Crystal and Molecular Structure of the Potassium Salt of Polymeric Manganese(III) Malonate, $K[Mn(C_3H_2O_4)_2(CH_3OH)]$

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The crystal structure of the compound hitherto regarded as $K[Mn(C_3H_2O_4)_2(OH_2)_2]$ has been found to be $K[Mn(C_3H_2O_4)_2(CH_3OH)]$ as established by *X*-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with $a = 8.55(2)$, $b = 8.56(1)$, $c = 8.95(1)$ Å, $\alpha = 113.60(9)$, $\beta = 94.78(10)$, $\gamma = 99.97(10)°$, and $Z = 2$. The structure has been solved using Patterson and Fourier methods, least-squares refinement giving a final $R = 0.051$ and $R' = 0.042$ for 1 231 reflections with $I > 1.96\sigma(I)$. The two different manganese atoms occupy special positions and have different octahedral environments. In one case, two malonate ligands and two methanol molecules are involved in co-ordination, while in the second only malonate groups are involved.

THE chemistry of manganese in its higher oxidation states has not been as exhaustively explored as one might have expected, considering the importance of this branch of co-ordination chemistry. In addition to interest in the role of Mn^{III}- or Mn^{IV}-containing systems in biological activity,[1] there is particular interest in the catalytic activity, analytical use (such as in redox processes between potassium permanganate and various reagents), or industrial application of similar, but artificial compounds.[2,3] In contrast with other co-ordination compounds, the high photosensitivity and general instability of many of these systems seem to reveal quite new opportunities for preparative chemistry.[4,5] Particular emphasis should be put on the malonate (mal) complexes of trivalent manganese, since they are far more stable than the related oxalato-complexes or other compounds (acetoacetonates, benzoates, *etc.*[6,7]). For this reason, the malonate complexes can be used as a starting point for experiments which require a relatively long time to perform, such as *X*-ray analysis. Our experiments in this field have allowed us to determine the crystal structures of $K[Mn(mal)_3]\cdot 2H_2O$ and of the two forms of $K[Mn(mal)_2(OH_2)_2]\cdot 2H_2O$.[8,9] Subsequent investigation has revealed the structure of the green crystals obtained in the reaction between potassium permanganate and malonic acid in a non-aqueous medium (anhydrous methanol). The compound has previously been described by the formula $K[Mn(mal)_2(OH_2)_2]$.[10,11]

EXPERIMENTAL

Materials.—Malonic acid (Fluka), $K[MnO_4]$ (AnalaR), methanol (Austranal), methylene chloride (POCh), and cyclohexanol (POCh) were used without further purification.

Preparation.—When prepared according to the method given by Cartledge and Nichols [10] the complex consisted of very small crystals. Larger ones, of identical morphology when observed under a microscope, were obtained after a slight modification had been adopted. Thus malonic acid (0.260 g) was dissolved in a mixture containing methylene chloride (6 cm^3), cyclohexanol (6 cm^3), and absolute methanol (5 cm^3) and then potassium permanganate was added (0.158 g). The mixture was placed in a refrigerator (*ca.* 5 °C) for 3 d after which clusters of green triclinic crystals appeared on the bottom of the beaker. Some of these had quite well developed faces, and were satisfactory for single-crystal diffractometry. The crystals were removed from the mother-liquor and dried in air. (It is noteworthy that this complex did not crystallize even when small amounts of water were added to the reaction mixture.)

Crystal Data.—$K[Mn(C_3H_2O_4)_2(CH_3OH)]$, Triclinic, $M = 330.2$, $a = 8.55(2)$, $b = 8.56(1)$, $c = 8.95(1)$ Å, $\alpha = 113.60(9)$, $\beta = 94.78(10)$, $\gamma = 99.97(10)°$, $U = 582.7$ Å^3, $D_m = 1.86$ g cm^{-3}, $Z = 2$, $D_c = 1.88$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) $= 132.8$ cm^{-1}, space group $P\bar{1}$.

Intensity Measurements.—A crystal with dimensions not greater than 0.09 mm in each direction was mounted on a Syntex $P2_1$ four-circle diffractometer and data were collected with Cu-K_α radiation and a graphite monochromator. 1 470 Reflections were measured within the limit $2\theta \leqslant 114.5°$, 1 231 of which with $I > 1.96\,\sigma(I)$ were used for structure determination. Two standard reflections were monitored after every 15 reflections. The 2θ—ω scan technique was employed. The intensities were corrected for Lorentz and polarization effects but not for absorption and extinction. The neutral-atom scattering factors employed in calculations were those given in ref. 12. All the calculations were performed on a NOVA 1200 minicomputer with programs supplied by Syntex.[13]

Determination and Refinement of the Structure.—The positions of the Mn and K atoms were found by a three-dimensional Patterson synthesis and space group $P\bar{1}$ was assumed. Successive difference-Fourier syntheses revealed the positions of all non-hydrogen atoms, including O and C atoms from the methanol molecule. The structure was then refined, first with isotropic and then with anisotropic temperature factors, to $R = 0.061$. A difference-Fourier synthesis at this stage showed the positions of all H atoms. Further refinement with isotropic temperature factors for H atoms gave a final R value of 0.051 and $R' = 0.042$. The final difference-Fourier synthesis was featureless. Lists of thermal parameters and structure factors are available as Supplementary Publication No. SUP 22730 (17 pp.).*

RESULTS AND DISCUSSION

The final atomic co-ordinates are listed in Table 1, interatomic distances and angles in Table 2. A view of the crystal structure down the *c* axis and the atom-numbering scheme are shown in the Figure. The polymeric structure consists of carboxylate-bridged *trans*-bis(malonato)dimethanolmanganate(III) and bis-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 1

Atomic positional parameters

Atom	*X*	*Y*	*Z*
Mn(1)	0	0	0
Mn(2)	½	½	0
K	0.722 6(2)	0.964 3(2)	0.320 1(2)
O(1)	0.004 4(6)	0.065 8(6)	0.230 1(6)
O(2)	0.220 0(6)	−0.018 0(6)	0.018 5(6)
O(3)	0.482 3(6)	0.657 3(6)	0.216 3(6)
O(4)	0.290 4(6)	0.356 8(6)	−0.030 2(6)
O(7)	0.598 4(8)	0.339 8(8)	0.108 0(8)
O(11)	0.109 0(7)	0.166 6(8)	0.492 1(7)
O(22)	0.447 9(7)	0.016 9(7)	0.153 2(6)
O(33)	0.358 1(7)	0.793 5(8)	0.417 3(7)
O(44)	0.064 3(6)	0.288 4(6)	0.058 4(6)
C(1)	0.126 8(10)	0.133 4(10)	0.349 8(10)
C(2)	0.324 8(10)	0.036 8(9)	0.152 4(10)
C(3)	0.350 8(10)	0.685 4(10)	0.276 4(10)
C(4)	0.180 6(10)	0.395 4(10)	0.058 2(9)
C(5)	0.293 4(11)	0.171 7(11)	0.310 7(10)
C(6)	0.191 6(10)	0.587 7(10)	0.168 4(11)
C(7)	0.708 1(16)	0.392 9(15)	0.258 4(13)
H(7)	0.582(9)	0.251(8)	0.067(9)
H(71)	0.828(15)	0.392(15)	0.302(14)
H(72)	0.747(10)	0.514(12)	0.319(10)
H(73)	0.672(16)	0.341(17)	0.351(16)
H(51)	0.372(9)	0.189(9)	0.403(9)
H(52)	0.314(8)	0.284(9)	0.306(8)
H(61)	0.101(9)	0.602(9)	0.251(9)
H(62)	0.171(10)	0.645(10)	0.099(10)

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) Distances

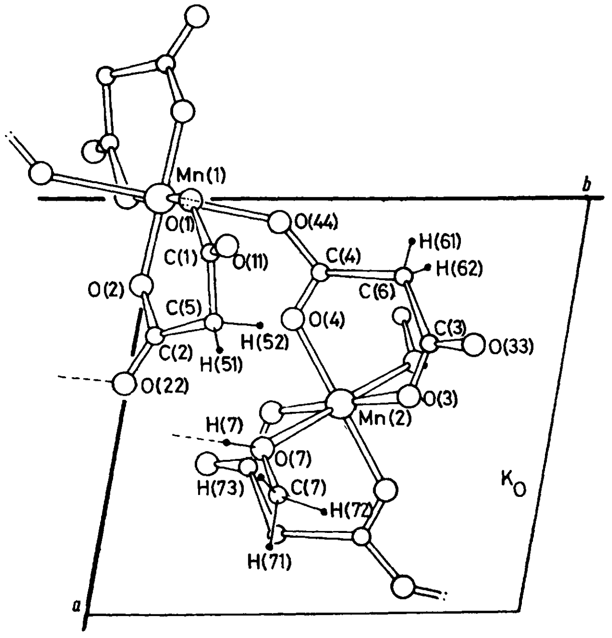
Mn(1)–O(1)	1.901(5)	Mn(2)–O(3)	1.901(4)
Mn(1)–O(2)	1.913(5)	Mn(2)–O(4)	1.918(5)
Mn(1)–O(44)	2.262(5)	Mn(2)–O(7)	2.203(7)
O(1)–C(1)	1.298(9)	O(3)–C(3)	1.304(10)
O(2)–C(2)	1.298(9)	O(4)–C(4)	1.280(9)
C(1)–O(11)	1.219(10)	C(3)–O(33)	1.218(10)
C(2)–O(22)	1.219(10)	C(4)–O(44)	1.230(10)
C(1)–C(5)	1.507(12)	C(3)–C(6)	1.492(12)
C(2)–C(5)	1.508(11)	C(4)–C(6)	1.523(12)
C(5)–H(51)	0.97(8)	C(6)–H(61)	1.11(8)
C(5)–H(52)	0.96(8)	C(6)–H(62)	0.95(9)
O(7)–C(7)	1.431(13)	C(7)–H(71)	1.06(14)
C(7)–H(72)	0.94(11)	C(7)–H(73)	1.13(15)
O(7)–H(7)	0.68(8)	H(7) · · · O(22$^{\mathrm{I}}$)	2.13(7)
O(7) · · · O(22$^{\mathrm{I}}$)	2.748(8)		
K · · · O(1$^{\mathrm{II}}$)	2.714(5)	K · · · O(3$^{\mathrm{III}}$)	2.802(5)
K · · · O(4$^{\mathrm{IV}}$)	2.904(5)	K · · · O(22$^{\mathrm{V}}$)	2.740(6)
K · · · O(11$^{\mathrm{VI}}$)	2.796(6)	K · · · O(33$^{\mathrm{VII}}$)	2.676(6)

(*b*) Angles

O(1)–Mn(1)–O(2)	91.5(3)	O(3)–Mn(2)–O(4)	92.1(2)
Mn(1)–O(1)–C(1)	129.3(5)	Mn(2)–O(3)–C(3)	127.7(5)
Mn(1)–O(2)–C(2)	127.9(5)	Mn(2)–O(4)–C(4)	127.3(5)
Mn(1)–O(44)–C(4)	137.8(5)	Mn(2)–O(7)–C(7)	129.7(7)
O(1)–C(1)–O(11)	121.2(8)	O(3)–C(3)–O(33)	120.4(8)
O(11)–C(1)–C(5)	119.8(8)	O(33)–C(3)–C(6)	120.5(8)
O(1)–C(1)–C(5)	119.0(8)	O(3)–C(3)–C(6)	119.1(8)
O(2)–C(2)–O(22)	121.9(8)	O(4)–C(4)–O(44)	124.6(8)
O(22)–C(2)–C(5)	119.4(8)	O(44)–C(4)–C(6)	117.3(7)
O(2)–C(2)–C(5)	118.8(7)	O(4)–C(4)–C(6)	118.1(7)
C(1)–C(5)–C(2)	115.2(8)	C(3)–C(6)–C(4)	115.3(8)
O(7)–H(7) · · · O(22$^{\mathrm{I}}$)	152(8)		

Roman numeral superscripts indicate the following equivalent positions: I $1 - x, -y, -z$; II $1 + x, 1 + y, z$; III x, y, z; IV $1 - x, 1 - y, -z$; V $x, 1 + y, z$; VI $1 - x, 1 - y, 1 - z$; VII $1 - x, 2 - y, 1 - z$.

(malonato)manganate(III) anions, and potassium cations. The anions are interlinked by hydrogen bonds. Each of the two different manganese atoms is bound to four oxygen atoms of the malonate ligands at a distance of 1.91(1) Å, which corresponds to the Mn–O(malonate) distances found previously in $[\mathrm{Mn(mal)_2(OH_2)_2}]^-$ anions.[8,9] The occupancy of the two remaining sites in the co-ordination octahedron is different for both manganese atoms. The Mn(1) atoms are linked to one of the oxygen atoms [O(44), see Figure] of the carboxy-groups of the malonate ligands chelating the Mn(2) atoms. In this way the carboxy-group O(44)–C(4)–O(4) becomes bidentate. The Mn(1)–O(44) bond length of 2.26(1) Å indicates that this bond is rather weak. In the case of the atom Mn(2), the two remaining positions are occupied by methanol molecules. The Mn–O(methanol) bond length of 2.203(7) Å is shorter than that [2.329(7) Å] observed[14] in $[\mathrm{Mn(tpp)(N_3)(CH_3OH)]\cdot CH_3OH}$.* In terms of manganese–oxygen distances, the distortion around the two different manganese(III) ions seems to be of the same type and may be classified as tetragonal elongation of the co-ordination octahedron. The situation is similar to that found earlier in $[\mathrm{Mn(mal)_2(OH_2)_2}]^-$ and $[\mathrm{MnF_4(OH_2)_2}]^-$ anions.[8,9,15]



View of the structure of $\mathrm{K[Mn(mal)_2(CH_3OH)]}$ projected on the (001) plane

The complex under discussion is relatively stable compared with other crystals containing methanol molecules. It is clear that the specific polymeric structure of the complex and the existence of hydrogen bonding is connected with this stability. The hydrogen bonds are formed between the hydrogen atoms of hydroxy-groups of the methanol molecules and the oxygen atoms O(22) of the malonate ligands which chelate the atom Mn(1) in a neighbouring cell. These bonds (the lengths and angles of which are presented in Table 2) may act as an additional ' anchorage ' for the methanol molecules in the crystal lattice. There are few papers which describe structures where methanol molecules act as ligands.[16-19] In the known structures,

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* tpp = 5,10,15,20-Tetraphenylporphyrinate(2−).

the bond lengths and the angle M–O–C (for the co-ordinated methanol) correspond well with the respective values determined here (Table 2).

In the investigated crystals the two different chelate rings adopt the 'envelope' conformation as in most complexes of the malonate ligand.[20] The fact that the atom O(44) is co-ordinated to Mn(1) does not account for the difference in length between the bonds C(4)–O(4) and C(4)–O(44). This seems to indicate that the double-bond character of C(4)–O(44) is partially preserved.

Each of the potassium cations is surrounded by six oxygen atoms lying at distances varying from 2.68(2) to 2.90(2) Å (Table 2), forming a considerably deformed shape.

The mechanism of reaction between potassium permanganate and malonic acid is not clear. Both in aqueous and in non-aqueous media (such as methanol) the product is the malonate complex of trivalent manganese. No intermediate complexes of Mn^{IV} or Mn^{V} could be isolated, in contrast to the formally analogous reaction between potassium permanganate and oxalic acid where the formation of manganese(IV) oxalate complexes is observed. The question remains as to whether the isolation of malonate complexes of Mn^{IV} is possible under mild conditions. Work in connection with this problem is in progress.

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