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Manganous Citrate Decahydrate

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Abstract. Crystals of manganese citrate, $[Mn(H_2O)_6]$ $[MnC_6H_5O_7(H_2O)_2]$ $2H_2O$, were prepared by evaporation of an aqueous mixture of freshly precipitated manganous hydroxide and citric acid. They are monoclinic, space group $P2_1/n$, $Z=2$, F.W. 723·19, $a=$ 20·575 (5), $b=6{\cdot}755$ (2), $c=9{\cdot}230$ (2) Å, $\beta=96{\cdot}74°$ (1), $V=1273{\cdot}97$ Å^3, $D_x=1{\cdot}89$, $D_{\text{meas}}=1{\cdot}88$ g cm^{-3}, λ(Mo $K\alpha$)$=0{\cdot}7107$ Å. The final residual $R=0{\cdot}045$. All hydrogen atoms were located and were refined isotropically. The structure is isomorphous with that of the magnesium salt [Johnson *Acta Cryst.* (1965). **18**, 1004]. Each citrate ion forms a tridentate chelate to one manganous ion.

Experimental. A roughly spherical crystal, 0·26 mm diameter, was used in the collection of three-dimensional data on a Syntex automated diffractometer with monochromatic Mo $K\alpha$ radiation using the θ–2θ scan technique. Intensities were measured for 3731 unique reflections. Values for $\sigma(F)$ were derived from counting statistics and measured instrumental uncertainties. The formula used was: $\sigma(F)=F/2\{\sigma^2(I)/I^2+\delta^2\}^{1/2}$ [where $\sigma(I)$ is derived from counting statistics alone and δ is the measured instrumental uncertainty]. Reflections for which the measured intensity, I_{obs}, was less than $2{\cdot}33\sigma(I)$ were considered to be unobserved. For these 'unobserved reflections', when $I\geq\sigma(I)$, the

Table 1. *Atomic parameters for manganese citrate*

Positional parameters are listed as fractions of cell edges.

Anisotropic temperature factors are expressed as

$$\exp\left[-(\tfrac{1}{4})\left(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots\right)\right]$$

and isotropic temperature factors as

$$\exp\left(-B\sin^2\theta/\lambda^2\right)$$

with values of B given in Å^2. Estimated standard deviations, determined from the inverted full matrices, are listed beside each parameter, with respect to the last decimal place given.

	$x\times10^5$	$y\times10^4$	$z\times10^4$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	0	0	0	1·62 (2)	1·61 (2)	1·53 (2)	0·07 (2)	−0·04 (2)	0·03 (2)
Mn(2)	21778 (2)	5140·6 (6)	5400·8 (4)	1·50 (2)	1·47 (2)	1·46 (1)	−0·17 (2)	−0·13 (1)	−0·12 (1)
O(1)	18672 (9)	−56 (3)	8339 (2)	1·70 (7)	1·83 (7)	1·53 (7)	0·26 (8)	−0·16 (6)	−0·29 (7)
O(2)	20744 (11)	−2426 (3)	6811 (2)	2·96 (8)	2·34 (8)	2·33 (9)	1·05 (8)	−0·46 (8)	−0·88 (8)
O(3)	2549 (10)	4940 (3)	2914 (2)	2·07 (7)	2·05 (8)	2·96 (9)	0·04 (8)	−1·20 (7)	0·54 (8)
O(4)	12844 (10)	5271 (3)	3877 (2)	1·90 (7)	2·42 (9)	2·44 (8)	−0·57 (8)	−0·70 (7)	0·98 (7)
O(5)	23341 (9)	2181 (3)	4525 (2)	1·52 (7)	2·08 (8)	2·48 (9)	−0·22 (7)	0·40 (6)	−0·67 (7)
O(6)	16588 (10)	26 (3)	3321 (2)	2·14 (7)	2·35 (8)	1·62 (7)	−0·30 (8)	0·18 (6)	−0·67 (8)
O(7)	15438 (9)	3074 (3)	6479 (2)	2·17 (8)	1·38 (7)	1·10 (6)	−0·03 (7)	−0·17 (6)	- 0·03 (6)
O(8)	26057 (11)	6813 (3)	3786 (2)	2·94 (8)	2·68 (9)	2·00 (8)	0·12 (8)	0·67 (8)	0·45 (8)
O(9)	4049 (10)	−1191 (3)	2110 (2)	2·25 (8)	1·88 (8)	2·20 (9)	−0·28 (7)	−0·60 (7)	0·41 (7)
O(10)	8938 (11)	1685 (3)	− 150 (3)	2·27 (8)	2·47 (9)	3·73 (11)	−0·50 (8)	0·83 (8)	−1·06 (9)
O(11)	− 4541 (11)	2427 (3)	1047 (2)	2·62 (8)	2·29 (8)	2·44 (9)	0·49 (8)	−0·69 (7)	−0·54 (8)
O(12)	13989 (11)	5558 (4)	748 (3)	2·27 (8)	3·00 (10)	2·78 (10)	0·11 (8)	0·21 (8)	0·09 (8)
C(1)	17273 (13)	−1050 (4)	7166 (3)	1·69 (10)	1·38 (10)	1·24 (9)	−0·32 (9)	−0·02 (8)	0·19 (8)
C(2)	11368 (13)	− 340 (4)	6171 (3)	1·50 (8)	1·44 (10)	1·42 (9)	−0·35 (8)	−0·11 (8)	0·12 (8)
C(3)	12912 (13)	1627 (4)	5423 (3)	1·47 (8)	1·34 (9)	1·10 (9)	−0·09 (8)	−0·05 (8)	−0·13 (8)
C(4)	6589 (13)	2496 (4)	4632 (3)	1·39 (8)	1·60 (10)	1·68 (10)	−0·04 (9)	0·10 (8)	0·17 (9)
C(5)	7415 (14)	4366 (4)	3750 (3)	1·75 (10)	1·63 (10)	1·48 (10)	0·08 (9)	−0·20 (9)	0·06 (8)
C(6)	18023 (13)	1246 (4)	4335 (3)	1·45 (10)	1·32 (9)	1·26 (10)	0·09 (8)	−0·05 (8)	0·20 (8)

Table 1 (*cont.*)

	$x\times10^3$	$y\times10^3$	$z\times10^3$	B
H(1)	77 (1)	− 12 (4)	672 (3)	1·8 (6)
H(2)	103 (2)	−129 (6)	548 (4)	3·6 (9)
H(3)	36 (1)	267 (4)	538 (3)	1·1 (6)
H(4)	45 (2)	153 (5)	398 (4)	2·4 (7)
H(5)	173 (2)	262 (5)	707 (4)	1·8 (8)
H(6)	281 (2)	627 (6)	326 (4)	3·4 (11)
H(7)	239 (2)	768 (7)	345 (5)	4·8 (11)
H(8)	32 (2)	−222 (6)	230 (4)	3·4 (10)
H(9)	72 (2)	− 89 (6)	238 (4)	2·8 (10)
H(10)	116 (2)	118 (6)	− 58 (4)	3·7 (10)
H(11)	99 (2)	262 (6)	3 (4)	3·1 (10)
H(12)	− 71 (2)	288 (6)	68 (6)	3·7 (11)
H(13)	− 27 (2)	304 (6)	160 (4)	3·9 (10)
H(14)	135 (2)	560 (6)	148 (5)	2·4 (11)
H(15)	178 (2)	593 (6)	65 (4)	3·4 (9)

measured value of I was used in computing F and when $I<\sigma(I)$, F was computed using the value $0·77\sigma(I)$. The intensity data were converted to structure amplitudes by application of Lorentz and polarization factors and a spherical absorption correction (Johnson, 1963) with $\mu[\mathrm{Mo}\ K\alpha]=16·5\ \mathrm{cm}^{-1}$. They were placed on an absolute scale by means of a Wilson plot.

The structure was determined from the Patterson map and refined by full-matrix least-squares methods with the hydrogen atoms treated isotropically and all others anisotropically. The weights used were $1/[\sigma^2(F_o)]$ with unobserved reflections assigned zero weight. The quantity minimized was $\sum\omega\{||F_o|-|F_c||\}^2$. The final refinement resulted in a residual, R, of 0·045 and a weighted R value of 0·042. Final atomic parameters are given in Table 1. A table of calculated and observed structure factors has been deposited with the National Lending Library as Supplementary Publication No. SUP 30040.*

The atomic scattering factors used for manganese, oxygen and carbon atoms were those in *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms those of Stewart, Davidson & Simpson (1965). The anomalous dispersion corrections for manganese, $\Delta f'=0·295$ and $\Delta f''=0·729$ respectively, are listed by Cromer & Liberman (1970). Computer programs used in this determination were the X-ray 70 System (Stewart, Kundell & Baldwin, 1970), *UCLALS*4 (Full-Matrix Least-Squares; Gantzel, Sparks, Long & Trueblood, 1969), modified by H. L. Carrell and a program to compute interatomic distances, planes and torsion angles (*ALLD* written by H. L. Carrell & A. Caron).

Discussion. This study was undertaken in order to provide data for an accurate comparison with the results from studies in solution (Grzybowski, Tate & Datta, 1970; Villafranca & Mildvan, 1971, 1972; Glusker & Carrell, 1973). Distances and angles are listed in Table 2 with a comparison with distances for the magnesium salt. Most of the differences in interatomic distances are very small. Those in the metal–oxygen distances indicate that the ionic radius of the manganous ion is 0·10 Å greater than that of magnesium ion. The main changes in bond lengths are the lengthening of C(1)–O(1) by 0·012 Å (e.s.d. 0·002 Å for each structure determination) and the shortening of C(3)–O(7) by 0·009 Å. The distances involved in the hydrogen bonding of H(5) are slightly different in the two salts. In the manganese salt the distances O(7)···O(1) and O(7)···O(2$^{\mathrm{I}}$) are 2·756 and 3·104 Å respectively while in the magnesium salt these distances are 2·788 and 2·985 Å. These changes are discussed in detail elsewhere (Glusker & Carrell, 1973).

Table 2. *Interatomic distances and angles*

Distances	Manganous salt (e.s.d. 0·002)	Magnesium salt (e.s.d. 0·002)
C(1)–C(2)	1·513 Å	1·515 Å
C(4)–C(5)	1·523	1·518
C(3)–C(6)	1·558	1·555
C(2)–C(3)	1·547	1·541
C(3)–C(4)	1·532	1·532
C(1)–O(1)	1·278	1·266
C(1)–O(2)	1·239	1·246
C(5)–O(3)	1·252	1·254
C(5)–O(4)	1·267	1·259
C(6)–O(5)	1·258	1·260
C(6)–O(6)	1·256	1·250
C(3)–O(7)	1·434	1·443

Angles	Manganous salt (e.s.d. 0·1)	Magnesium salt (e.s.d. 0·1)
O(1)–C(1)–O(2)	122·6°	123·2°
O(3)–C(5)–O(4)	122·7	123·0
O(5)–C(6)–O(6)	123·9	124·1
O(1)–C(1)–C(2)	115·7	116·2
O(2)–C(1)–C(2)	121·6	120·5
O(3)–C(5)–C(4)	117·1	117·2
O(4)–C(5)–C(4)	120·2	119·8
O(5)–C(6)–C(3)	118·0	117·0
O(6)–C(6)–C(3)	118·1	118·9
O(7)–C(3)–C(2)	111·0	111·7
O(7)–C(3)–C(4)	106·4	106·7
O(7)–C(3)–C(6)	109·4	108·4
C(1)–C(2)–C(3)	110·5	111·0
C(3)–C(4)–C(5)	115·5	115·3
C(2)–C(3)–C(6)	109·6	110·6
C(4)–C(3)–C(6)	110·8	110·4
C(2)–C(3)–C(4)	109·5	108·9

Distances	Manganous salt (e.s.d. 0·002)	Magnesium salt (e.s.d. 0·001)
M(1)–O(9)	2·180 Å	2·081 Å
M(1)–O(10)	2·181	2·080
M(1)–O(11)	2·169	2·061
M(2)–O(1′)	2·167	2·072
M(2)–O(2″)	2·123	2·019
M(2)–O(4)	2·181	2·077
M(2)–O(5)	2·194	2·081
M(2)–O(7)	2·224	2·118
M(2)–O(8)	2·140	2·031

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* Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

A comparison of $Mn^{2+} \cdots H$ distances from this study with those found by n.m.r. studies in the absence and presence of the enzyme aconitase (Villafranca *et al.*, 1972) indicates that the model involving a ternary enzyme–manganous citrate complex with the citrate ion directly chelated to the metal ion is probably correct.

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SHORT COMMUNICATION

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Acta Cryst. (1973). B29, 640

The crystallography of nitramine–solvent complexes. II.* Classification and crystallographic data of some complexes of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX).

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Crystallographic data of some further complexes of the title compound with organic solvents are given. The complexes are classified into types depending on the internal symmetry within the crystals.

The crystalline complexes of BSX, formed with various solvents by simple recrystallisation, can be divided into four main groups; within each group the cell dimensions are similar and the internal symmetry the same. Table 1 shows the four types of complex formed with a number of organic solvents. Those marked (2:1) have that molecular ratio of BSX to solvent and the remainder have a 1:1 ratio. These ratios were obtained from crystal density and unit-cell dimension measurements and confirmed by thermogravimetric analysis or in some cases from n.m.r. spectra of solutions.

Unit-cell dimensions and space groups were determined for most of the complexes from oscillation and Weissenberg photographs using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Crystal data for the complexes are shown in Table 2. Crystals grown from benzene and monofluorobenzene (type *D*) were too small to determine unit-cell dimensions.

Table 1. *BSX complexes*

Type *A*. Monoclinic
- Acetonitrile
- Acetone
- Nitromethane
- Pyridine
- *N,N*-Dimethylformamide
- *N,N*-Dimethylacetamide
- Dichloromethane
- Dibromomethane
- *N*-Methyl-2-pyrrolidinone
- Nitrobenzene (2:1)
- Acetophenone (2:1)
- Acetylacetone (2:1)
- Cyclohexanone (2:1)
- Pentafluorobenzene (2:1)
- 1,1,2,2-Tetrachloroethane (2:1)

Type *B*. Monoclinic
- 4-Hydroxybutanoic acid lactone
- 1,4-Thioxane (2:1)
- 3-Bromopyridine (2:1)
- 3-Methylpyridine (2:1)

Type *C*. Monoclinic
- 1,4-Dioxane

Type *D*. Triclinic
- Benzene
- Monofluorobenzene

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* Part I: Claringbull & Small, *Acta Cryst.* B27, 863–864.