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Pentapotassium dicitrato(4−)manganate(III) pentahydrate

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The centrosymmetric crystal structure pentapotassium dicitrato(4−)manganate(III) pentahydrate, $K_5[Mn(C_6H_4O_7)_2]\cdot 5H_2O$, has two independent anions, both of which lie at inversion centers in the triclinic unit cell. The Mn atoms are *O,O′,O″*-chelated by the citrate entity and the six O atoms surrounding each Mn atom constitute an octahedron. The K atoms interact with the anions and the water molecules, leading to the formation of a network structure that also features extensive hydrogen bonding.

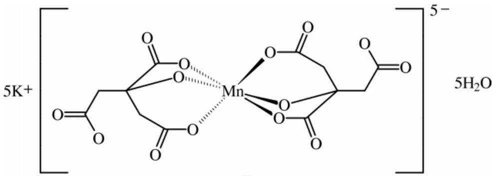
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.062
wR factor = 0.161
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The citrate ion, in the form of its transition-metal derivatives, has been extensively studied, and for the Mn–citrate system in particular, the synthesis has been investigated in order to understand the influence of pH on the nature and composition of the product. At a pH of 1.5–3.0 and in the presence of ammonium hydroxide, Mn^{2+} reacts with citric acid to form neutral $[Mn^{II}(C_6H_6O_7)_2]\cdot H_2O$ (Deng *et al.*, 2003), whereas at a pH of 7, the reaction yields $(NH_4)_4[Mn^{II}(C_6H_5O_7)_2]$, the ammonium counter-ion being incorporated into the crystal structure in this example. On the other hand, at a somewhat higher pH of 8, the Mn^{3+} product, $(NH_4)_5[Mn^{III}(C_6H_4O_7)_2]\cdot 2H_2O$ (Matzapetakis *et al.*, 2000) could be isolated. The use of potassium hydroxide as the base in place of ammonium hydroxide furnishes the corresponding pentapotassium manganate(III) complex, (I), at pH 9, and it crystallizes with five water molecules per . The potassium cation is able to bind to more water molecules than the ammonium cation; this feature has also been observed for the related citratovanadates(V), $K_2[VO_2(C_6H_6O_7)]_2\cdot 4H_2O$ and $(NH_4)_2[VO_2(C_6H_6O_7)]_2\cdot 2H_2O$ (Zhou *et al.*, 1995), and $K_4[VO(C_6H_6O_7)]_2\cdot 6H_2O$ and $(NH_4)_4[VO(C_6H_6O_7)]_2\cdot 2H_2O$ (Tsaramyrsi *et al.*, 2001; Velayutham *et al.*, 1998).



(I)

The Mn atom is *O,O′,O″*-chelated by the $[C_6H_4O_7]^{4-}$ ion, which uses two carboxyl and the alkoxyl O atom to bond in a *fac* manner (Fig. 1 and Table 1). The two independent Mn atoms both lie at inversion centers. The negative charge of the anion is balanced by five potassium cations, but the stability of

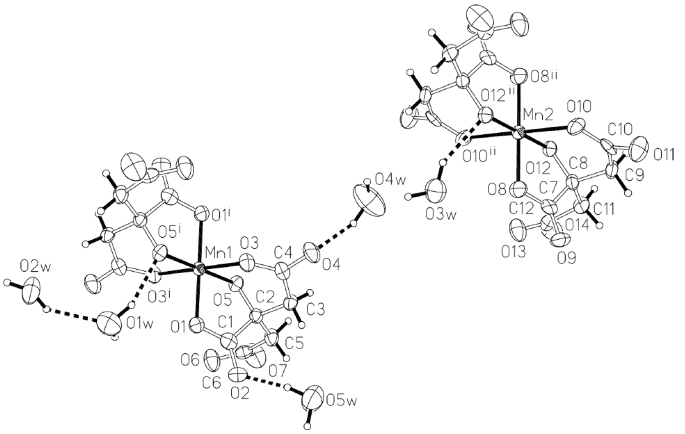


Figure 1
*ORTEP*II (Johnson, 1976) plot of the two symmetry-independent dicitratomanganate(III) ions and the water molecules, with displacement ellipsoids drawn at the 75% probability level. The K^+ ions have been omitted. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$.]

this salt is better explained in terms of stabilization by the lattice water molecules, which form extensive hydrogen bonds (Table 2), as well as interacting with the potassium ions.

Experimental

Manganese(II) dichloride (0.99 g, 5 mmol) and citric acid monohydrate (2.10 g, 10 mmol) were dissolved in water (10 ml). Aqueous potassium hydroxide was added in drops until the solution registered a pH of 9.0. The solution was filtered and the filtrate was set aside for several days to allow the brown crystals to separate from solution. IR (KBr): $\nu_{as}(CO_2)$ 1637, 1593; $\nu_s(CO_2)$ 1403, 1379 cm^{-1}.

Crystal data

$K_5[Mn(C_6H_4O_7)_2]\cdot 5H_2O$
$M_r = 716.70$
Triclinic, $P\bar{1}$
$a = 6.8304$ (4) Å
$b = 9.2270$ (5) Å
$c = 20.197$ (1) Å
$\alpha = 78.294$ (1)°
$\beta = 82.734$ (1)°
$\gamma = 74.892$ (1)°
$V = 1199.7$ (1) Å^3
$Z = 2$
$D_x = 1.984$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3636 reflections
$\theta = 2.3$–28.3°
$\mu = 1.51$ mm^{-1}
$T = 298$ (2) K
Plate, brown
0.19 × 0.19 × 0.04 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.711$, $T_{max} = 0.942$
7084 measured reflections
4168 independent reflections
3444 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.0$°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 8$
$l = -24 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.161$
$S = 1.15$
4168 reflections
337 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.8327P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.979 (3)	Mn2—O8	1.976 (3)
Mn1—O3	2.174 (3)	Mn2—O10	2.216 (3)
Mn1—O5	1.872 (3)	Mn2—O12	1.870 (3)
O1—Mn1—O1^i	180	O8—Mn2—O8^{ii}	180
O1—Mn1—O3	88.5 (1)	O8—Mn2—O10	87.0 (1)
O1—Mn1—O3^i	91.5 (1)	O8—Mn2—O10^{ii}	93.0 (1)
O1—Mn1—O5	84.2 (1)	O8—Mn2—O12	84.2 (1)
O1—Mn1—O5^i	95.8 (1)	O8—Mn2—O12^{ii}	95.8 (1)
O3—Mn1—O5	86.7 (1)	O10—Mn2—O10^{ii}	180
O3—Mn1—O3^i	180	O10—Mn2—O12	86.3 (1)
O3—Mn1—O5^i	93.3 (1)	O10—Mn2—O12^{ii}	93.7 (1)
O5—Mn1—O5^i	180	O12—Mn2—O12^{ii}	180

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*2···O5^i	0.98	2.00	2.919 (6)	157
O2*w*—H2*w*1···O9^{iii}	0.98	1.95	2.902 (5)	165
O2*w*—H2*w*2···O1*w*	0.99	2.14	2.830 (6)	125
O3*w*—H3*w*2···O11^{iv}	0.97	2.22	2.828 (5)	120
O3*w*—H3*w*1···O12^{ii}	0.97	2.13	2.992 (5)	148
O4*w*—H4*w*1···O4	0.97	1.92	2.828 (6)	153
O4*w*—H4*w*2···O3*w*	0.97	2.56	2.903 (7)	101
O5*w*—H5*w*1···O2	0.98	1.82	2.792 (6)	171
O5*w*—H5*w*2···O11^v	0.98	2.06	2.822 (6)	134

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $x, y, z - 1$; (iv) $-x, 2 - y, 2 - z$; (v) $-x, 1 - y, 2 - z$.

The C-bound H atoms were positioned geometrically and were included in the refinement in the riding-model approximation. The positions of the water H atoms were generated by *HYDROGEN* (Nardelli, 1999) but these were not refined. The displacement parameters of all H atoms were set to 1.2 times U_{eq} of their parent atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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