

New Dinuclear Mn(II) Phenanthroline Adipato Complex: Synthesis and Structural and Thermal Characterization of $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$

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Reaction of freshly precipitated $\text{Mn}(\text{OH})_{2-2x}(\text{CO}_3)_x \cdot y\text{H}_2\text{O}$, adipic acid and phenanthroline in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ afforded a new dinuclear Mn(II) complex, $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$ **1**, aside the known $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ **2**. Single crystal X-ray analyses showed that complex **1** consists of the centrosymmetric dinuclear molecules resulting from two $[\text{Mn}(\text{phen})(\text{H}_2\text{O})]^{2+}$ moieties bridged by two twisted tridentate adipato ligands. The Mn atoms are each in severely distorted octahedral geometry defined by two N atoms of one phen ligand, three carboxyl O atoms of two adipato ligands and one H_2O molecule with $d(\text{Mn}-\text{N}) = 2.246$ and 2.296 \AA and $d(\text{Mn}-\text{O}) = 2.066 - 2.339 \text{ \AA}$. The complex molecules are assembled *via* $\pi-\pi$ stacking interactions into 2D layers, which are held together by both strong $\text{O}-\text{H} \cdots \text{O}$ and weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds. The thermal behavior of **1** and **2** upon heating in argon stream is discussed.

Key words: Manganese, Phenanthroline Complex, $\pi-\pi$ Stacking Interactions, Thermal Behavior

Introduction

Our recent research interest has been intensively focused on the construction of coordination polymers based on self-assembly of transition metal cations with α,ω -dicarboxylate anions in the presence of neutral heteroaromatic N-donor chelating ligands such as bipyridine and phenanthroline [1–6]. The α,ω -dicarboxylate anions proved to be efficient and flexible bridging spacers to constitute 1D, 2D and 3D coordination polymers [7] and the heteroaromatic N-donor ligands to function as a basis for $\pi-\pi$ stacking interactions [8]. Self-assembly of Mn^{2+} ions with phen and succinate ions results in various interesting structural motifs such as chelated mononuclear $[\text{Mn}(\text{phen})_2(\text{C}_4\text{H}_4\text{O}_4)]$ [9] and bridged dinuclear $[\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_4(\text{C}_4\text{H}_4\text{O}_4)_2]$ [9, 10] complex molecules aside the mononuclear $[\text{Mn}(\text{phen})(\text{H}_2\text{O})_3(\text{C}_4\text{H}_4\text{O}_4)]$ compound [11]. The employment of glutarate in place of succinate anion led to mononuclear $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_5\text{H}_6\text{O}_4)]$ molecule [12], glutarato-bridged dumbbell-like dinuclear $[\text{Mn}_2(\text{phen})_4(\text{C}_5\text{H}_6\text{O}_4)]^{2+}$ cations [13] and glutarato-bridged ribbon-like $1\text{D} \infty \{[\text{Mn}(\text{phen})]_2\text{L}_{4/2}\}$ zigzag chains with alternative 8- and 16-membered

rings [14]. Reportedly, reaction of manganese adipate monohydrate with phen in aqueous ethanol gave $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ consisting of crystal H_2O molecules and $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)]$ complexes [15]. Hitherto, however, no glutarato- and adipato-bridged cyclic dinuclear Mn(II) complex molecules have been reported. Our investigation showed that freshly precipitated $\text{Mn}(\text{OH})_{2-2x}(\text{CO}_3)_x \cdot y\text{H}_2\text{O}$ reacts with adipic acid and phenanthroline in aqueous methanol to yield a new dinuclear Mn(II) complex, $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$ (**1**), aside the known $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ (**2**) reported by McCann and coworkers [15]. Here we present our results about syntheses and crystal structure of **1** and about the thermal behavior of **1** and **2**.

Experimental Section

Measurements of physical properties

All chemicals of p. a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Heraeus Rapid-CHNO elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range $4000 - 400 \text{ cm}^{-1}$ on a Shimadzu FTIR-

Table 1. Crystal and refinement data for $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$

Formula; mole mass	$\text{C}_{18}\text{H}_{18}\text{MnN}_2\text{O}_5$; 397.28 amu
Crystal shape	orange plate
Crystal size	$0.311 \times 0.222 \times 0.133$
Space group, formula units	$P\bar{1}$ (no. 2), 2
Unit cell dimensions	$a = 8.260(2) \text{ \AA}$, $b = 9.787(2) \text{ \AA}$ $c = 11.954(2) \text{ \AA}$, $\alpha = 70.52(1)^\circ$ $\beta = 75.42(2)^\circ$, $\gamma = 72.22(1)^\circ$
V ; D_x	$855(5) \text{ \AA}^3$; 1.543 g cm^{-3}
Measurement	Bruker P4 four-circle diffractometer, Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$); $\vartheta/2\vartheta$ scan mode, $2^\circ \leq 2\vartheta \leq 55^\circ$
Structure refinement	Empirical absorption correction (ψ -scan method); direct methods, difference Fourier syntheses; full-matrix least-squares refinement, $w = [\sigma^2(F_o^2) + (0.0224P)^2 + 1.08P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$, SHELXS-97 [18], SHELXL-97 [18]
μ ; Transmission	$0.0804 \text{ (mm}^{-1}\text{)}$; $0.734 - 0.786$
Extinction coefficient	$0.0039(8)$
N (parameter)	246
N (hkl) (meas./unique)	4709/3897
N (hkl) ($I > 2(I)$)	2760
R_1 ; wR_2 ($I \geq 2\sigma(I)$) ^a	0.0482; 0.1046
R_1 ; wR_2 (all data) ^a	0.0762; 0.1168
Goodness of fit on F^2	1.048
$\delta\rho_{\text{min}}$; $\delta\rho_{\text{max}}$	-0.381 ; $0.378 \text{ [e} \cdot \text{\AA}^{-3}\text{]}$

$$^a wR_2 = \sum wF_o^2 F_c^2 / \sum w(F_o^2)^2)^{1/2}$$

8900 spectrometer. The combined measurements on thermogravimetric and differential thermal analyses (TG/DTA) were carried out between 25–500 °C on powdered samples in an argon stream using a Seiko Exstar6000 TG/DTA6300 equipment with a heating rate of 10 °C/min.

Preparation

For an optimized synthesis, freshly precipitated $\text{Mn}(\text{OH})_{2-2x}(\text{CO}_3)_x \cdot y\text{H}_2\text{O}$ is necessary.

Dropwise addition of 4.0 ml of a 1 M solution of Na_2CO_3 to a stirred aqueous solution of 0.433 g (2.50 mmol) of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 5.0 ml of H_2O gave a white precipitate, which was separated by centrifugation and washed with distilled water several times until no SO_4^{2-} anions were detectable. 0.504 g (2.5 mmol) of phenanthroline monohydrate and 20 ml of CH_3OH were successively added to a stirred aqueous solution of 0.375 g (2.5 mmol) of adipic acid in 20 ml of H_2O to form a clear solution, to which the above fresh $\text{Mn}(\text{OH})_{2-2x}(\text{CO}_3)_x \cdot y\text{H}_2\text{O}$ precipitate was added. The mixture was stirred for 30 min and a little insoluble solid was filtered off. The yellow filtrate (pH = 5.93) was allowed to stand at room temperature. Slow evaporation during one week afforded well-

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for non-hydrogen atoms in $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Mn	0.56904(7)	0.65244(5)	0.79001(4)	0.0352(2)
N(1)	0.4757(4)	0.7588(3)	0.6124(2)	0.0388(6)
N(2)	0.7233(4)	0.5032(3)	0.6671(2)	0.0377(6)
O(1)	0.7767(3)	0.5749(3)	0.7364(2)	0.0409(5)
O(2)	0.8023(3)	0.7627(3)	0.8967(2)	0.0475(6)
O(3)	0.6142(4)	1.2080(3)	0.9479(2)	0.0659(8)
O(4)	0.6037(3)	1.1805(3)	1.1411(2)	0.0573(7)
O(5)	0.4346(3)	0.4827(3)	0.8855(2)	0.0388(6)
C(1)	0.3546(5)	0.8831(4)	0.5865(3)	0.0509(9)
C(2)	0.3082(6)	0.9486(5)	0.4720(4)	0.062(1)
C(3)	0.03893(6)	0.08822(5)	0.3835(4)	0.065(1)
C(4)	0.05166(5)	0.7483(5)	0.4067(3)	0.052(1)
C(5)	0.6048(6)	0.6679(6)	0.3206(3)	0.064(1)
C(6)	0.7251(6)	0.5422(6)	0.3472(3)	0.063(1)
C(7)	0.7738(5)	0.4807(4)	0.4648(3)	0.0477(9)
C(8)	0.9005(5)	0.3503(5)	0.4975(4)	0.061(1)
C(9)	0.9354(5)	0.2979(5)	0.6119(4)	0.059(1)
C(10)	0.8422(5)	0.3786(4)	0.6951(3)	0.0485(9)
C(11)	0.6874(4)	0.5554(4)	0.5530(3)	0.0381(7)
C(12)	0.5586(4)	0.6905(4)	0.5243(3)	0.0377(7)
C(13)	0.8512(4)	0.6779(3)	0.8328(3)	0.0353(7)
C(14)	0.9960(4)	0.6984(4)	0.8752(3)	0.0401(8)
C(15)	0.9315(4)	0.7607(4)	0.9839(3)	0.0403(8)
C(16)	0.8105(4)	0.9152(4)	0.9582(3)	0.0407(8)
C(17)	0.7562(5)	0.9759(4)	1.0669(3)	0.0470(9)
C(18)	0.6489(4)	1.1351(4)	1.0485(3)	0.0416(8)

shaped orange crystals of $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$ (**1**) (yield: ca. 47% based on the initial $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ input). After separation, the filtrate was further kept at room temperature and greenish yellow prismatic crystals of the known $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ (**2**) grew within the next day (yield: ca. 35% based on the initial $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ input). Analysis for $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$ (**1**): calcd. C 54.42, H 4.57, N 7.05; found: C 54.79, H 4.69, N 7.28. IR (cm^{-1}): 3383m, 2943m (sh), 2905w, 2860w, 2799vw, 1580vvs (sh), 1543vs (sh), 1516vs (sh), 1458m (sh), 1427vs (sh), 1414vvs (sh), 1356m (sh), 1344m (sh), 1310m, 1240w, 1188m, 1144m, 1099m, 864m (sh), 849s (sh), 775m, 729s (sh) (sh = sharp).

X-ray structural analyses

A suitable single crystal was selected under a polarizing microscope and fixed with epoxy cement on the tip of a fine glass fibre, which was then mounted on a Bruker P4 diffractometer for cell determination and data collection. The lattice parameters were refined from the 2ϑ values ($10 - 25^\circ$) of 25 carefully centered reflections. The reflection intensities with $2\vartheta_{\text{max}} = 55^\circ$ were collected at 293 K using the ϑ - 2ϑ scan technique. On the basis of the monitored reflec-

tions, the employed single crystals exhibited no detectable decay during the data collection. The data were corrected for L_p and absorption effects. SHELXS-97 [16] and SHELXL-97 [17] programs were used for structure determination and refinement. The structures were solved by using direct methods. The hydrogen atoms associated with carbon atoms were generated geometrically, and the aqueous hydrogen atoms were located from the difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques [17], and hydrogen atoms with isotropic displacement parameters. Detailed informations about the crystal data and structure determination are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are listed in Table 2 and selected interatomic distances and bond angles are given in Table 3. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 206604 ($C_{18}H_{18}MnN_2O_5$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and IR spectrum

Repeated experiments showed that reaction of freshly precipitated $Mn(OH)_{2-2x}(CO_3)_x \cdot yH_2O$, adipic acid and phenanthroline in a mixed solvent comprising equivooluminal H_2O and CH_3OH produced a clear solution with $pH = 5.93$. Slow evaporation at room temperature resulted firstly in formation of orange crystals of the title dinuclear complex $Mn_2(phen)_2(H_2O)_2(C_6H_8O_4)_2$ (**1**) and then greenish yellow crystals of the known $[Mn(phen)_2(H_2O)(C_6H_8O_4)] \cdot 7H_2O$ (**2**) after separation of **1**. If the initial aqueous methanolic solution was adjusted to $pH = 7.70$ by dropwise adding Na_2CO_3 , slow evaporation afforded a mixture of **1** and **2**. Although a lot of efforts have been dedicated, no pure complex **2** was obtained prior to **1**. The fact suggests that crystal growth of **1** is kinetically more favorable and presence of **1** deters formation of **2** and, on the other hand, the nature of the product is pH dependent.

The IR spectrum shows a broad band centered at 3383 cm^{-1} due to the O–H stretching vibrations of the aqua ligand. In comparison with the IR spectrum of phenanthroline monohydrate and that of phenanthroline, which was obtained from dehydration of phenanthroline monohydrate under dynamic vacuum at $120\text{ }^\circ\text{C}$, the absorptions at 1516, 1144, 1099, 864,

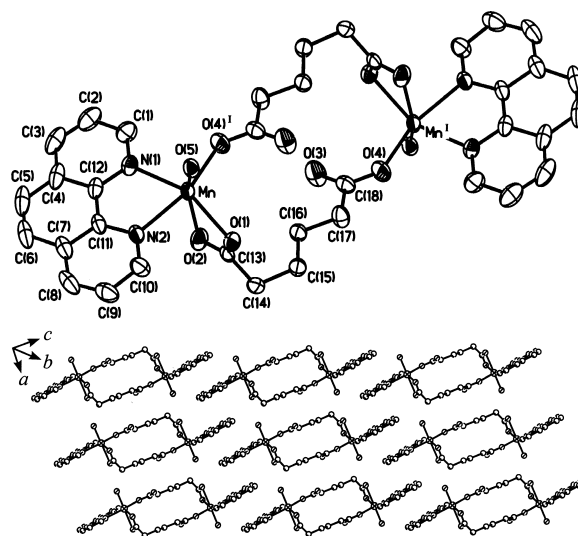


Fig. 1. (Top) Ortep view of the dinuclear $[Mn_2(phen)_2(H_2O)_2(C_6H_8O_4)_2]$ complex molecule with atomic labelling for **1** (the displacement ellipsoids are drawn at 45% probability and H atoms have been omitted for clarity); (Bottom) Supramolecular assembly of dinuclear $[Mn_2(phen)_2(H_2O)_2(C_6H_8O_4)_2]$ complex molecules *via* intermolecular π – π stacking interactions into a 2D layer parallel to $(01\bar{1})$.

$849, 775, 729\text{ cm}^{-1}$ with medium to strong intensity are related to the heteroaromatic N-donor ligand and those at 2943, 2905, 2860 cm^{-1} to the C–H and C–C vibrations of the adipato ligands. The sharp strong absorptions at 1580 and 1543 cm^{-1} and the strong sharp band at 1427 cm^{-1} could be assigned, respectively, to the symmetric and asymmetric stretching vibrations of COO groups, indicating different coordination modes of the terminal carboxylate groups of the adipate anion.

Structure description

The title Mn(II) complex **1** consists of centrosymmetric dinuclear $[Mn_2(phen)_2(H_2O)_2(C_6H_8O_4)_2]$ molecules, whose centers are situated at the crystallographic $1d$ positions. As shown in Fig. 1, the complex molecules are generated from two $[Mn(phen)(H_2O)]^{2+}$ moieties bridged by two twisted $(C_6H_8O_4)^{2-}$ adipate anions. The Mn atoms are in a severely distorted octahedral environment defined by two N atoms of one phen ligand, three carboxyl O atoms of two adipato ligands and one water O atom. The Mn–N distances are 2.246 and 2.296 Å, and the Mn–O distances vary from 2.066 to 2.339 Å. The

Mn–O(1)	2.192(2)	C(2)–C(3)	1.352(6)	C(11)–C(12)	1.422(5)
Mn–O(2)	2.339(3)	C(3)–C(4)	1.401(6)	O(1)–C(13)	1.268(4)
Mn–O(4) ⁱ	2.066(2)	C(4)–C(5)	1.422(6)	O(2)–C(13)	1.253(4)
Mn–O(5)	2.126(3)	C(4)–C(12)	1.418(4)	C(13)–C(14)	1.499(5)
Mn–N(1)	2.246(3)	C(5)–C(6)	1.324(6)	C(14)–C(15)	1.525(4)
Mn–N(2)	2.296(3)	C(6)–C(7)	1.439(5)	C(15)–C(16)	1.517(4)
N(1)–C(1)	1.319(4)	C(7)–C(8)	1.391(6)	C(16)–C(17)	1.517(4)
N(1)–C(12)	1.361(4)	C(7)–C(11)	1.405(4)	C(17)–C(18)	1.513(4)
N(2)–C(10)	1.314(4)	C(8)–C(9)	1.362(6)	O(3)–C(18)	1.230(4)
N(2)–C(11)	1.362(4)	C(9)–C(10)	1.404(5)	O(4)–C(18)	1.258(4)
C(1)–C(2)	1.400(5)				
O(1)–Mn–O(2)	57.6(1)	O(2)–Mn–O(5)	155.0(1)	O(5)–Mn–N(1)	106.0(1)
O(1)–Mn–O(4) ⁱ	103.6(1)	O(2)–Mn–N(1)	95.9(1)	O(5)–Mn–N(2)	87.4(1)
O(1)–Mn–O(5)	98.2(1)	O(2)–Mn–N(2)	87.4(1)	N(1)–Mn–N(2)	73.2(1)
O(1)–Mn–N(1)	150.4(1)	O(4) ⁱ –Mn–O(5)	96.5(1)	O(1)–C(13)–O(2)	120.2(3)
O(1)–Mn–N(2)	91.3(1)	O(4) ⁱ –Mn–N(1)	90.7(1)	O(3)–C(18)–O(4)	126.0(3)
O(2)–Mn–O(4) ⁱ	95.3(1)	O(4) ⁱ –Mn–N(2)	163.8(1)		
Torsion angles (°)					
C(13)–C(14)–C(15)–C(16)	–62.9(4)	C(15)–C(16)–C(17)–C(18)	174.4(3)		
C(14)–C(15)–C(16)–C(17)	–177.4(3)				
Hydrogen bonding contacts					
D–H···A	D–H	H···A	D···A	D–H···A	
O(5)–H(18a)···O(1) ⁱⁱ	1.05	1.73	2.735	159	
O(5)–H(18b)···O(3) ⁱⁱⁱ	0.74	1.86	2.602	176	
C(2)–H(2)···O(2) ^{iv}	0.93	2.49	3.146	126	

Tab. 3. Selected interatomic distances (in Å) and angles (in degree) for $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$.

Symmetry codes: ⁱ $-x+1, -y+2, -z+2$; ⁱⁱ $-x+1, -y+1, -z+2$; ⁱⁱⁱ $x, y-1, z$; ^{iv} $-x+1, -y+2, -z+1$.

cisoid and transoid bond angles around the central Mn atom fall in the region 57.6 – 106.0° and 150.4 – 163.8° , respectively (Table 3). Different from the known $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ **2**, where the twisted adipate anion functions as monodentate ligand [15], the terminal carboxylate group of the tridentate adipate anion in the present complex either bidentately chelates or monodentately coordinates a Mn atom. Due to the formation of hydrogen bonds and significant π – π stacking interactions (see below), the present tridentate adipato ligand is also twisted and the torsion angle for the C(13)–C(14)–C(15)–C(16) chain close to the chelating terminal reaches $-62.9(4)^\circ$.

Within the crystal structure, the dinuclear complex molecules are arranged in such a way that each phen ligand is sandwiched by two antiparallel symmetry-equivalents of different dinuclear neighbors. The mean interplanar distance of 3.46 Å indicates significant intermolecular π – π stacking interactions, which are responsible for the supramolecular assembly of the complex molecules into 2D layers parallel to $(01\bar{1})$ as depicted in Fig. 1. The 2D layers are further connected by strong intermolecular O–H···O hydrogen bonds between coordinating water O and non-coordinating or chelating carboxyl O atoms and by weak intermolec-

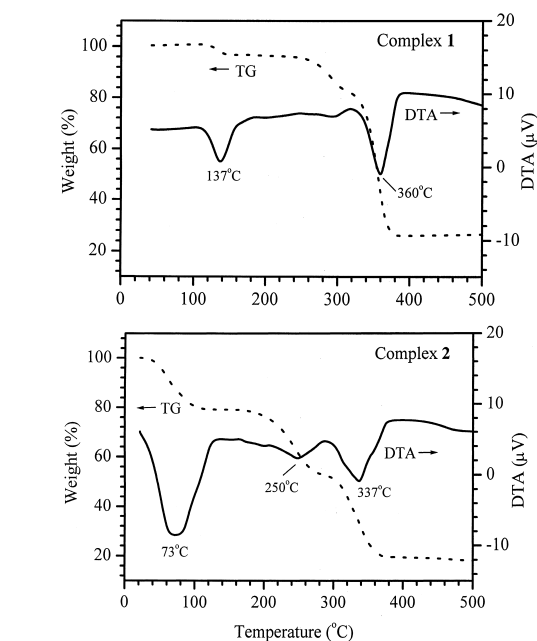


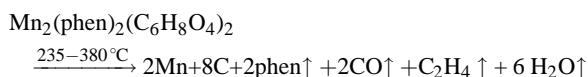
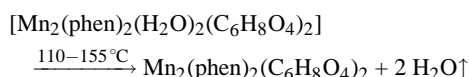
Fig. 2. TG (dashed lines) / DTA (solid lines) curves for $\text{Mn}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{O}_4)_2$ **1** (top) and $[\text{Mn}(\text{H}_2\text{O})(\text{phen})_2(\text{C}_6\text{H}_8\text{O}_4)] \cdot 7\text{H}_2\text{O}$ **2** (bottom).

ular C–H···O hydrogen bonds between phen C and chelating carboxyl O atoms (Table 3).

Thermal analyses

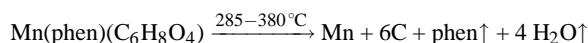
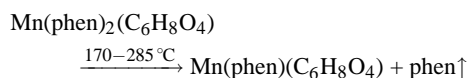
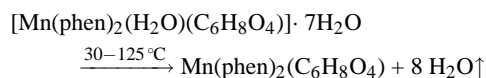
Fig. 2 demonstrates the combined TG/DTA curves of the dinuclear Mn(II) complex **1** and the mononuclear Mn(II) complex **2** registered upon heating over the temperature range 25–500 °C in an argon stream.

The endothermic dehydration of **1** starts at 110 °C and is finished at 155 °C, at which temperature the observed weight loss of 4.5% corresponds well to the calculated value of 4.5% for two moles of H₂O per formula unit. After experiencing a plateau, the TG curve upon further heating over the temperature range 235–380 °C indicates an additional weight loss of 69.3% in good accordance with liberation of two phen, two CO, one C₂H₄ and six H₂O molecules (calcd. 69.6%). The residue of 26.2% agrees well with data calculated for a mixture of 2Mn + 8C (calcd. 25.9%). According to the above description, the thermal decomposition of **1** could be formulated as follows:



As stated above, complex **2** comprises [Mn(phen)₂(H₂O)(C₆H₈O₄)] complex molecules and crystal water molecules. It decomposes in three steps upon heating. The sharp endothermic peak at 73 °C indicates

that complex **2** is easily completely dehydrated, the observed weight loss of 20.8% at 125 °C being in good agreement with the calculated value of 20.5% for one coordinating and seven crystal H₂O molecules per formula unit. Over 170–285 °C, additional weight loss of 25.7% corresponds well to sublimation of one phen molecule (calcd. 25.6%). Upon further heating up to 380 °C, the investigated sample loses additional weight of 34.1% close to the calculated value of 35.9% for one phen and four H₂O molecules. The whole thermal decomposition of **2** could be expressed as follows:



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