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Homo- and hetero-metallic manganese citrate complexes: Syntheses, crystal structures and magnetic properties

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Abstract

A series of Mn citrate coordination polymers $[NaMn(Hcit)]_n$ (**1**, H_4cit = citric acid), $[MnCa_2(Hcit)_2(H_2O)_4]_n$ (**2**), $[\{Mn(Hcit)(H_2O)_2\}_2Mn(H_2O)_4]_n$ (**3**) and $[\{Mn(Hcit)(H_2O)_2\}_2Mn(H_2O)_2]_n$ (**4**) have been synthesized by the solvothermal method and the conventional solvent method. **1** and **2** represent novel examples of bimetallic Mn citrate complexes with 3-D architectures. In the structure of **1**, $Mn(\mu\text{-}O)_3Na$ and $Mn(\mu\text{-}O)(\mu\text{-}OCO)Na$ units are alternately fused via edge-sharing to form Mn…Na…Mn chains and the citrate trianion links between the chains by terminal carboxylate groups. In the structure of **2** the Ca ions are correlated by carboxylate bridges to create a two-dimensional Ca-citrate layer at the a-c face and the Mn(II) ions form a helix chain along the *a* axis by carboxylate bridges. Each citrate trianion links 9 and 8 hetero-metal ions in **1** or **2**, respectively, through component carboxylate and hydroxyl groups. In **3** and **4** both the $Mn(Hcit)(H_2O)_2$ units are coupled to form centrosymmetrical dimer units, which construct the one-dimensional chain structure of **3** and the 3D network architecture of **4**. Infrared spectra and the magnetic properties are also discussed, being associated with the bridging coordination mode of the carboxylate group.

Keywords: Crystal structure; Manganese; Calcium; Citrate; Magnetic property

1. Introduction

Citric acid, a hydroxyl tricarboxylic acid and citrate ions play an important role in biosystems [1]. They can take part in some fundamental physiological processes, such as the acid cycle [1a] and carbohydrate metabolism [1b]. Citrate is correlated to the MoFe-protein containing homocitrate, and mutant forms of nitrogenase were found to contain citrate as an organic ligand [1c]. The polydentate citrate shows its prominent capacity to produce new cluster topologies by virtue of its coordinative flexibility. Hundreds of metal citrate complexes with diverse architectures have been reported [2–11]. We have noted that most of the metal citrate complexes are homo-metallic and that each citrate usually bridges 2–4 metal ions, and not more than 6 metal ions [11] to our knowledge. Few of the citrate complexes contain hetero-metal ions [10]. It is also noted that manganese citrate complexes are still rare, of which three mononuclear complexes [12] $(NH_4)_4[Mn^{II}(C_6H_5O_7)_2]$, $(NH_4)_5[Mn^{III}(C_6H_4O_7)_2]\cdot 2H_2O$ and $[(NH_2)_2C{=}NH_2]_4[Mn^{II}(C_6H_5O_7)_2(H_2O)_2]$ have been reported. Only two

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manganese citrate coordination polymers $\{[Mn^{II}(H_2O)_6][Mn^{II}(C_6H_5O_7)(H_2O)]_2 \cdot 2H_2O\}_n$ [13] and $[Mn(C_6H_6O_7)(H_2O)]_n$ [14] are known so far. Manganese has been known to be involved in the active centers of some metalloenzymes [15]. The participation of manganese in the oxygen-evolving complex (OEC) of photosystem II (PSII) has been proven to be unequivocal and especially important [16]. It is known that the OEC is a bimetallic cluster of 4Mn/Ca, in which calcium is also essential for catalytic activity [17] and the Ca^{2+} ion is believed to be linked by a carboxylic acid residue to the Mn aggregate [18]. Recently, crystallographic data have begun to give the topological arrangement of the Ca ion in the Mn_4 cluster of the OEC [19]. There are three Mn complexes in which calcium exists as a discrete counterion [20]. Recently the Mn/Ca complex $[Mn_{13}Ca_2O_{10}(OH)_2(OMe)_2(O_2CPh)_{18}(H_2O)_4]$, containing the $[Mn_4CaO_4]$ sub-unit, has been reported by Christou [21a] and one Mn/Ca coordination polymer [21b] was also reported. We have also reported several Mn dicarboxylate complexes [22]. In the preparation of novel Mn/Ca (or alkali) bimetallic and Mn citrate complexes, a synthetic system including Mn and Ca (or alkali) metal ions and citric acid has been used. Bimetallic Mn/Ca and Mn/Na citrate and two Mn citrate coordination polymers are obtained and reported in this paper.

2. Experimental

All manipulations were performed under aerobic conditions, and all commercially available reagents were used as received. IR spectra were recorded on a Magna-75-FT-IR spectrophotometer as KBr pellets. The variable temperature susceptibility was measured on a model CF-1 superconducting magnetometer with the crystalline sample kept in a capsule at 5–300 K. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms of the complexes determined. Elemental analyses were performed by Germany Elemental Analyzer Vario EL III.

2.1. $[MnNa(Hcit)]_n$ (**1**)

To 15 ml of methanolic solution containing CH_3ONa (0.22 g, 4.0 mmol), 0.39 g of $MnCl_2 \cdot 4H_2O$ (2.0 mmol) and 0.42 g of citric acid monohydrate (2.0 mmol) were added. The slurry mixture was sealed into a teflon tube with a space volume of 23 ml and heated for 3 days at 160 °C under autogenous pressure. Prism light red crystals (0.20 g, yield 38%) suitable for X-ray determination were collected. *Anal.* Calc. for $C_6H_5MnNaO_7$: C, 26.99; H, 1.89; Mn, 20.58. Found: C, 27.13; H, 1.98; Mn, 21.23%. IR (KBr, cm^{-1}): 1664(m), 1606(s), 1578(s), 1541(m), 1429(s), 1408(s), 1390(m), 1340(s).

2.2. $[MnCa_2(Hcit)_2(H_2O)_4]_n$ (**2**)

To 15 ml of H_2O, $MnCO_3$ (0.12 g, 1.0 mmol), $Ca(NO_3)_2$ (0.32 g, 1.95 mmol) and citric acid monohydrate (0.42 g, 2.0 mmol) were added and dissolved. The solution was sealed into a teflon tube with a space volume of 23 ml and heated at 160 °C under autogenous pressure for 3 days. Colorless plate crystals (0.35 g, yield 60%) suitable for X-ray determination were collected. *Anal.* Calc. for $C_{12}H_{18}Ca_2MnO_{18}$: C, 24.62; H, 3.10; Ca, 13.69; Mn, 9.39. Found: C, 24.68; H, 3.12; Ca, 13.71; Mn, 9.35%. IR (KBr, cm^{-1}): 3480(s), 3396(s), 1616(s), 1562(s), 1537(s), 1465(m), 1429(s), 1384(s).

2.3. $[\{Mn(Hcit)(H_2O)_2\}_2Mn(H_2O)_4]_n \cdot 6nH_2O$ (**3**)

Citric acid (0.42 g, 2.0 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (0.25 g, 1.0 mmol) were dissolved in 15 ml of MeOH/H_2O (v/v, 2:1), then 0.22 g of MeONa (4.0 mmol) was added. The solution was sealed into a teflon tube with a space volume of 23 ml and heated at 150 °C under autogenous pressure for 3 days. Colorless rhombic crystals (0.078 g, yield 31% based on Mn used) were collected. *Anal.* Calc. for $C_{12}H_{38}Mn_3O_{28}$: C, 18.12; H, 4.82; Mn, 20.73. Found: C, 18.36; H, 4.92; Mn, 20.96%. IR (KBr, cm^{-1}): 3446(br), 3396(s), 1616(s), 1574(s), 1419(s), 1394(s), 1375(s), 525(m).

2.4. $[\{Mn(Hcit)(H_2O)_2\}_2Mn(H_2O)_2]_n \cdot 4nH_2O$ (**4**)

Citric acid (0.42 g, 2.0 mmol) and $Mn(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1.0 mmol) were dissolved in 30 ml of DMF and the solution was stirred at room temperature for 2 h. Then 0.27 g of imidazole (4.0 mmol) was added and continuously stirred for 14 h to resulting in a red solution, which was allowed to stand for two months to deposit colorless block crystals of **4** (0.13 g, yield 54% based on Mn used). *Anal.* Calc. for $C_{12}H_{30}Mn_3O_{24}$: C, 19.93; H, 4.18; Mn, 22.79. Found: C, 19.92; H, 4.14; Mn, 22.93%. IR (KBr, cm^{-1}): 3426(br), 3253(w), 1564(s, br), 1439(s), 1417(s), 1389(s), 521(m).

2.5. $[Mn(H_2cit)(H_2O)]_n$ (**5**)

The synthetic procedure of **2** was utilized in the absence of $Ca(NO_3)_2$, affording colorless insoluble prism crystals which were collected resulting in 0.22 g (yield 84%). *Anal.* Calc. for $C_6H_8MnO_8$: C, 27.39; H, 3.07; Mn, 20.88. Found: C, 27.05; H, 3.16; Mn, 20.65%. IR (KBr, cm^{-1}): 3369(br), 2973(m), 2922(m), 2809(m), 2687(m), 2618(m), 2532(m), 1733(s), 1616(s), 1562(s), 1537(s), 1465(m), 1429(s), 1384(s). The crystal structure was identified by X-ray diffraction and was found to be identical with a known compound [14]. When $MnCO_3$: