxylate C–O bond lengths in the bi- and tridentate methoxyacetate groups are equivalent (C5–O5 1.2631(10) Å, C5–O6 1.2503(10) Å and C2–O2 1.2545(10) Å, C2–O3 1.2589(10) Å), and these C–O distances are between the mean values given by Allen *et al.* (1987) for a variety of carboxylic acid groups (C–OH = 1.308 Å and C=O=1.214 Å [34]).

The crystal structure of **1** is stabilized by medium-strength  $O-H \cdots O$  hydrogen bonds in which O7 of water at (x, y, z) acts as a hydrogen-bond donor to the carboxyl oxygens of adjacent molecules at  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$  and  $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ (figure 2). Thus, each water bridges two [Mn(C<sub>6</sub>O<sub>6</sub>H<sub>10</sub>)] molecules. In turn, each carboxyl of [Mn(C<sub>6</sub>O<sub>6</sub>H<sub>10</sub>)] is hydrogen bonded to water ligands of two different molecules. These interactions lead to the formation of a specific ring motif with binary graph-set notation of  $R_4^2$ (8) [35, 36]. This hydrogen-bond pattern results in a 3-D network with graph-sets  $R_4^4$ (24) and the formation of larger macrocycles (figure 3). The H–O and O···O bond distances, as well the O–H···O angles in [Mn(C<sub>6</sub>O<sub>6</sub>H<sub>10</sub>)(H<sub>2</sub>O)]<sub>n</sub> network [H7A···O6\* 1.89 Å, O7···O6\* 2.7678(10) Å, and O7–H7A···O6\* 167.8°; and H7B···O6# 2.08 Å, O7···O6# 2.6955(11) Å, and O7– H7B···O6# 173.5°; symmetry code: (\*)  $x, \frac{1}{2} - y, \frac{1}{2} + z;$  (#)  $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ], are in the range of the values reported by Jeffrey (1997) and Steiner (2002) [37, 38] for medium-strength hydrogen bonds [H···O 1.5–2.2 Å, O···O 2.5–3.2 Å, and O–H···O > 130°, respectively].

### 3.2. FT-IR spectrum of 1

The infrared spectrum of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  confirms the structural analysis (Supplementary material). The most intense band with maximum at 1586 cm<sup>-1</sup> corresponds to the anti-symmetric C–O vibration and shifts to lower frequencies when compared to the free ligand ( $v_{as}$  1747 cm<sup>-1</sup>). The symmetric stretch of carboxylate is located at 1423 cm<sup>-1</sup>. The difference between these peaks,  $\Delta v = 163$  cm<sup>-1</sup>, is considerably smaller than observed with the corresponding acid ( $\Delta v_{acid} = 322$  cm<sup>-1</sup>) and indicates bidentate coordination of the carboxylate to manganese(II) [39–41]. A narrow absorption band of medium intensity at *ca* 1107 cm<sup>-1</sup> may be attributed to the C–O vibration of the alcoholic group of the methoxyacetate ligands. A broad and intense band between 3800 and 2600 cm<sup>-1</sup> proves the presence of water and hydrogen bonds in the complex postulated in X-ray analysis. The narrow bands at 3151, 3133, and 3117 cm<sup>-1</sup>, disturbing the v(O-H) band contour shape, arise from the v(CH) and  $v(CH_2)$  stretching modes.

# 3.3. Thermal analysis of 1

The thermogravimetric curves (Supplementary material) show that decomposition takes place in three steps. The first endothermic peak in the temperature range of  $95-140^{\circ}$ C can be attributed to the removal of one lattice water with 6.28% weight

loss (Calcd 7.17%). A second endothermic peak observed at 279.55°C corresponds to partial ligand destruction (33.21%). Further decomposition of ligands began at 307°C and ended at 672°C. The final total mass loss of 71.28% corresponds to the decomposition of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  into MnO (Calcd 71.75%).

## 3.4. EPR study of 1

The solid state EPR spectrum of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  at a room temperature consists of the single signal with the Lorentzian shape and linewidth  $\Delta B = 35.7$  mT, centered around g = 2.0188 (Supplementary material has experimental and simulated spectrum). This spectrum can be interpreted using the theory of narrowing exchange which assumes that the exchange-induced fluctuations are sufficiently rapid to average the dipolar field and describes a linewidth using the following equation [42]:

$$\Delta\omega \approx \omega_{\rm p}^2/\omega_{\rm ex}$$

where  $\Delta \omega$  is the linewidth in frequency units;  $\omega_{ex}$  is the frequency associated with isotropic exchange;  $\omega_p$  includes the contributions due to anisotropic interactions: dipolar, crystal-field, antisymmetric exchange, etc.

The EPR measurements of 1 as aqueous solution brought more detailed information about the coordination sphere of Mn(II). The ground state of Mn(II) ( $3d^5$ ) is  ${}^6S_{5/2}$ . The EPR of Mn(II) ions can be adequately described by the spin-Hamiltonian:

$$H = g\mu_{\rm B}BS + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) + ASI$$

where S = 5/2 and I = 5/2; D and E are fine structure (fs) parameters; the last term means the hyperfine interaction; the g-factor and hyperfine structure parameter A are isotropic.

The resonance spectrum of Mn(II) features five separate "allowed" *fs* components:  $M_S = \pm 5/2 \leftrightarrow \pm 3/2$ ;  $M_S = \pm 3/2 \leftrightarrow \pm 1/2$ , and  $M_S = 1/2 \leftrightarrow -1/2$ , where  $M_S$  is the magnetic quantum number of the electron spin *S*. The position of the latter *fs* component is rather insensitive to strain or electric fields produced by defects. The others, however, possess a very strong angular dependence resulting in their complete "smearing out" in polycrystals, glasses and solutions.

The recorded EPR spectrum of aqueous solution of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  is shown in figure 4. It displays only the central *fs* component, a typical X-band Mn(II) central hyperfine sextet for disordered materials where a complete smearing of the hyperfine forbidden lines and a significant broadening of hyperfine allowed lines become visible.

The spectrum simulated with the best-fit EPR parameters: g = 2.0098,  $A = 89.2 \times 10^{-4}$  cm<sup>-1</sup>, and  $\Delta B = 8.5$  mT for each hyperfine component is shown in figure 4. The value of A is consistent with Mn(II) in octahedral coordination and comparable with that of the Mn(II)-hexaaqua ion [43–45].

# **3.5.** Magnetic properties of 1

The temperature dependence of the magnetic susceptibility was collected for solid sample of **1** from 10 to 300 K. The magnetic behavior of the title compound is presented in figure 5 in the forms of  $\chi_{\rm M}$  and  $\chi_{\rm M}T$  versus T, respectively. At room temperature,



Figure 4. X-band EPR spectrum of  $[Mn(C_6O_6H_{10})(H_2O)]_n$  in aqueous solution. EPR conditions: temperature, 298 K, microwave frequency, 9.70 GHz, microwave power, 20.12 mW, modulation amplitude 2 Gpp.



Figure 5. Thermal variation of  $\chi_M(\circ)$  and  $\chi_M T(\Box)$  for **1**. The solid lines show the best fits to the data of the infinite chain model [46].

 $\chi_{\rm M}T$  is 4.59 cm<sup>3</sup> K mol<sup>-1</sup>, which is slightly larger than the value of 4.38 cm<sup>3</sup> K mol<sup>-1</sup>, expected for one isolated manganese(II) ion having spin S = 5/2, with g equal to 2. As the temperature is lowered, the value of  $\chi_{\rm M}T$  decreases continuously upon cooling and reaches 3.92 cm<sup>3</sup> K mol<sup>-1</sup> at 10 K. Magnetic susceptibility data give an effective

moment of 6.06 BM at room temperature ( $\mu_{eff}$ =5.92 BM for uncoupled five independent spins of Mn(II), (S=5/2)). The variable temperature magnetic susceptibility data follow the Curie–Weiss law,  $\chi_{M} = C/(T-\theta)$ , with  $\theta = -0.56$  K and C = 4.62 cm<sup>3</sup> K mol<sup>-1</sup>, respectively. Decrease in  $\chi_{M}T$  value with decreasing temperature and the negative Weiss constant indicate antiferromagnetic interactions between Mn(II) ions at low temperature. A decrease in the low temperature  $\chi_{M}T$  data can also arise from zero-field splitting of the  ${}^{6}A_{1g}$  ground state from distortion of the Mn<sup>2+</sup> octahedron [46]. According to the crystal structure, there are two possible exchange pathways, the first through carboxylate groups of methoxyacetate between manganese(II) centers of an infinite Mn–O–C–O–Mn chain and the other via the methoxyacetate ligand.

The magnetic behavior can be interpreted using the infinite chain model for classical S = 5/2 spins derived by Fisher from the Heisenberg model [47, 48]. The spin Hamiltonian is described as:

$$\hat{H} = -J\sum S_i S_{i-1}$$

where J is the magnetic exchange coupling between two adjacent paramagnetic metal ions in the same chain. Taking into account the interchain exchanges,

$$\chi_M = \frac{\chi_{\rm chain}}{1 - [2zJ'/Ng^2\beta^2]\chi_{\rm chain}}$$

is used for molecular field correction, in which

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2 S(S+1)}{3kT} \frac{1+u}{1-u} \quad \text{and} \quad u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right].$$



Figure 6. Magnetization curves vs. applied magnetic field at  $2 \text{ K} (\Box)$  and  $300 \text{ K} (\circ)$ .

The best fit, shown as the solid line in figure 5, afforded:  $J = -0.74 \text{ cm}^{-1}$ , g = 2.06,  $zJ' = 0.41 \text{ cm}^{-1}$ , agreement factor  $R = \sum [(\chi_M)_{obs} - (\chi_M)_{Calcd}]^2 / \sum [(\chi_M)_{obs}]^2 = 1.82 \times 10^{-6}$ . The small negative value of J implies the existence of a weak antiferromagnetic interaction between manganese(II) centers of an infinite Mn–O–C–O–Mn chain. The positive zJ' value arises from weak ferromagnetic interchain interaction through the methoxyacetate ligands and by hydrogen bonds. Figure 6 shows the magnetization curves of **1** measured at 2 and 300 K with the applied magnetic field ranging from 0 to 7.5 kOe. The linear dependence of the magnetization of the sample with the applied field is characteristic for an antiferromagnetic interaction.

# 4. Conclusions

We have reported the synthesis, X-ray structure, thermal, spectroscopic, and magnetic properties of a metal-organic complex coordination polymer  $[Mn(C_6O_6H_{10})(H_2O)]_n$ which can easily be prepared by the reaction of manganese(II) carbonate and methoxyacetic acid in aqueous solution. Methoxyacetate is a diverse ligand toward manganese(II) binding as a bi- and tridentate ligand employing methoxy and carboxylate. Similar to other carboxylato-bridged manganese coordination polymers, e.g. aqua-bispyridine *bis*-4-chlorobenzoate manganese(II) [49], aqua-(p-methoxybenzoato-O, O')-(p-methoxybenzoato-O)-(1,10-phenanthroline)-manganese(II) p-methoxybenzoic acid [50] aqua-(2,2'-bipyridine)-(4-methoxybenzoato-O,O')-(4-methoxybenzoato-O)or manganese(II) 4-methoxybenzoic acid solvate [51], the uncoordinated carboxylic oxygen of 1 is involved in hydrogen bonds with coordinated water ligands of two different molecules. These intermolecular interactions result in a 3-D network. The antiferromagnetic properties of 1 closely reflect those reported in other carboxylatobridged manganese(II) complexes [52-54]. Our further work is focused on the influence of reaction conditions, such as pH, molar ratio or temperature, to the structure and properties of the manganese methoxyacetate complexes. The coordination polymer described here can have the potential importance in the study of manganese ions and the structures of the active sites in manganese enzymes where small-molecule complexes of Mn are often used as model systems [55].

# Supplementary material

CCDC-716104 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

#### Acknowledgements

The work of the author (B. Hachuła) was partially supported by the scholarship granted in 2008 within the framework of the "University as a Partner of the Economy Based on Science" (UPGOW) project, co-financed by the European Social Fund (EFS) of the European Union.

# References

- M.C. Wilce, C.S. Bond, N.E. Dixon, H.C. Freeman, J.M. Guss, P.E. Lilley, J.A. Wilce. *Proc. Natl. Acad. Sci. USA*, 95, 3472 (1998).
- [2] M. Sundaramoorthy, K. Kishi, M.H. Gold, T.L. Poulos. J. Biol. Chem., 269, 32759 (1994).
- [3] G.E. Borgstahl, H.E. Parge, M.J. Hickey, W.F. Beyer Jr., R.A. Hallewell, J.A. Tainer. Cell, 71, 107 (1992).
- [4] M.M. Palcic, J. Ripka, K.J. Kaur, M. Shoreibah, O. Hindsgaul, M. Pierce. J. Biol. Chem., 265, 6759 (1990).
- [5] S. Yousefi, E. Higgins, Z. Daoling, A. Pollex-Kruger, O. Hindsgaul, J.W. Dennis. J. Biol. Chem., 266, 1772 (1991).
- [6] T.A. Beyer, R.L. Hill. J. Biol. Chem., 255, 5373 (1980).
- [7] J.O. Lee, L.A. Bankston, M.A. Arnaout, R.C. Liddington. Structure, 3, 1333 (1995).
- [8] A. Qu, D.J. Leahy. Proc. Natl. Acad. Sci. USA, 92, 10277 (1995).
- [9] R.H. Holm, P. Kennepohl, E.I. Salomon. Chem. Rev., 96, 2239 (1996) and references therein.
- [10] C.-Y. Cheng, S.-L. Wang. Acta Cryst., C47, 1734 (1991).
- [11] T. Lis. Acta Cryst., B33, 2964 (1977).
- [12] T. Lis, J. Matuszewski. Acta Cryst., B35, 2212 (1979).
- [13] T. Lis. Acta Cryst., B36, 701 (1980).
- [14] T. Lis. Acta Cryst., B38, 937 (1982).
- [15] H.L. Carrell, J.P. Glusker. Acta Cryst., B29, 638 (1973).
- [16] T. Lis, J. Matuszewski, B. Jeżowska-Trzebiatowska. Acta Cryst., B33, 1943 (1977).
- [17] T. Lis. Acta Cryst., C39, 39 (1983).
- [18] T.S. Yaukey, O.W. Steward, S.-C. Chang. Acta Cryst., C54, 1081 (1998).
- [19] S. Sain, T.K. Maji, G. Mostafa, T.-H. Lu, N.R. Chaudhuri. Inorg. Chim. Acta, 51, 12 (2003).
- [20] Y.-F. Deng, Z.-H. Zhou. J. Coord. Chem., 62, 778 (2009) and references cited herein.
- [21] L.-H. Li, R.N. Wine, R.E. Chapin. J. Androl., 17, 538 (1996).
- [22] O.M. Tirado, E.D. Martínez, O.C. Rodriguéz, M. Danielsen, D.M. Selva, J. Reventós, F. Munell, C.A. Suárez-Quian. *Biol. Reprod.*, 68, 1437 (2003).
- [23] L. Aasmoe, M. Mathiesen, G. Sager. Xenobiotica, 29, 417 (1999).
- [24] P.J. Beattie, M.J. Welsh, M.J. Brabec. Toxicol. Appl. Pharmacol., 76, 56 (1984).
- [25] P.M. Foster, S.C. Lloyd, D.M. Blackburn. Toxicology, 43, 17 (1987).
- [26] S.J. Rawlings, D.E. Shuker, M. Webb, N.A. Brown. Toxicol. Lett., 28, 49 (1985).
- [27] A. Starek, P. Nowak. Acta Pol. Pharm., 63, 89 (2006).
- [28] Oxford Diffraction, CrysAlis CCD & CrysAlis RED, Version 1.171.29, Oxford Diffraction Ltd, Wrocław, Poland (2008).
- [29] G.M. Sheldrick. Acta Cryst., A64, 112 (2008).
- [30] L.J. Farrugia. J. Appl. Cryst., 30, 565 (1997).
- [31] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek. J. Appl. Cryst., 39, 453 (2006).
- [32] Y. Rodríquez-Martín, C. Ruiz-Pérez, J. González-Platas, J. Sanchiz, F. Lloret, M. Julve. Inog. Chim. Acta, 315, 120 (2001).
- [33] J. Drummond, J.S. Wood. J. Chem. Soc. A, 226 (1970).
- [34] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor. J. Chem. Soc., Perkin Trans., 2, S1 (1987).
- [35] M.C. Etter, J.C. MacDonald, J. Bernstein. Acta Cryst., B46, 256 (1990).
- [36] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang. Angew. Chem. Int. Ed. Engl., 34, 1555 (1995).
- [37] G.A. Jeffrey. An Introduction to Hydrogen Bonding, p. 12, Oxford University, New York (1997).
- [38] T. Steiner. Angew. Chem. Int. Ed., 41, 48 (2002).
- [39] A.I. Grigor'ev. Zh. Neorg. Khim., 13, 802 (1963).
- [40] D.A. Edwards, R.N. Hayward. Can. J. Chem., 46, 3443 (1968).
- [41] G.B. Deacon, R.J. Phillips. Coord. Chem. Rev., 33, 227 (1980).
- [42] A. Abragam, B. Bleaney. Electron Paramagnetic Resonance of Transition Metal Ions, p. 454, 518, Clarendon Press, Oxford (1970).
- [43] G.H. Reed, G.D. Markham. In *Biological Magnetic Resonance*, L.J. Berliner, J. Reuben (Eds), Vol. 6, pp. 73–142, Plenum Press, New York (1984).

- [44] V.K. Jain, G. Lehmann. Phys. Status Solidi B, 159, 495 (1990).
- [45] B. Ke. *Photosynthesis: Photobiochemistry and Photobiophysics*, Ch. 19, pp. 337–354, Kluwer Academic Publishers, Dordrecht (2001).
- [46] R.L. Carlin. Magnetochemistry, Springer-Verlag, New York (1986).
- [47] M.E. Fisher. Am. J. Phys., 32, 343 (1964).
- [48] O. Kahn. Molecular Magnetism, p. 258, VCH Publishers, New York (1993).
- [49] R. Sarma, A. Perumal, J.B. Baruah. J. Coord. Chem., 62, 1513 (2009).
- [50] J. Wang, L. Ping, Y. Chen, Z. Liu. Acta Cryst., E60, m628 (2004).
- [51] J. Wang, M.-H. Huang, W.-D. Cheng, P. Liu. Chin. J. Struct. Chem., 26, 33 (2007).
- [52] X.-M. Lu, P.-Z. Li, X.-T. Wang, S. Gao, X.-J. Wang, S. Wang, Y.-H. Deng, Y.-J. Zhang, L. Zhou. Polyhedron, 27, 2402 (2008).
- [53] J.-M. Shi, W. Xu, W. Xu, C.-J. Wu, W.-T. Yu. Transition Met. Chem., 28, 308 (2003).
- [54] J.-M. Shi, H.-L. Yin, C.-J. Wu. J. Coord. Chem., 58, 915 (2005).
- [55] Z. Zhi, L.-R. Zhang, S. Gang, G. Yang, J. Hua, L. Gao, S. Feng. Inorg. Chem., 39, 1990 (2000).