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The Crystal Structures of $\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$

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The crystal structures of potassium *trans*-diaquabis(malonato)manganese(III) dihydrate and tripotassium tris(malonato)manganese(III) dihydrate were determined by single-crystal diffraction. $\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$ (I) crystallizes in space group *Pbcn*, with $a = 6.842$ (3), $b = 13.491$ (7), $c = 14.115$ (6) Å; $\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$ (II) crystallizes in *C2/c* (rather than *Cc*), with $a = 14.799$ (8), $b = 7.850$ (4), $c = 16.210$ (8) Å, $\beta = 108.51$ (4)°. The Mn–O bond distances in (II) are in the range 1.92–2.04 Å and are longer than the average Mn–O(malonate) bond length of 1.90 (1) Å in compound (I).

Introduction

Literature on the preparation, kinetics and spectra of Mn complexes with carboxylic acids is extensive. Investigations of complexes of Mn with oxalate and malonate ions are of special interest. Air-stable compounds of Mn^{III} with malonic acid (Meyer & Schramm, 1922; Cartledge & Nichols, 1940; Bullock, Patel & Salmon, 1969) have been obtained. The present paper discusses the crystal structures of $\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$.

Experimental

Preparation

$\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$ was obtained by the method of Bullock, Patel & Salmon (1969) as green crystals. Red crystals of this compound prepared by the method of Bullock, Patel & Salmon were not suitable for X-ray analysis. Crystals of $\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$ suitable for single-crystal diffraction were obtained as follows: to a moist potassium malonate (prepared from stoichiometric proportions of potassium carbonate and malonic acid) was added well powdered, green $\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$. The reaction mixture was then put into an ice-box ($\sim 0^\circ\text{C}$) and after one day well formed red crystals appeared and were dried with a filter paper and ethanol.

Crystal data

$\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$ (I), $M_r = 370.2$, orthorhombic, $a = 6.842$ (3), $b = 13.491$ (7), $c = 14.115$ (6) Å, $V = 1302.9$ Å³; $D_m = 1.88$, $Z = 4$, $D_c = 1.89$ g cm⁻³; $\mu(\text{Cu } K\alpha) = 121.3$ cm⁻¹. Space group *Pbcn* from systematic absences.

$\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$ (II), $M_r = 420.5$, monoclinic, $a = 14.799$ (8), $b = 7.850$ (4), $c = 16.210$ (8) Å, $\beta = 108.51$ (4)°, $V = 1785.7$ Å³; $D_m = 1.90$, $Z = 4$, $D_c = 1.91$ g cm⁻³; $\mu(\text{Cu } K\alpha) = 132.1$ cm⁻¹. Space group *Cc* or *C2/c* from systematic absences.

Intensity measurements

In both cases a Syntex P2₁ diffractometer, with Cu $K\alpha$ radiation and a graphite monochromator, was used for lattice-parameter and intensity measurements. The intensities were measured by the 2θ – ω scan technique. An irregular polyhedron of (I) with dimensions 0.15 × 0.15 × 0.10 mm was selected and 1244 independent reflexions were measured, of which 874 were ‘observed’ with $I > 1.96\sigma(I)$. In the case of (II), an almost spherical crystal with a diameter of 0.10 mm was used and 1786 independent reflexions were measured, 1456 of which were ‘observed’ with $I > 1.96\sigma(I)$. The reflexions were collected within the limit $\theta \leq 73^\circ$. The data were corrected for Lorentz and polarization effects. For (II) the absorption correction was applied as for a spherical crystal with $\mu R = 0.7$. In both cases the standard reflexion was measured every 40 reflexions; no significant changes in intensity were observed.

Determination of the structures

All calculations were performed on a NOVA 1200 computer with programs supplied by Syntex (Syntex XTL structure determination system). Scattering factors for Mn³⁺, K⁺, O, C and H atoms were those in *International Tables for X-ray Crystallography* (1974).

In (I) Mn and K atoms were found from the three-dimensional Patterson synthesis. Difference Fourier syntheses, after preliminary refinements of the heavy atoms, showed the positions of all the remaining non-H atoms. The refinement with the full-matrix least-squares program, first with isotropic and then with anisotropic thermal parameters, gave $R = 0.067$ and $R_w = 0.085$. A difference map based on the final parameters was essentially flat; H atoms were not resolvable. The final atomic coordinates and their estimated standard deviations are listed in Table 1.*

For the crystal of (II), two space groups were possible from the systematic absences: Cc and $C2/c$. The Mn atoms were found from the three-dimensional Patterson map and the centrosymmetric space group $C2/c$ was assumed. A Fourier synthesis, after preliminary refinements of the Mn atoms, showed the positions of the K atoms. The difference Fourier synthesis based on the Mn and K structure showed all the remaining non-H atoms. The structure was then refined, first with isotropic and then anisotropic temperature factors for all non-H atoms, to $R = 0.050$ and $R_w = 0.050$. A difference Fourier synthesis at this stage showed two H atoms from the water molecule and two H atoms from the C(2) atom. Further refinement with fixed parameters for H atoms reduced R to 0.045 and R_w to 0.042. The final atomic coordinates and their estimated standard deviations are listed in Table 2. The temperature factors for all atoms are acceptable, only B_{33}

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32363 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters of K[Mn(H₂O)₂(mal)₂].2H₂O*

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0	0	0
K	0	0.2092 (3)	$\frac{1}{4}$
O(1)	-0.0034 (14)	0.1303 (4)	0.0516 (4)
O(2)	-0.1066 (12)	0.0450 (5)	-0.1158 (5)
O(11)	-0.0506 (12)	0.2902 (5)	0.0590 (5)
O(22)	-0.2302 (12)	0.1464 (6)	-0.2211 (5)
H ₂ O(1)	0.3142 (11)	0.0216 (5)	-0.0543 (6)
H ₂ O(2)	0.3037 (12)	0.0698 (6)	0.2678 (6)
C(1)	-0.0382 (14)	0.2134 (7)	0.0110 (7)
C(2)	-0.1392 (15)	0.1324 (8)	-0.1479 (7)
C	-0.0473 (15)	0.2217 (7)	-0.0984 (7)

Table 2. *Final positional parameters of K₃[Mn(mal)₃].2H₂O*

The H atoms positions are unrefined (all $B = 3.5 \text{ \AA}^2$).

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0	0.1727 (2)	$\frac{1}{4}$
K(1)	0.2343 (1)	0.4500 (2)	0.2910 (1)
K(2)	$\frac{1}{4}$	$\frac{1}{4}$	0
O(1)	0.0756 (2)	0.3469 (4)	0.3335 (2)
O(2)	-0.0903 (2)	0.1742 (5)	0.3131 (2)
O(3)	-0.0808 (3)	-0.0138 (5)	0.1738 (2)
O(4)	0.1357 (3)	0.4666 (5)	0.4626 (2)
O(5)	-0.1238 (3)	0.1194 (5)	0.4330 (2)
O(6)	-0.1638 (3)	-0.2393 (5)	0.1852 (3)
H ₂ O	0.2758 (3)	0.1239 (5)	0.3645 (2)
C(1)	0.0826 (4)	0.3612 (6)	0.4139 (3)
C(2)	0.0268 (4)	0.2432 (7)	0.4530 (3)
C(3)	-0.0687 (3)	0.1740 (6)	0.3975 (3)
C(4)	-0.0875 (4)	-0.1642 (6)	0.2005 (3)
C(5)	0	-0.2573 (12)	$\frac{1}{4}$
H(1)	0.318	0.136	0.432
H(2)	0.205	0.090	0.364
H(3)	0.016	0.305	0.504
H(4)	0.070	0.141	0.477

= 23.8 for C(5) is very large. This atom lies on the twofold axis (in the space group $C2/c$). It is possible that the complex investigated really crystallizes in the noncentrosymmetric space group. However, refinement in space group Cc was not successful. Therefore only the results of the refinement in $C2/c$ are reported. The final difference synthesis in this group was quite flat, except for the sphere about C(5) where three peaks appeared, corresponding in height to the H atoms of the earlier difference synthesis.

Description of the structures and discussion

Crystals of (I) comprise complex $[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2]^-$ anions, potassium cations and water molecules. The arrangement of the molecules in projection on the (100) plane is shown in Fig. 1. The principal intramolecular distances and angles in the complex anion are given in Table 3. The complex anion possess $\bar{1}$ point symmetry, as required by the space group, and for chemical purposes may be considered to possess mmm symmetry. The two Mn—O(malonate) bonds are equal, within experimental error, and the average distance of 1.90 (1) Å is rather short compared with the values of 1.93–2.17 Å for Mn^{III}—O(formate) bonds found in $\text{K}_3\{\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}_3\text{O}(\text{HCOO})_9]_2\}$ (Lis & Jeżowska-Trzebiatowska, 1977). The value of 2.30 (1) Å for the Mn—H₂O bond distance is rather long for coordinated water and suggests that this bond is rather weak. No other Mn^{III}—H₂O distances with which the present bond length can be compared, have been reported. It is

interesting to note that the $\text{Mn}^{\text{II}}-\text{H}_2\text{O}$ bond lengths of 2.19 Å in $[(\text{CH}_3)_3\text{NH}]\text{MnCl}_3 \cdot 2\text{H}_2\text{O}$ (Caputo, Willett & Muir, 1976) and 2.17 Å in $\text{K}_2\text{Mn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (Schulz, 1974) are shorter. The bond distances and angles in the malonate ion are normal and agree well with the values reported for malonic acid (Goedkoop & MacGillivray, 1957), benzylmalonic acid (Lepore, Lepore & Ganis, 1975), and fluoromalonic acid (Kanters, Roelofsen & Kroon, 1975).

In the crystal, three hydrogen bonds of lengths 2.70 (1), 2.80 (1) and 2.73 (2) Å linking $\text{H}_2\text{O}(1)$ to $\text{O}(11)$, $\text{H}_2\text{O}(1)$ to $\text{H}_2\text{O}(2)$ and $\text{H}_2\text{O}(2)[x, y, z]$ to $\text{H}_2\text{O}(2)[1-x, y, \frac{1}{2}-z]$ can be distinguished.

The K^+ cation lies on a twofold axis. The eight O atoms surrounding the K^+ ion are at distances varying from 2.71 to 3.00 Å, forming a rather irregular shape.

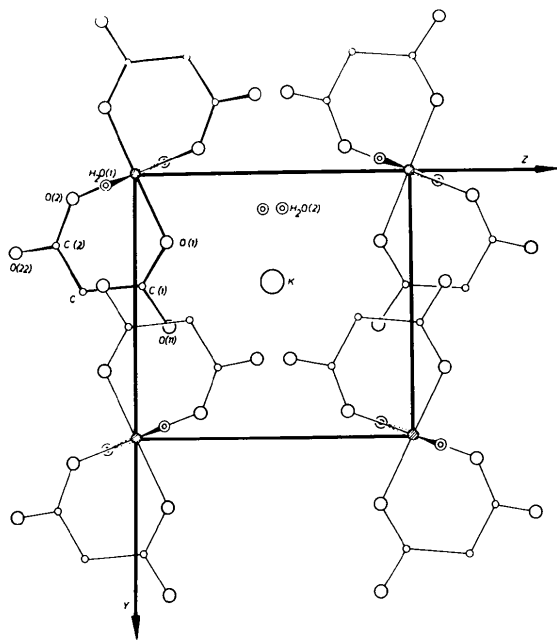


Fig. 1. The crystal structure of $\text{K}[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2] \cdot 2\text{H}_2\text{O}$: projection on the (100) plane.

Table 3. Bond lengths (Å) and angles (°) in the $[\text{Mn}(\text{H}_2\text{O})_2(\text{mal})_2]^-$ ion

Mn—O(1)	1.903 (5)	Mn—O(2)	1.890 (7)
O(1)—C(1)	1.280 (11)	O(2)—C(2)	1.282 (12)
C—C(1)	1.550 (13)	C—C(2)	1.529 (14)
C(1)—O(11)	1.240 (12)	C(2)—O(22)	1.222 (12)
Mn—H ₂ O(1)	2.301 (7)		
Mn—O(1)—C(1)	129.8 (7)	Mn—O(2)—C(2)	131.9 (7)
O(1)—C(1)—O(11)	120.0 (9)	O(1)—C(1)—C	121.1 (9)
O(11)—C(1)—C	118.7 (9)	O(2)—C(2)—O(22)	122.0 (9)
O(2)—C(2)—C	119.5 (9)	O(22)—C(2)—C	118.3 (9)
C(2)—C—C(1)	114.5 (8)		

The crystals of (II) are built of $[\text{Mn}(\text{mal})_3]^{3-}$ anions, K^+ cations and water molecules. The arrangement of the molecules in projection on the (010) plane is shown in Fig. 2. The principal intramolecular distances and angles in the complex anion are given in Table 4.

The $[\text{Mn}(\text{mal})_3]^{3-}$ ion is approximately a trigonally distorted octahedron with small deviations from D_3 symmetry, arising from lattice forces which vary as a result of the packing of the complex, from Jahn–Teller distortion in Mn^{III} complexes, and from crystallographic symmetry which imposes a C_2 axis on the D_3 geometry. It was predicted (Dunitz & Orgel, 1957) that the Mn^{III} complexes susceptible to a Jahn–Teller mechanism might distort their immediate octahedral configuration to four shorter and two longer (or two shorter and four longer) metal–ligand bond lengths. The Mn—O distances of 1.92, 2.00 and 2.04 Å in the $[\text{Mn}(\text{mal})_3]^{3-}$ ions plainly indicate the distortion from octahedral symmetry, although it is not the classical model of ‘two shorter and four longer’ or ‘two longer and four shorter’ distances. The $\text{H}_2\text{O}-\text{O}(3)$ hydrogen bond probably influences the lengthening of the Mn—O(3) bond and because of this the geometry of the complex anion is

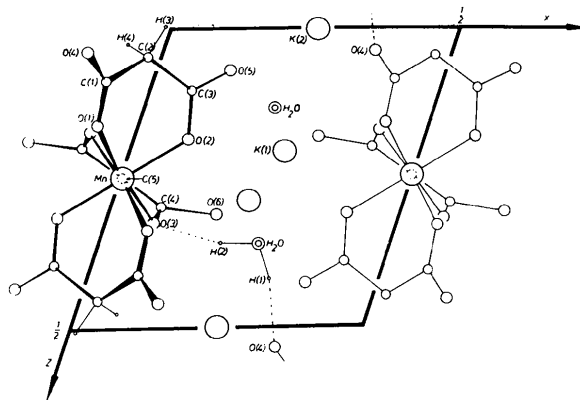


Fig. 2. The crystal structure of $\text{K}_3[\text{Mn}(\text{mal})_3] \cdot 2\text{H}_2\text{O}$: projection on the (010) plane.

Table 4. Bond lengths (Å) and angles (°) in the $[\text{Mn}(\text{mal})_3]^{3-}$ ion

Mn—O(1)	1.998 (3)	Mn—O(2)	1.923 (3)
Mn—O(3)	2.040 (3)	O(1)—C(1)	1.279 (5)
O(2)—C(3)	1.303 (5)	O(3)—C(4)	1.272 (6)
O(4)—C(1)	1.237 (6)	O(5)—C(3)	1.216 (6)
O(6)—C(4)	1.227 (6)	C(1)—C(2)	1.507 (7)
C(3)—C(2)	1.516 (6)	C(4)—C(5)	1.482 (7)
Mn—O(1)—C(1)	126.7 (3)	Mn—O(2)—C(3)	125.4 (3)
Mn—O(3)—C(4)	123.7 (3)	O(1)—C(1)—O(4)	122.6 (5)
O(1)—C(1)—C(2)	119.8 (4)	O(4)—C(1)—C(2)	117.7 (4)
O(2)—C(3)—O(5)	121.4 (4)	O(2)—C(3)—C(2)	119.6 (4)
O(5)—C(3)—C(2)	119.0 (4)	O(3)—C(4)—O(6)	122.9 (5)
O(3)—C(4)—C(5)	119.5 (5)	O(6)—C(4)—C(5)	117.6 (5)
C(1)—C(2)—C(3)	120.2 (4)	C(4)—C(5)—C(4)	120.9 (5)

Table 5. Hydrogen-bond lengths (Å) and angles (°) in K₃[Mn(mal)₃].2H₂O

X-H...Y	X...Y	X-H	H...Y	X-H...Y
H ₂ O-H(1)-O(4)	2.782 (4)	1.08	1.81	147.2
H ₂ O-H(2)-O(3)	2.958 (5)	1.08	1.92	159.2

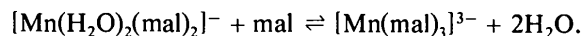
more distorted. The geometry and the average values of the intramolecular bond lengths and angles of malonate ions, except the C(5)-C(4) bond, agree well with those found in the [Mn(H₂O)₂(mal)₂]⁻ complex ions.

Two hydrogen bonds found in (II) are shown with dotted lines in Fig. 2. Their bond lengths and angles are given in Table 5. It is possible that these hydrogen bonds contribute to the stability of the crystal structure and one of them (see above) influences the lengthening of the Mn-O(3) bond.

The complexity of the coordination polyhedra around the potassium ions is similar to that found in other potassium salts.

As reported earlier (Bullock, Patel & Salmon, 1969) both (I) and (II), being high-spin *d*⁴ complexes, obeyed the Curie-Weiss law with magnetic moments close to 4.9 BM. This value is identical with the theoretical value of 4.90 BM obtained for the spin-only approximation, and can now be confirmed by the fact that the Mn-Mn distances are very long (long enough to eliminate any interaction between Mn atoms).

The interrelationships between compounds I and II may be expressed by the equation:



In all probability the very weak Mn-H₂O(1) bonds in (I) can be very easily disrupted in aqueous solution, and at high malonate-ion concentrations, [Mn(mal)₃]³⁻ may be formed.

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