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Synthesis and characterization of triaquabis(1,1-cyclobutanedicarboxylato-O,O′,O″,O‴)dimanganese(II)

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Abstract

The manganese(II) complex, $[Mn_2(C_6H_6O_4)_2(H_2O)_3]$ was synthesized and characterized by X-ray crystallography, IR spectra and thermal analysis. The manganese salt crystallizes in the monoclinic system, space group $C2/c$. Mn ions are coordinated to six oxygen atoms. The coordination polyhedron around the Mn ion can be described as a distorted octahedron. The manganese(II) complex has a chain structure. The repeating dimeric unit consists of Mn(II) atoms bridged by oxygens from two carboxylate ligands and one water molecule. The carboxylate ligands occur as tridentate-bridging and monodentate. The compound dehydrates at 403 K and then decomposes at 500 K first to Mn_2O_3 which transforms into Mn_3O_4 at 1183 K. The thermal decomposition is connected with release of water (405 K), carbon dioxide (470 K) and hydrocarbons (595 K). The IR spectra of the salt are discussed.

Keywords: Manganese complexes; 1,1-Cyclobutanedicarboxylate complexes; Crystal structures; IR spectra; Thermal analysis; TG-FTIR analysis

1. Introduction

Manganese is one of the trace elements which plays an important role in some biological systems. It is essential for the oxidation of water to O_2 in photosynthetic processes. Manganese participates in the disproportionation of hydrogen peroxide (catalase activity) in microorganisms [1,2] and in the formation of various metalloenzymes such as superoxide dismutase, pyruvate carboxylase [2,3], arginase and enolase [2,4,5]. These facts have contributed to an increase of interest in the coordination chemistry of manganese, especially complexes with carboxylato ligands.

The present work reports the crystal structure and properties of the manganese(II) complex with 1,1-cyclobutanedicarboxylic acid. The first results were presented at ICCC [6]. 1,1-Cyclobutanedicarboxylic acid is a component of carboplatin, which is widely used as a drug in cancer chemotherapy [7–10].

2. Experimental

2.1. Synthesis

1,1-Cyclobutanedicarboxylic acid was dissolved in boiling water. The resulting solution was then neutralized by the addition of manganese(II) carbonate. The solution was filtered to remove any excess manganese(II) carbonate and the filtrate was then reduced in volume to yield the metal complex. The single crystals were obtained by recrystallization from an aqueous solution after a few weeks. Cream crystals were isolated, washed with ethanol and dried at room temperature. The contents of carbon and hydrogen were determined on the basis of elemental analysis using a CHN 2400 Perkin–Elmer analyser. Chemical analysis confirms the composition (Table 1).

2.2. Magnetism

Magnetic susceptibility measurement was conducted at 294 K using a magnetic susceptibility balance MSB-MKI, Sherwood Scientific Ltd, Cambridge. The data

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Table 1
Elemental analyses and magnetic moment of manganese(II) 1,1-cyclobutanedicarboxylate trihydrate

M (%)		C (%)		H (%)		μ_{eff} (BM)	Colour
Calc.	Found	Calc.	Found	Calc.	Found		
24.53	24.47	32.15	32.57	4.02	3.73	5.69	cream

were corrected for diamagnetic susceptibilities. The effective magnetic moment was calculated by the equation $\mu_{eff} = 2.828(\chi_{cor}T)^{1/2}$.

2.3. X-ray structure determination

The crystal system, space group and approximately unit cell dimensions were determined from the radiation on Weissenberg photographs. Intensities of reflection were measured on Kuma KM-4, using Mo Kα radiation. The crystallographic data and the refinement procedure details are given in Table 2. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXS-97 and refined by the full-matrix least-square methods using the SHELXL-97 program [11,12]. The positions of all hydrogen atoms were determined from the difference Fourier map. Several cycles of refinement of coordinates and thermal parameters (anisotropic for non-hydrogen and isotropic for hydrogen atomic) reduced the R-value to 0.0279. Scattering factors were those incorporated in SHELXL-97. Selected bonding parameters and torsion angles are listed in Tables 3 and 4. The distances Mn···Mn were measured using the MERCURY-1.1 program.

Table 2
Crystal data and structure refinement

Formula	$C_{12}H_{18}Mn_2O_{11}$
M_r	448.14
Crystal system	monoclinic
Space group	$C2/c$
T (K)	100(1)
Wavelength (Å)	0.71073
a (Å)	19.661(4)
b (Å)	8.112(2)
c (Å)	10.062(2)
β (°)	98.23(3)
Volume (Å^3)	1588.3(5)
Z	4
$F(0\,0\,0)$	912
Absorption coefficient (mm^{-1})	1.649
D_{calc} (Mg m^{-3})	1.874
Crystal size (mm)	0.20 × 0.15 × 0.12
Reflections measured	5259
θ range for data collection (°)	3.49–28.38
Index ranges	$-25 \leq h \leq 25$, $-10 \leq k \leq 10$, $-13 \leq l \leq 10$
Data $[I > 2\sigma(I)]$/parameters	1621/150
Goodness-of-fit on F^2	1.053
Final R indices $[I > 2\delta(I)]$	$R_1 = 0.0279$, $wR_2 = 0.0743$
R indices (all data)	$R_1 = 0.0295$, $wR_2 = 0.0757$
Largest diff. peak and hole (e Å^{-3})	0.549 and −0.465

2.4. IR

The IR spectra of complex were recorded over the range 4000–400 cm^{-1} using a FTIR 1725X Perkin–Elmer spectrometer. The samples were prepared as KBr discs.

2.5. Thermal analysis

The thermal stability and decomposition of the prepared complexes in air were determined with the aid of Setsys 16/18, recording TG, DTA and DTG curves. Samples (8 mg) were heated in Al_2O_3 crucibles at 293–1273 K in flowing air atmosphere with a heating rate of 10 K min^{-1}. The products of decomposition were calculated from TG curves (Fig. 2). Netzsch TG apparatus coupled with a Bruker FTIR IF566 spectrophotometer identified the gas-phase products of decom-

Table 3
Selected bond lengths (Å) and angles (°)

Bond lengths			
Mn(1)–O(1)	2.1421(13)	Mn(1)–O(3)	2.2527(12)
Mn(1)–O(3)^{i}	2.1641(12)	O(3)–Mn(1)^{i}	2.1641(12)
Mn(1)–O(4)^{ii}	2.1678(12)	O(4)–Mn(1)^{iv}	2.1678(12)
Mn(1)–OW1	2.1899(13)	OW2–Mn(1)^{iii}	2.2484(11)
Mn(1)–OW2	2.2484(11)		
O(1)–C(5)	1.269(2)	O(3)–C(6)	1.288(2)
O(2)–C(5)	1.249(2)	O(4)–C(6)	1.243(2)
Bond angles			
O(2)–C(5)–O(1)	123.84(15)	O(4)–C(6)–O(3)	124.05(14)
O(1)–Mn(1)–O(3)^{i}	158.09(5)	O(3)^{i}–Mn(1)–O(3)	74.98(5)
O(1)–Mn(1)–O(4)^{ii}	102.32(5)	O(4)^{ii}–Mn(1)–O(3)	96.65(5)
O(3)^{i}–Mn(1)–O(4)^{ii}	86.71(5)	OW1–Mn(1)–O(3)	95.11(5)
O(1)–Mn(1)–OW1	88.78(5)	OW2–Mn(1)–O(3)	176.76(4)
O(3)^{i}–Mn(1)–OW1	86.74(5)	Mn(1)^{iii}–OW2–Mn(1)	105.61(7)
O(4)^{ii}–Mn(1)–OW1	164.57(5)	Mn(1)^{i}–O(3)–Mn(1)	105.02(5)
O(1)–Mn(1)–OW2	94.98(5)	C(5)–O(1)–Mn(1)	118.73(10)
O(3)^{i}–Mn(1)–OW2	105.56(5)	C(6)–O(3)–Mn(1)^{i}	123.28(10)
O(4)^{ii}–Mn(1)–OW2	86.58(4)	C(6)–O(3)–Mn(1)	130.81(10)
OW1–Mn(1)–OW2	81.76(4)	C(6)–O(4)–Mn(1)^{iv}	138.11(10)
O(1)–Mn(1)–O(3)	84.09(5)		

Symmetry code: (i) $-x, -y, -z+1$; (ii) $x, -y, z-1/2$; (iii) $-x, y, -z+1/2$; (iv) $x, -y, z+1/2$.

Table 4
Selected torsion angles (°)

Atom	Atom	Atom	Atom	Angle (°)
O(1)	Mn(1)	OW2	Mn(1)^{iii}	152.40(3)
O(3)^{i}	Mn(1)	OW2	Mn(1)^{iii}	−35.30(3)
O(4)^{ii}	Mn(1)	OW2	Mn(1)^{iii}	50.32(3)
OW1	Mn(1)	OW2	Mn(1)^{iii}	−119.56(4)
O(3)	Mn(1)	OW2	Mn(1)^{iii}	−134.4(7)
O(1)	Mn(1)	O(3)	Mn(1)^{i}	173.47(5)
O(3)^{i}	Mn(1)	O(3)	Mn(1)^{i}	0.0
O(4)^{ii}	Mn(1)	O(3)	Mn(1)^{i}	−84.77(5)
OW1	Mn(1)	O(3)	Mn(1)^{i}	85.23(5)
OW2	Mn(1)	O(3)	Mn(1)^{i}	100.0(7)
Mn(1)	O(1)	C(5)	C(1)	57.75(16)
Mn(1)^{iv}	O(4)	C(6)	C(1)	147.67(12)
Mn(1)^{i}	O(3)	C(6)	C(1)	162.94(10)
Mn(1)	O(3)	C(6)	C(1)	−4.59(19)

Symmetry code: (i) $-x, -y, -z+1$; (ii) $x, -y, z-1/2$; (iii) $-x, y, -z+1/2$; (iv) $x, -y, z+1/2$.

position (Fig. 3). The samples (10.2 mg) were heated to 1273 K in Al_2O_3 erucibles, in an argon atmosphere, at a heating rate of 10 K min^{-1}.

3. Results and discussion

3.1. Magnetism

The magnetic moment of the manganese(II) complex (5.69 BM) is in the range of values expected for a high-spin complex.

3.2. X-ray structure determination

Crystals of manganese(II) 1,1-cyclobutanedicarboxylate are monoclinic, and have space group *C*2/*c*. The polymeric structure of the complex comprises of a dimeric $[Mn_2(C_6H_6O_4)_2(H_2O)_3]$ repeating unit. The structure is shown in Fig. 1. The distance between neighboring Mn(II) atoms in the dimeric units is 3.505 Å. The water molecule and two carboxylate groups from two different ligands link the dimeric units, yielding infinite chains that run parallel to the *c* axis; where neighboring chains are connected via hydrogen bonds. The distance between neighboring Mn(II) atoms in chains is 3.582 Å, the shortest interchain Mn···Mn separation is 5.431 Å. Each Mn(II) ion is six coordinated and the coordination is that of a significantly distorted octahedron. Each manganese(II) cation is surrounded by four carboxylate oxygen atoms from three different 1,1-cyclobutanedicarboxylic anions and by two water oxygen atoms. The Mn–O$_{carboxyl}$ distances vary in the range 2.1421(13)–2.2527(12) Å while the M–O$_{water}$ bond lengths are 2.1899(13) and 2.2484(11) Å (Table 3). The angles, which are 90° or 180° in a regular octahedral arrangement, range from 74.98(5)° to 105.56(5)° and from 158.09(5)° to 176.76(4)°, respectively. The carboxylate groups in the complex studied have the tridentate-bridging (O(3)–C(6)–O(4)) and monodentate (O(1)–C(5)–O(2)) character. The carboxylate groups O(3)–C(6)–O(4) and (O(1)–C(5)–O(2) are rotated by 63.0(1)° and 55.0(1)° from C1–C2–C4 plane of the cyclobutane ring. The C–O bonds are within the

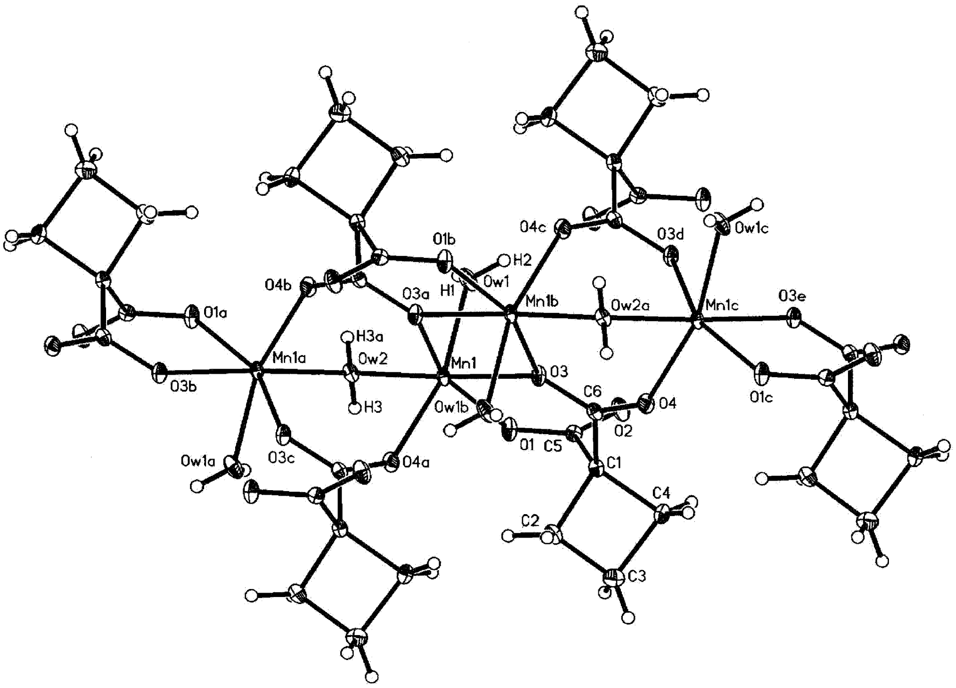

Fig. 1. The structure of $[Mn_2(C_6H_6O_4)_2(H_2O)_3]$.

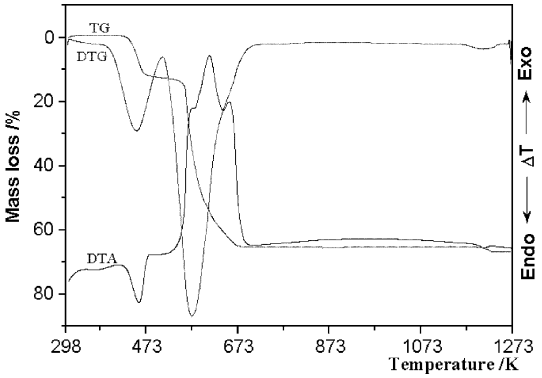

Fig. 2. TG, DTA and DTG curves of manganese(II) 1,1-cyclobutanedicarboxylate.

range from 1.243(2) to 1.288(2) Å and the O–C–O angles are 123.84(15)° and, 124.05(14)°.

The $C_{carboxyl}$–C_{ring} bonds length and all distances C–C in the ring are similar to those in 1,1-cyclobutanedicarboxylic acid [13]. The cyclobutane ring, like the free acid, is puckered with internal rotation (torsion) angles of approximately 17° (15° in free acid) [13,14].

The water molecules (OW1 and OW2) take part in hydrogen bonds as proton acceptors; the distances are 2.6309(17)–2.7864(17) Å (Table 5).

3.3. IR

The IR spectrum of the manganese(II) complex displays very strong absorptions at 1610, 1561 cm^{-1} and 1340 cm^{-1}; which are due to the characteristic $\nu_{as}(COO)$ and $\nu_s(COO)$ stretching modes of the carboxyl group; the splittings ($\Delta\nu$) are 270 and 221 cm^{-1}. The first value of $\nu_{as}(COO)$ shifts to higher frequencies and $\nu_s(COO)$ is the same compared to sodium salts with 1,1-cyclobutanedicarboxylic acid. In addition, the first value $\Delta\nu$ being higher than the $\Delta\nu$ value of sodium suggests that one carboxylate group is unidentate. The second value $\Delta\nu$ is characteristic for a chelating bidentate group; the value $\nu_{as}(COO)$ shifts to lower frequencies and $\nu_s(COO)$ is the same indicating an unsymmetrical bridging bidentate carboxylate group. This different nature of the carboxylic group might be connected with the unusual coordination mode of the carboxylic group [15–17]. In the structure of manganese(II) 1,1-cyclobutanedicarboxylate, the carboxylic group occurs as unidentate and tridentate groups (Table 3).

Table 5
Hydrogen-bonds lengths (Å) and angles (°) for manganese(II) 1,1-cyclobutanedicarboxylate

D–H···A	D–H	H···A	D···A	∠DH···A
OW1–H(1)···O(1)^{v}	0.84(3)	1.91(3)	2.7415(18)	171(3)
OW1–H(2)···O(2)^{vi}	0.79(3)	2.07(3)	2.7864(19)	151(2)
OW2–H(3)···O(2)^{vii}	0.87(2)	1.77(2)	2.6309(17)	170(2)

Symmetry code: (v) $-x, -y+1, -z+1$; (vi) $-x, y, -z+3/2$; (vii) $x, -y+1, z-1/2$.

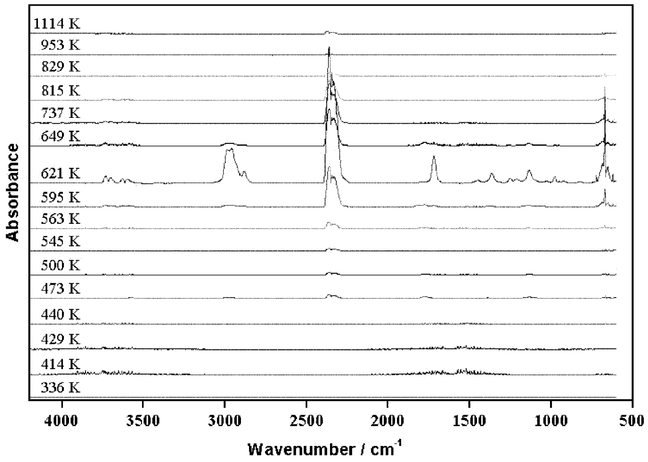

Fig. 3. FTIR spectra of gaseous products of thermal decomposition of manganese(II)1,1-cyclobutanedicarboxylate trihydrate.

In the spectrum strong bands characteristic for water molecules are observed; the bands at 3403 cm^{-1} are assigned to OH stretching vibrations and at 1667 cm^{-1} to the deformation vibration $\delta(H_2O)$ [18].

3.4. Thermal analysis

Manganese(II) 1,1-cyclobutanedicarboxylate is stable at room temperature. Upon heating the dehydration process begins at 403 K and the complex loses three water molecules becoming anhydrous. A calculated weight loss due to removal of all water molecules is 12.06%, while the measured weight losses are 12.50%. In the first stage, the dehydration process is reflected by FTIR spectra of the gaseous decomposition at 405 K; characteristic valence and deformation vibration bands of water molecules appear in the wavenumber ranges of 4000–3500 cm^{-1} and 2050–1250 cm^{-1}, respectively. The anhydrous complex is stable up to 500 K and then it decomposes into Mn_2O_3 (found and calculated weight losses are 64.92 and 64.75%, respectively). At 470 K weak bands characteristic for carbon dioxide (2350–2250 cm^{-1} and 750–600 cm^{-1}) appear. At 595 K temperature bands in the wavenumber ranges 3050–2850 cm^{-1} and 1500–850 cm^{-1} are observed. This region is characteristic for stretching (ν(CH)) and skeleton (γ(C–C)) vibrations. These bands are connected with occurrence of gaseous hydrocarbons, probably with cyclobutane, alkanes and alkenes. Upon further heating, these bands disappear at 665 K. During heating up to 1183 K Mn_2O_3 transforms into Mn_3O_4, which is the final product of decomposition (found weight loss 66.03%, calculated 65.94%). The decomposition scheme for manganese(II) can be presented as follows;

$$Mn_2(C_6H_6O_4)_2\cdot 3H_2O \xrightarrow{\text{Endo}} Mn_2(C_6H_6O_4)_2 \xrightarrow{\text{Exo}} Mn_2O_3 \xrightarrow{\text{Endo}} Mn_3O_4$$

4. Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition number 202260 (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). (only 2 hyphens in fax number).

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References

[1] R.H. Holm, P. Kennepohl, E.J. Solomon, Chem. Rev. 96 (1996) 2239.

[2] J.E. Penner-Hahn, Encyclopaedia of Inorganic Chemistry, vol. 4, Wiley, Chichester, 1994.

[3] A. Garcia-Deibe, M.R. Bermejo, A. Sousa, C.A. McAuliffe, P. McGlynn, P.T. Ndifon, R.G. Pritchard, J. Chem. Soc. Trans. (1993) 1605.

[4] G.Ch. Dismukes, Chem. Rev. 96 (1996) 2909.

[5] J.E. Sheats, R.S. Czernuszewicz, G.Ch. Dismukes, A.L. Rheingold, V. Petrouleas, J. Stubbe, W.H. Armstrong, R.H. Beer, S.J. Lippard, J. Am. Chem. Soc. 109 (1987) 1435.

[6] Z. Rzaczynska, A. Bartyzel, A. Ostasz, T. Glowiak, 35th International Conference on Coordination Chemistry ICCC35, Heidelberg, July 21–26, 2002.

[7] J. Kuduk-Jaworska, Poszukiwania cytostatycznych zwiazków koordynacyjnych platyny, Wydawnictwo Uniwersytetu Wroclawskiego, Wrocław, 1993.

[8] A.D.Q. Ferreira, A. Bino, D. Gibson, Inorg. Chim. Acta 265 (1997) 155.

[9] T. Rau, M. Shoukry, R. van Eldik, Inorg. Chem. 36 (1997) 1454.

[10] M.M.A. Mohamed, M. Shoukry, Polyhedron 20 (2001) 343.

[11] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

[12] G.M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[13] L. Soltzberg, T.N. Margulis, J. Chem. Phys. 55 (1971) 4907.

[14] D.D. Santarsiero, J. Chem. Phys. 92 (1990) 3794.

[15] Z. Sun, P.K. Gantzel, D.N. Hendrickson, Polyhedron 17 (1998) 1511.

[16] B.S. Manhass, A.K. Trikha, J. Indian Chem. Soc. (1982) 315.

[17] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.

[18] K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, Wiley, New York, 1986.