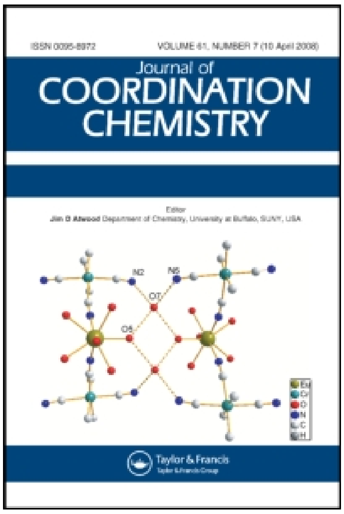

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Manganese citrate complexes: syntheses, crystal structures and thermal properties

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Manganese citrate complexes: syntheses, crystal structures and thermal properties

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Manganese citrate complexes $M_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ [$M = NH_4^+$ (**1**); K^+ (**2**)] and $[Mn(H_2O)_2]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 4nH_2O$ (**3**) (H_4cit = citric acid) were prepared by reaction of $MnCl_2$ and citric acid when the pH was adjusted to 4.5 by NH_4OH, KOH and NaOH, respectively. The isolated complexes were characterized by elemental analyses, IR spectra and X-ray crystal structures. Citrate binds the Mn(II) tridentately via its α-hydroxyl, α-carboxylate and one of the β-carboxylate groups. The carboxylate-bridged di-manganese cores in **1** and **2** were interlocked by β-carboxylates of the citrate chains into 2-D layers, forming a 3-D network by ammonium in **1** and K^+ in **2**. Complex **3**, with a tetrahedral water pentamer, forms a 3-D structure through linking the dimeric unit $[Mn_2(Hcit)_2(H_2O)_4]$ by uncoordinated oxygens of β-carboxylate groups. The structural diversities of these complexes demonstrate that counter-cations play essential roles in the construction of the different frameworks of manganese(II) citrate complexes. Decompositions of **1** and **3** result in formations of pure Mn_3O_4 phase at 500°C.

Keywords: Manganese; Citric acid; Water clusters; X-ray crystal structure

1. Introduction

Manganese carboxylate complexes have long been of special interest since they are known to exist at the active sites of some metalloenzymes and proteins [1], especially as model compounds for photosynthetic oxygen-evolving center (OEC) [2]. Citric acid, an α-hydroxyl tricarboxylic acid, has been known for its abundance in physiological fluids and its chemical versatility toward biologically relevant metal ions [3, 4]. It is central to the citric acid cycle and forms complexes with many metal ions, which increases solubility and leads to enhanced bioavailability and subsequent absorption by biological issues. Such metal ions include Ti^{4+}, V^{5+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}.

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Of these, manganese has been identified as a key metal ion involved in the active sites of essential metalloenzymes related to physiological protective metabolic functions [5]. For an example, ferrous citrate activates the catalytic activity of the enzyme aconitase, and manganese competes with ferrous ion for a position on the active site of enzyme with high activity [6]. On the other hand, manganese carboxylate (especially citrate) complexes are technologically important in producing high-tech materials in highly homogeneous and well-crystallized products [7–9].

Complex formation between manganese(II) and citrate has been studied extensively by spectroscopic and structural studies [10–16]. Previous solution studies addressing the nature of manganese(II) citrate species in aqueous solutions showed the importance of pH [10]. Efforts have been made to isolate and structurally characterize manganese(II) citrate complexes, such as $[Mn(H_2cit)(H_2O)]$ [11], $[Mn(H_2O)_6]_n[Mn_2(Hcit)_2(H_2O)_2]_n \cdot 2nH_2O$ [12], $(NH_4)_4[Mn(Hcit)_2]$ [13], $[GunH]_4[Mn(Hcit)_2(H_2O)_2]$ (GunH = guanidinium) [14], $K_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ [15], $[NaMn(Hcit)]_n$ and $[Mn(H_2O)_4]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 6nH_2O$ [16]. Formation of metal citrate complexes is frequently influenced by pH values, mole ratio, temperature and concentration of the reactants [17]. By control of reaction conditions, such as pH, molar ratio, and temperature, it is possible to elaborate different complexes with specific structures. However, to the best of our knowledge, the influence of countercations in the formation of metal citrate complexes is less well understood [18]. To better understand formation of manganese citrate complexes influenced by countercations, we herein report the preparation of three polymeric manganese citrate complexes, $M_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ [$M = NH_4^+$ (**1**); K^+ (**2**)] and $[Mn(H_2O)_2]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 4nH_2O$ (**3**), from reactions of manganese(II) with citric acid at pH = 4.5. The isolated manganese(II) citrate complexes illustrate the coordination diversity of citrate toward manganese(II), displaying different structural features. Also, we studied the thermal decomposition of the manganese citrate complexes to explore the application of these complexes in producing homogeneous and well-crystallized oxide materials.

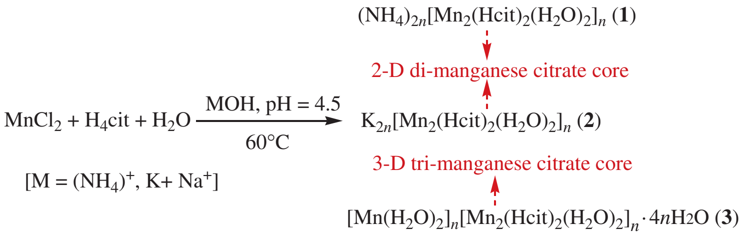
2. Experimental

2.1. *General*

All chemical reagents were analytically pure and used without purification. Elemental microanalyses were performed on an EA 1100 elemental analyzer. Infrared spectra were recorded from KBr pellets on a Nicolet FT-IR 360 spectrophotometer from $4000 \sim 400\,cm^{-1}$. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using a Netzsch STA 409EP thermal analysis system with a heating rate of $10^\circ C\,min^{-1}$ over $25 \sim 600^\circ C$. X-ray diffraction patterns were obtained using a Rigaku D/Max-C powder diffractometer using Cu Kα radiation at 40 kV and 30 mA at a scan rate of $4^\circ min^{-1}$.

2.2. *Synthesis*

The synthesis of compounds **1**–**3** is summarized in scheme 1. Solid $MnCl_2 \cdot 4H_2O$ (1.98 g, 10 mmol) and citric acid monohydrate (2.10 g, 10 mmol) were dissolved in



Scheme 1. Syntheses of manganese(II) citrate complexes.

deionized H_2O (10 mL). To this solution was added either:

2.2.1. An aqueous solution of NH_4OH (15 wt%) to give a solution of pH 4.5. The solution was kept in a 60°C water bath for 24 h, whereupon light pink crystals precipitated. The product was collected, washed with water three times and air-dried to give light pink crystals of $(NH_4)_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ (**1**) in 80% yield based on manganese (2.25 g). $C_6H_{11}O_8NMn$ (280.10): Calcd. C, 25.7; H, 4.0; N, 5.0. Found: C, 25.6; H, 4.2; N, 4.6. IR(KBr): 3415m, 3187s, 1633vs, 1602vs, 1435s, 1415s, 1376s, 1298m, 1283m, 1250m, 1063m, 844w, 819w, 715w, 629w, 554w.

2.2.2. An aqueous solution of KOH (4 M) to give a solution of pH 4.5. The solution was kept in a 60°C water bath for 48 h and light pink crystals precipitated. The product was collected, washed with water three times and air-dried to give light pink crystals of $K_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ (**2**) in 70% yield based on manganese (2.18 g). $C_6H_7O_8KMn$ (301.16): Calcd. C, 23.9; H, 2.3. Found: C, H. IR(KBr): 3298m, 3173m, 1631vs, 1601vs, 1435s, 1415s, 1386s, 1370s, 1298m, 1273m, 1250m, 1062m, 842w, 823w, 715w, 627w, 553w. The crystal structure was identified by X-ray diffraction and was found to be identical with a known compound [15].

2.2.3. An aqueous solution of NaOH (4 M) to give a solution of pH 4.5. The solution was kept in a 60°C water bath for 48 h and light pink crystals precipitated. The product was collected, washed with water three times and air-dried to give light pink crystals of $[Mn(H_2O)_2]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 4nH_2O$ (**3**) in 60% yield based on manganese (1.45 g). $C_{12}H_{30}O_{24}Mn_3$ (723.18): Calcd. C, 19.9; H, 4.2. Found: C, 20.1; H, 4.1. IR(KBr): 3368b, 1575vs, 1446m, 11403s, 1270m, 1127m, 846w, 721m, 639m, 548w. The crystal structure was identified by X-ray diffraction and was found to be identical with a known compound [16].

2.3. *X-ray data collection, structure solution and refinement*

Crystals of **1**–**3** were measured on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The data were corrected for Lorentz and polarization effects. An absorption correction was applied using SADABS [19]. The structures were primarily solved by direct methods using SHELXS-97 [20] and refined by full-matrix least-squares on F^2 with SHELXL-97 [21]. All hydrogen atoms were located from a difference Fourier map and refined isotropically. All nonhydrogen atoms were refined anisotropically. Summaries of crystallographic data for **1** are given in table 1. Selected bond distances and angles of **1** are listed in table 2.

Table 1. Crystal data and structure refinement for $(NH_4)_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$.

Complexes	**1**
Empirical formula	$C_6H_{11}O_8NMn$
Formula weight	280.10
Crystal system	Monoclinic
Color	Light pink
Space group	$P2_1/c$
Units of cell dimensions (Å, °)	
a	11.8952(3)
b	8.4967(2)
c	9.6999(2)
β	96.439(1)
V (Å^3)	974.18(4)
Z	4
D_{Calcd} (g cm^{-3})	1.910
Crystal size (mm^3)	0.19 × 0.15 × 0.13
θ range (°)	1.72 to 28.16
T (K)	296(2)
λ (Mo-Kα) (Å)	0.7107
$[R_{(int)}]$	0.0524
Data/restraints/parameters	2126/14/166
Goodness-of-fit on F^2	1.048
R_1[a], wR_2[b] $[I > 2\sigma(I)]$	0.034, 0.088
R_1, wR_2 (all data)	0.039, 0.090
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	0.452, −0.318

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(|F_o|)$, [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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

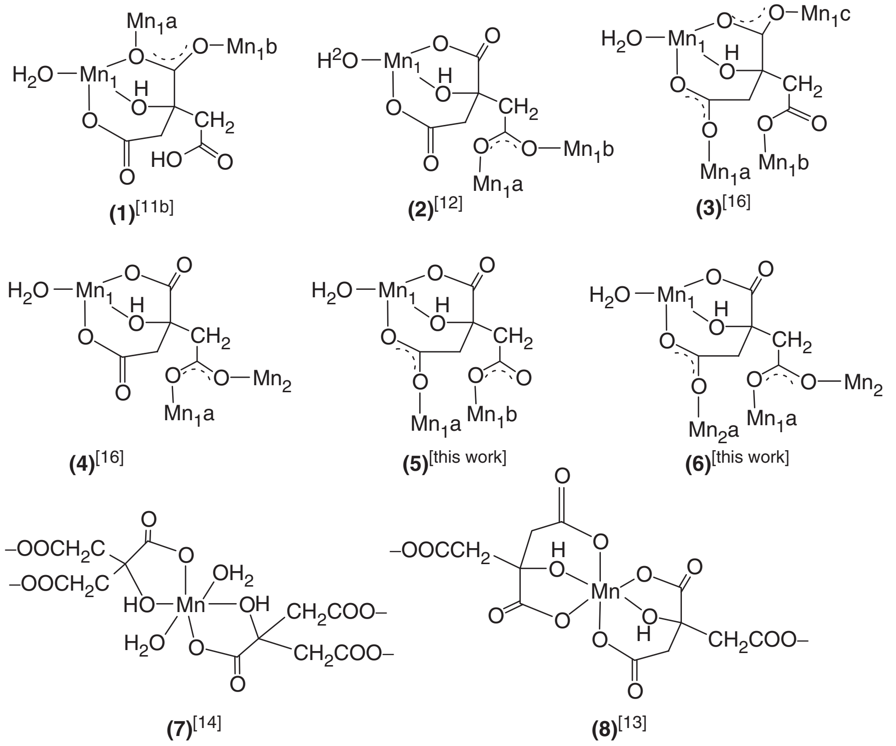
Mn(1)–O(1)	2.204(2)	Mn(1)–O(2)	2.181(2)	Mn(1)–O(2)	2.181(2)
Mn(1)–O(1w)	2.146(2)	Mn(1)–O(5a)	2.181(2)	Mn(1)–O(6b)	2.181(2)
O(1)–Mn(1)–O(2)	71.91(6)	O(1)–Mn(1)–O(4)	81.82(6)	O(1)–Mn(1)–O(5a)	106.76(6)
O(1)–Mn(1)–O(6b)	87.68(6)	O(1)–Mn(1)–O(1w)	160.30(7)	O(2)–Mn(1)–O(4)	83.81(6)
O(2)–Mn(1)–O(5a)	172.05(6)	O(2)–Mn(1)–O(6b)	93.90(6)	O(2)–Mn(1)–O(1w)	89.05(7)
O(4)–Mn(1)–O(5a)	88.24(6)	O(4)–Mn(1)–O(6b)	169.45(7)	O(4)–Mn(1)–O(1w)	91.35(8)
O(5a)–Mn(1)–O(6b)	93.88(6)	O(1w)–Mn(1)–O(5a)	91.39(8)	O(1w)–Mn(1)–O(6b)	98.92(8)

Symmetry codes: (a) $-x, -y, -z$; (b) $x, -y + 1/2, z + 1/2$.

3. Results and discussion

3.1. *Synthesis*

Scheme 1 shows the reactions of manganese chloride and citric acid in the presence of different bases. In all of the cases, $MnCl_2 \cdot 4H_2O$ (1.98 g, 10 mmol) and citric acid (2.10 g, 10 mmol) in a 1 : 1 molar ratio were used to initiate the reactions at pH = 4.5 in aqueous solutions. Complexes **1** and **2** have 1 : 1 ligand/metal compositions, while a 2 : 3 ligand/metal moiety was achieved for **3**. The scheme illustrates the sensitivity of the reaction toward countercations in aqueous solutions. The bases used for these syntheses, NH_4OH for **1**, KOH for **2**, and NaOH for **3**, were essential for the reactions. Compared with the pH value and molar ratio, the sensitivity of the reactions of metal ions and citric acid toward countercations is not reported. As the size of the cations decreased, we see a corresponding increase in the dimensionality of the manganese citrate motifs, from 2-D network in **1** and **2**, to a 3-D network in **3**. A similar



Scheme 2. The different coordination modes of known manganese(II) citrate complexes which have been characterized structurally [11–16].

result was observed previously, which demonstrates different sizes of the contercations bring about different dimensionalities of cobalt citrate complexes [18c].

The three complexes are difficult to dissolve in water and common organic solvents, such as ethanol, acetone etc., even after strong heating. The synthesized manganese(II) citrate complexes exhibit various structural features. Scheme 2 displays the known coordination modes of citrate toward manganese(II) [11–16]. Citrate employs its α-carboxylate group as a bridging ligand to coordinate manganese(II) at low pH; however, it employs β-carboxylate groups as the bridge ligands to coordinate manganese(II) ions under weak acid condition in the presence of different counterions and temperature. It coordinates manganese(II) tridentately only via its α-hydroxyl, α-carboxylate and one of the β-carboxylate groups as a basic feature in neutral environment.

3.2. *Description of the crystal structures*

The X-ray structure determination revealed **1** consists of discrete ammonium cations and polymeric $[Mn_2(Hcit)_2(H_2O)_2]^{2-}$ anions. As shown in figure 1, the anion is a new dinuclear structure with two Mn(II) ions linked by coordinated β-carboxylate oxygens of citrate. Each citrate ligand is triply deprotonated, coordinating to Mn(II), giving rise to two distorted octahedral units within the dimer. In each octahedron, the citrate binds

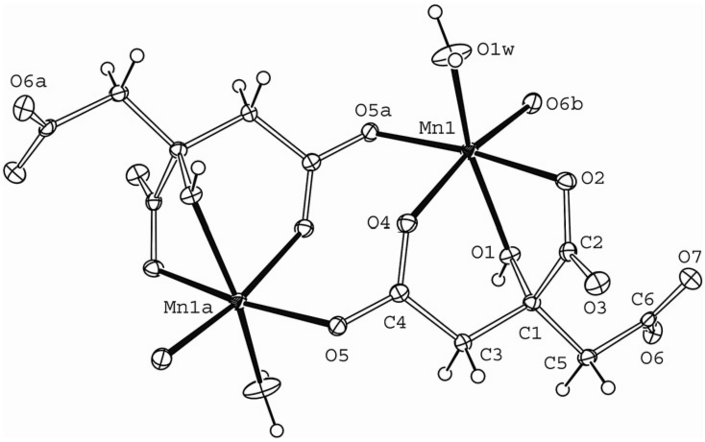


Figure 1. ORTEP plot of the di-manganese core in $(NH_4)_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ (**1**). Thermal ellipsoids are drawn by ORTEP and represent 30% probability surface.

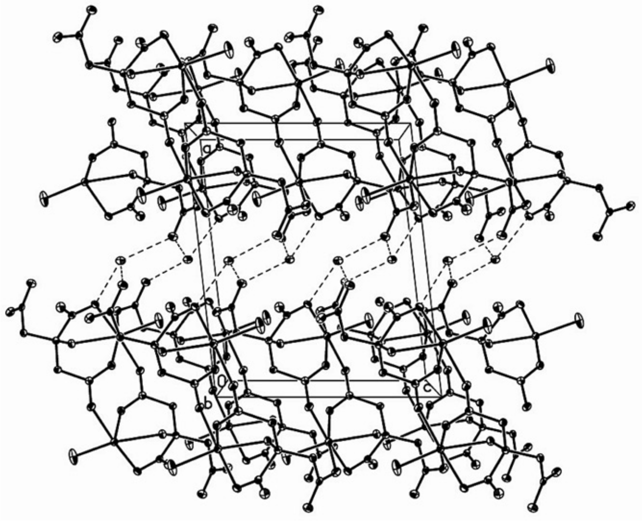


Figure 2. The 2-D layered structure of the di-manganese cores in **1**. Hydrogen atoms have been omitted for clarity.

as a tridentate ligand, employing the α-hydroxyl and the α-carboxylate groups, as well as one of the β-carboxylate groups. Furthermore, the β-carboxylate group coordinates to Mn1a ion linking two Mn ions into a dimer, which results in a Mn1–Mn1a separation of 5.062(2) Å. The remaining β-carboxylate group does not participate in coordination to the same Mn(II), but spans over to another dimeric $[Mn_2(Hcit)_2(H_2O)_2]^{2-}$ and coordinates to a Mn(II), assembling the $[Mn_2(Hcit)_2(H_2O)_2]^{2-}$ unit into a planar polymeric structure. As shown in figure 2, **1** forms a layered structure via hydrogen-bonding interactions of ammonium cations and the oxygens of carboxylate groups [N1–H2 $\cdots$ O2: 2.869(3) Å, 176(2)°, (x, y, z); N1–H5 $\cdots$ O6: 2.970(2) Å, 162(2)°, $(1-x, -0.5+y, -0.5-z)$; N1–H4 $\cdots$ O7: 2.918(3) Å, 175(2)°, $(1-x, -y, -z)$;

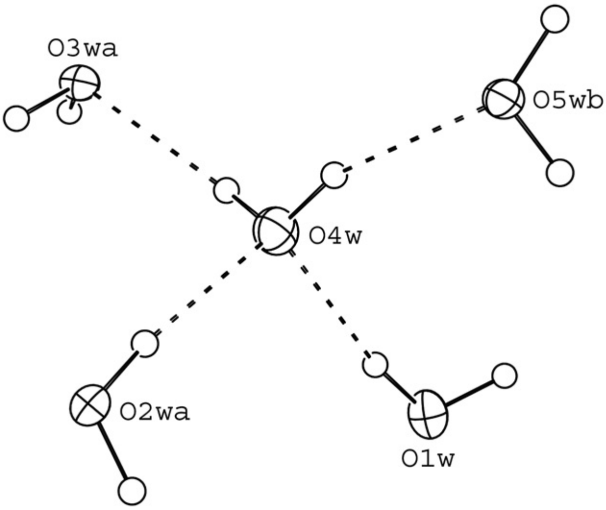


Figure 3. ORTEP plot of the pentameric water cluster showing hydrogen-bonding interactions in **3**. Thermal ellipsoids are drawn by ORTEP and represent 30% probability surface.

N1–H3 ⋯ O7: 2.892(3) Å, 167(2)°, (x, $-0.5-y$, $0.5+z$)]. In the six coordination apexes around Mn(II), O6b, the coordination water molecule (O1w) and O1 and O4 from α-hydroxyl and β-carboxylate groups occupy the equatorial plane, while O2 and O5a from α- and β-carboxylate groups occupy the axial positions. Bond valence sum (BVS) calculations [22] give the values of 2.141 for Mn1 in **1**, indicating that the Mn centers are +2. This dimeric structure is rare for metal citrate complexes [23].

Structures of **2** and **3** have been reported [15, 16]. Further analysis of the crystal packing reveals that **3** contains a pentameric water cluster. Figure 3 shows the ORTEP plot of the pentameric water cluster showing hydrogen bonding interactions. The pentameric water cluster occupies the voids in the metal-oraganic framework (MOF) (figure 4). Among the water pentamer, the O1w and O2wa behave as H donors, O3wa and O5wb as H acceptors, while the centered O4w is both acceptor and donor in the hydrogen-bonding scheme. O1w and O2wa involve one hydrogen bond from water-carboxylate interaction, the O3w involves two hydrogen bonds with two water-carboxylate interactions, and O5wb, as a double donor and a single acceptor, involves three hydrogen bonds. Thus, the O3wa, O4w and O5wb show tetra-coordination and O1w and O2wa that are coordinated Mn^{2+} show tri-coordination. In this water pentamer, the average O ⋯ O distance is 2.765 Å, which is comparable to the value of 2.759 Å in ice I_h at −90°C [24]. The average angle is 111.0°, but vary widely (99.2° ∼ 123°), comparable to the value of 109.3° in hexagonal ice. Theoretical studies indicate that the water pentamer with a cyclic quasi-planar ring is most stable [25] and this stable conformer has been experimentally observed [26]. However, the so-called "Walrafen" pentamer [27], which was trapped in **3**, was observed here. This shows that other water pentamer conformations can also be stabilized by particular crystal hosts.

Hydrogen-bonding geometry (Å, °) for **3** is listed in table 3. Some of the average Mn–O bond distances (Å) in the manganese(II) citrate complexes are listed in table 4. The Mn–O distances observed in **1**–**3** are comparable to those seen in other manganese(II) citrate complexes [11–16].

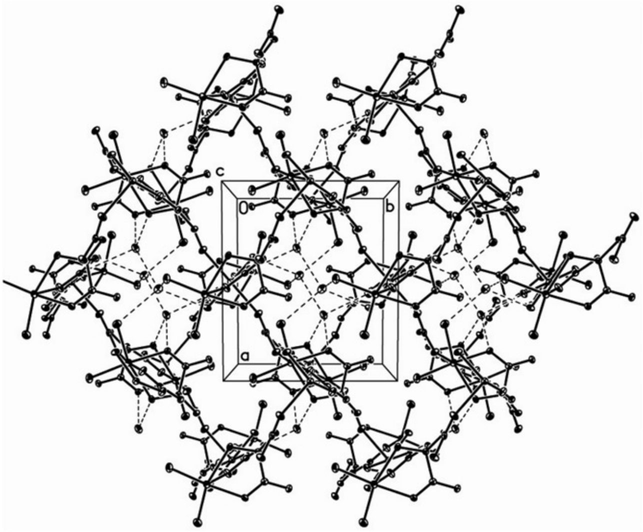


Figure 4. A view of the MOF in **3** showing the pentameric water cluster; hydrogen atoms are omitted for clarity.

Table 3. Hydrogen-bonding geometry (Å, °) for **3**.

D–H···A	D–H	H···A	D···A	D–H···A	Symmetry codes
O1w–H1w1···O7	0.85	1.99	2.817(3)	163(3)	$1-x, -y, -z$
O1w–H1w2···O4w	0.85	1.92	2.764(4)	171(3)	x, y, z
O2w–H2w1···O3	0.85	1.90	2.739(3)	170(3)	$x, y+1, z$
O2w–H2w2···O4w	0.85	1.92	2.764(3)	173(3)	$0.5-x, 0.5+y, 0.5-z$
O3w–H3w1···O4	0.85	1.83	2.666(3)	166(3)	x, y, z
O3w–H3w2···O3	0.86	1.84	2.696(3)	175(3)	$0.5-x, 0.5+y, 0.5-z$
O4w–H4w1···O5w	0.84	1.94	2.752(3)	162(3)	$x-1, y, z$
O4w–H4w2···O3w	0.83	1.98	2.780(3)	161(4)	$0.5-x, -0.5+y, 0.5-z$
O5w–H5w1···O2	0.85	1.87	2.697(3)	167(3)	$1-x, -y, -z$
O5w–H5w2···O5	0.84	1.90	2.746(3)	174(3)	$1.5-x, 0.5+y, 0.5-z$
O1–H1···O5w	0.84	1.84	2.670(4)	171(3)	x, y, z

Table 4. Comparison of the bond distances (Å) in manganese(II) citrate complexes.

Complex	Mn–O (hydroxyl)	Mn–O (α-carboxylate)	Mn–O (β-carboxylate)	Ref.
$[Mn(H_2cit)(H_2O)]_n$	2.139(3)	$2.191(3)_{av}$	2.195(3)	[11b]
$[Mn(H_2O)_6]_n[Mn_2(Hcit)_2(H_2O)_2]_n \cdot 2nH_2O$	2.224(2)	2.194(2)	$2.157(2)_{av}$	[12]
$[C(NH_2)_3]_4[Mn(Hcit)_2(H_2O)_2]$	2.196(1)	2.116(1)		[14]
$(NH_4)_4[Mn(Hcit)_2]$	2.225(2)	2.162(3)	2.117(2)	[13]
$[Mn(H_2O)_4]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 6nH_2O$	2.280(4)	2.193(4)	$2.150(4)_{av}$	[16]
$[NaMn(Hcit)]_n$	2.265(3)	2.196(3)	$2.156(3)_{av}$	
$(NH_4)_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ (**1**)	2.241(2)	2.132(2)	$2.186(2)_{av}$	This work
$K_{2n}[Mn_2(Hcit)_2(H_2O)_2]_n$ (**2**)	2.189(2)	2.175(2)	$2.133(2)_{av}$	
$[Mn(H_2O)_2]_n[Mn_2(Hcit)_2(H_2O)_4]_n \cdot 4nH_2O$ (**3**)	2.278(2)	2.184(2)	$2.145(2)_{av}$	

3.3. *IR spectra*

The absence of characteristic IR spectra around $1700\,\mathrm{cm}^{-1}$ expected for the vibration of protonated carboxylate groups (COOH) indicates that the carboxylate groups of the citrate in **1**–**3** are deprotonated. Broad bands in the region $3300{\sim}3500\,\mathrm{cm}^{-1}$ can be assigned to stretching vibrations of the hydroxyl of citrate and water molecules. In addition, all of the complexes exhibit strong characteristic features of the carboxylate of citrate. Specifically, antisymmetric stretching vibrations $\nu_{\mathrm{as}}(\mathrm{COO}^-)$ appear 1between 1633 and $1602\,\mathrm{cm}^{-1}$ for **1**, 1631 and $1601\,\mathrm{cm}^{-1}$ for **2**, and near $1575\,\mathrm{cm}^{-1}$ for **3**. The symmetric stretching vibrations $\nu_{\mathrm{s}}(\mathrm{COO}^-)$ are observed between 1435 and $1376\,\mathrm{cm}^{-1}$ for **1**, 1435 and $1370\,\mathrm{cm}^{-1}$ for **2**, and near $1446\,\mathrm{cm}^{-1}$ for **3**. All of the bands are shifted to lower frequencies compared to those of free citric acid, denoting changes in vibrational status upon complexation to manganese.

3.4. *Thermal studies*

The DTA and TG analyses of **1** and **3** were studied from 25~600°C (figure S1 and S2). The thermogravimetric analyses display three consecutive processes, namely, dehydration, decomposition/oxidation reactions of the organic ligand and inorganic residue formation. Complex **1** loses its crystal lattice water molecules with an endothermic peak at 170°C, while **3** loses its coordination water molecules at a relatively high temperature of 280°C, with the corresponding weight loss. Subsequent decompositions of **1** and **3** are in the range 300 ~ 500°C, with intense exothermic processes at 340 ~ 450 and 350 ~ 490°C, respectively, with weight loss due to the vigorous combustion of the residual organics. The powders of **1** and **3** annealed in air at 500°C had XRD pattern typical for a well-crystallized pure $\mathrm{Mn_3O_4}$ phase (figure S3); powders of **1** and **3** annealed in air at 600°C had XRD patterns for the mixture of $\mathrm{Mn_2O_3}$ and $\mathrm{Mn_3O_4}$ phases (figure S4). $\mathrm{Mn_3O_4}$ was usually synthesized by high-temperature calcinations of manganese oxides with a higher valence of manganese, hydroxides, and hydroxyoxides or oxysalts of manganese at about 1000°C in air [28]. Herein, **1** and **3** can act as precursors for preparation of $\mathrm{Mn_3O_4}$ at lower temperature than the general approach.

4. Conclusion

We synthesized and characterized manganese complexes with citrate ligands in the presence of different bases. The data presented in this work, as well as the results from the past solution studies of manganese(II) citrate system [10], confirm the diversity of citrate as a ligand toward manganese(II). This study indicates the countercations in aqueous solution play an important role in constructing the different structures of manganese citric complexes. Complexes **1** and **3** are single molecular precursors for preparation of $\mathrm{Mn_3O_4}$ at 500°C.

Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 238251 for **1**. 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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