

Structure of Potassium Tris(oxalato)manganate(III) Trihydrate

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Abstract. $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$, monoclinic, $P2_1/c$, $a = 7.72$ (1), $b = 19.88$ (3), $c = 10.41$ (1) Å, $\beta = 108.22$ (3)°, $V = 1517.4$ Å³, $M_r = 490.3$, $Z = 4$, $D_x = 2.15$, $D_c = 2.15$ Mg m⁻³, $\mu(Mo K\alpha, \lambda = 0.71069 \text{ Å}) = 1.8$ mm⁻¹. The discrete $[Mn(ox)_3]^{3-}$ (ox = oxalato) anions exhibit orthorhombic deviation from D_3 symmetry owing to the Jahn–Teller effect. There are three pairs of different Mn–O(*trans*) distances: short, 1.899 (9) and 1.915 (9) Å; intermediate, 2.016 (9) and 2.019 (10) Å; and long, 2.073 (10) and 2.076 (8) Å. The crystals are not exactly isomorphous with $K_3[Cr(ox)_3] \cdot 3H_2O$ and $K_3[Al(ox)_3] \cdot 3H_2O$ but the structures are related by a pseudo mirror plane perpendicular to y at $b = \frac{1}{2}$. The structure was refined to $R = 4.8\%$ and $R_w = 4.7\%$ for 1206 diffractometer data obtained in a darkened room.

Introduction. Since much interest in recent years has been shown in the chemistry of Mn^{III}, whereas only limited structural data are available, we decided to investigate the structures of some of its complexes. Such structural results are useful when applied to problems connected with the bio-inorganic role of Mn (Lawrence & Sawyer, 1978). The well-known complexes formed in the reaction between $KMnO_4$ and oxalic acid have been characterized (Cartledge & Ericks, 1936) and reviewed (Davies, 1969; Harriman, 1979) but their instability made X-ray experiments difficult. The present study is a continuation of our earlier experiment and its preliminary results have been reported (Matuszewski, Lis & Jeżowska-Trzebiatowska, 1978). 1601 reflections were collected at that time, including 785 which had $I > 1.96\sigma(I)$, and the structure was solved on the assumption that $K_3[Mn(ox)_3] \cdot 3H_2O$ is isomorphous with $K_3[Cr(ox)_3] \cdot 3H_2O$. Both the experiment itself and its results left much to be desired ($R = 9.5\%$) so we decided to re-examine the structure.

The preparation was conducted according to the following procedure. To a mixture of 7.2 g $H_2C_2O_4 \cdot 2H_2O$ (0.08 mol) and 3.7 g $K_2C_2O_4 \cdot H_2O$ (0.02 mol) suspended in water (~2 ml), well powdered $KMnO_4$ was added in small portions (3.2 g, 0.02 mol), the temperature being kept at ~273 K. A few drops of the solution were placed on a Petri plate and put into a

refrigerator (~280 K). After one day deep-purple crystals appeared. A crystal 0.15 × 0.25 × 0.10 mm was mounted on a Syntex $P2_1$ four-circle diffractometer and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation. The stability of the complex was presumed to be dependent on light as well as temperature, so data were collected as rapidly as possible. The experiment was carried out in a darkened room and first the intensities of 785 reflexions were measured [those which were observed in the previous experiment with $I > 1.96\sigma(I)$]. After these reflexions had been collected with no observable loss of intensity

Table 1. Final positional parameters with e.s.d.'s in parentheses

	x	y	z	B_{eq} (Å ²)
Mn	0.2646 (3)	0.3716 (1)	0.2518 (3)	1.72
O(1)	0.1577 (11)	0.4300 (5)	0.3667 (11)	2.49
O(2)	0.4849 (9)	0.3872 (5)	0.3971 (10)	1.99
O(3)	0.3369 (12)	0.4403 (5)	0.1276 (11)	2.12
O(4)	0.0418 (10)	0.3721 (5)	0.1071 (10)	2.70
O(5)	0.3926 (11)	0.3003 (5)	0.1774 (9)	3.50
O(6)	0.1856 (10)	0.2848 (5)	0.3294 (9)	2.63
O(11)	0.2383 (11)	0.4705 (5)	0.5790 (11)	3.00
O(22)	0.5970 (10)	0.4368 (5)	0.6007 (10)	2.13
O(33)	0.2263 (11)	0.4793 (5)	−0.0859 (10)	2.85
O(44)	−0.1003 (10)	0.4170 (5)	−0.0969 (10)	2.91
O(55)	0.4535 (15)	0.1914 (5)	0.1845 (10)	6.25
O(66)	0.2104 (13)	0.1725 (5)	0.3235 (10)	4.85
C(1)	0.2698 (16)	0.4425 (8)	0.4805 (17)	2.34
C(2)	0.4744 (17)	0.4217 (8)	0.5021 (16)	1.82
C(3)	0.2165 (18)	0.4475 (7)	0.0112 (17)	2.20
C(4)	0.0365 (16)	0.4100 (7)	0.0045 (17)	2.12
C(5)	0.3787 (17)	0.2395 (7)	0.2142 (12)	2.81
C(6)	0.2473 (16)	0.2295 (7)	0.2983 (12)	2.77
K(1)	0.4785 (4)	0.5760 (2)	0.1615 (4)	2.63
K(2)	0.0367 (4)	0.5790 (2)	0.3355 (4)	2.90
*K(3)	0.7554 (6)	0.4117 (2)	0.2552 (6)	3.20
*K(33)	0.8806 (29)	0.2432 (20)	0.4060 (34)	11.73
H ₂ O(1)	0.6275 (15)	0.3292 (7)	0.0316 (12)	7.16
H ₂ O(2)	0.7965 (15)	0.2133 (6)	0.1640 (12)	7.47
*H ₂ O(3)	0.9178 (17)	0.3169 (8)	0.4466 (15)	5.99
*H ₂ O(33)	0.831 (10)	0.373 (5)	0.364 (9)	9.84

* The occupancy factors of K(3) and H₂O(3) are 0.83 and of K(33) and H₂O(33) are 0.17.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Mn—O(1)	2.019 (10)	Mn—O(4)	1.899 (9)
Mn—O(2)	1.915 (9)	Mn—O(5)	2.016 (9)
Mn—O(3)	2.073 (10)	Mn—O(6)	2.076 (8)
C(1)—O(1)	1.254 (19)	C(1)—O(11)	1.256 (19)
C(2)—O(2)	1.315 (17)	C(2)—O(22)	1.197 (17)
C(3)—O(3)	1.284 (19)	C(3)—O(33)	1.214 (18)
C(4)—O(4)	1.298 (18)	C(4)—O(44)	1.246 (18)
C(5)—O(5)	1.282 (15)	C(5)—O(55)	1.207 (16)
C(6)—O(6)	1.280 (15)	C(6)—O(66)	1.217 (15)
C(1)—C(2)	1.579 (19)	C(3)—C(4)	1.560 (19)
C(5)—C(6)	1.546 (17)		
O(1)—Mn—O(2)	82.3 (4)	O(1)—Mn—O(3)	103.3 (4)
O(1)—Mn—O(4)	91.7 (4)	O(1)—Mn—O(5)	166.4 (4)
O(1)—Mn—O(6)	91.3 (4)	O(2)—Mn—O(3)	92.3 (4)
O(2)—Mn—O(4)	170.4 (4)	O(2)—Mn—O(5)	89.8 (4)
O(2)—Mn—O(6)	97.1 (4)	O(3)—Mn—O(4)	81.7 (4)
O(3)—Mn—O(5)	88.0 (4)	O(3)—Mn—O(6)	163.6 (4)
O(4)—Mn—O(5)	97.5 (4)	O(4)—Mn—O(6)	90.5 (4)
O(5)—Mn—O(6)	78.7 (3)		
Mn—O(1)—C(1)	112.6 (9)	Mn—O(2)—C(2)	118.1 (8)
Mn—O(3)—C(3)	113.9 (9)	Mn—O(4)—C(4)	116.3 (9)
Mn—O(5)—C(5)	116.8 (8)	Mn—O(6)—C(6)	116.0 (7)
O(1)—C(1)—O(11)	127.3 (14)	O(2)—C(2)—O(22)	127.3 (13)
O(3)—C(3)—O(33)	129.0 (14)	O(4)—C(4)—O(44)	124.2 (13)
O(5)—C(5)—O(55)	125.4 (12)	O(6)—C(6)—O(66)	127.9 (12)
O(1)—C(1)—C(2)	116.6 (13)	O(2)—C(2)—C(1)	109.7 (11)
O(3)—C(3)—C(4)	111.1 (12)	O(4)—C(4)—C(3)	116.3 (12)
O(5)—C(5)—C(6)	115.0 (10)	O(6)—C(6)—C(5)	113.2 (10)
O(11)—C(1)—C(2)	116.1 (13)	O(22)—C(2)—C(1)	123.0 (13)
O(33)—C(3)—C(4)	119.9 (13)	O(44)—C(4)—C(3)	119.5 (13)
O(55)—C(5)—C(6)	119.6 (11)	O(66)—C(6)—C(5)	118.8 (11)

for two check reflexions, the measurement was continued until the total number of reflexions was 2338. Not only were the two check reflexions examined after every 40 reflexions, but also some other reflexions were remeasured from time to time in order to estimate the rate of decomposition of the crystal. It became evident that the decomposition of the compound is mainly caused by light at room temperature (Simmons & Wendlandt, 1971). A 2θ - ω scan technique was employed. Of 2140 independent reflexions, 1206 with $I > 3\sigma(I)$ were used for structure determination. All calculations were based on programs supplied by Syntex on a Nova 1200 minicomputer. At the beginning the old model of the structure was refined with the new set of experimental data. The structure was refined first with isotropic and then anisotropic temperature factors; R stopped at 10.1%. Furthermore, bond lengths and angles as well as a final difference synthesis were unacceptable. Since no reasonable solution could be deduced from the Patterson synthesis, direct methods were applied with *MULTAN*. As $K_3[Mn(ox)_3] \cdot 3H_2O$ very nearly crystallizes in the space group $C2/c$, this pseudo-symmetry weakens reflexions with $h + k = 2n + 1$, so a renormalization procedure was applied during the calculations. The new model based on the best E map

revealed an interesting feature: the only difference between the previously suggested structure and the new one is that they are mirror-related, the pseudo plane being parallel to xz at $b = \frac{1}{2}$. The refinement converged at $R = 7.6\%$ ($R_{iso} = 9.5\%$). However, for the same reasons as previously the structure could not be accepted.

Recently, Taylor (1978) reinvestigated the crystal structures of $K_3[Cr(ox)_3] \cdot 3H_2O$ and $K_3[Al(ox)_3] \cdot 3H_2O$ and found one of the K^+ cations and one of the water molecules to be partially cooperatively disordered. The same suggestion might account for the effects obtained by us. After careful inspection of a difference synthesis two peaks were selected according to this assumption and a few cycles of refinement were re-run. Occupancy factors of 0.83 and 0.17 for K(3) and K(33) [and consequently for $H_2O(3)$ and $H_2O(33)$] were then assumed for further refinement. The refinement stopped at $R = 4.8$ and $R_w = 4.7\%$, all temperature factors and bond lengths being acceptable. A final difference synthesis was featureless, and H atoms from water molecules were not resolvable.*

Table 1 presents the atomic coordinates, while Table 2 contains the main bond lengths and angles.

Discussion. The structure consists of discrete $[Mn(ox)_3]^{3-}$ anions, K^+ cations and water molecules. One of the K^+ cations and one water molecule are partially cooperatively disordered.

The inner structure of tri(bidentate) $[Mn(L)_3]$ -type complexes has been exhaustively discussed as they are expected to show fine structural effects such as Jahn-Teller distortion of the coordination octahedron (when only the immediate environment of the metal atom is taken into account, Fackler & Avdeef, 1974). As $[Mn(ox)_3]^{3-}$ is the simplest and best known of this type, it would also be the basic example of such effects. Three pairs of different Mn—O lengths make the octahedron orthorhombically distorted, the situation being similar to that in $[Mn(trop)_3]$ (Fackler & Avdeef, 1974) or $[Mn(mal)_3]^{3-}$ (Lis, Matuszewski & Jezowska-Trzebiatowska, 1977). However, in $[Mn(trop)_3]$ as well as in $[Mn(ox)_3]^{3-}$ similar bonds are *trans* to one another and in $[Mn(mal)_3]^{3-}$ such bonds are *cis*. A schematic drawing of the complex anion is shown in Fig. 1. The geometry of the ligands shows no extraordinary deviations from the known examples, neutron diffraction results for free oxalic acid (Sabine & Cox, 1969) being the proper reference for our results.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35225 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

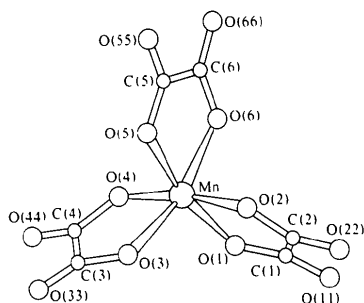


Fig. 1. The complex anion viewed down *a*.

There is no clear difference (in the limits of 3σ) between the bonds C—O(endocyclic) (single-numbered O atoms in Table 2) and C—O(exocyclic) (double-numbered O atoms in Table 2). The oxalate ligands are not planar. The —C—C(=O)—O⁻ groups are planar and twist angles as defined by Siems & Lohn (1972) range from 6.0 to 7.4°. The C—C lengths are comparable to those found in oxalic acid dihydrate (Sabine & Cox, 1969), [Mn(C₂O₄)]·2H₂O (Deyrieux, Berro & Peneloux, 1973) and Cs₂[Mn₂(C₂O₄)₃]·3H₂O (Siems & Lohn, 1972). Three water molecules are distributed in the crystal lattice in such a way that the crystal packing is similar to that in K₃[Cr(ox)₃]·3H₂O and K₃[Al(ox)₃]·3H₂O (Taylor, 1978). Each of the K(1), K(2) and K(3) cations is surrounded by six O atoms at

distances varying from 2.63 (1) to 2.99 (1) Å. The problem of cooperative disordering of K(3)—K(33) and H₂O(3)—H₂O(33) seems to be of the same nature as in K₃[Cr(ox)₃]·3H₂O or K₃[Al(ox)₃]·3H₂O (Taylor, 1978).

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Potassium Formate

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Abstract. CHO₂⁻·K⁺, orthorhombic, *Cmcm*, *Z* = 4, *a* = 5.887 (1), *b* = 6.791 (2), *c* = 7.024 (2) Å, *V* = 280.8 (1) Å³ at 295 K, *D_c* = 1.99 Mg m⁻³, *μ* = 1.57 mm⁻¹; 576 non-equivalent diffractometer data up to $\sin \theta/\lambda = 0.97$ Å⁻¹; final *R(F)* = 0.026, *R_w(F)* = 0.027. The K atom has an eightfold coordination of O atoms. Four K—O bonds of 3.0025 (7) Å form a chelate-like structure, while the other four with the shorter distance of 2.8195 (6) Å interconnect different formate groups.

Introduction. K formate was prepared by neutralizing a solution of formic acid in methanol with K carbonate. Because the solution contains water, evaporation will

normally not result in the crystallization of K formate. However, by drying the solution in a desiccator over P₂O₅, large prismatic crystals of K formate appeared. Because of their deliquescent nature the crystals had to be handled with considerable care. A specimen 0.5 × 0.6 × 0.6 mm was cut from a large crystal and sealed in a capillary, partly filled with P₂O₅.

Precession photographs showed the space group to be *Cmc*2₁, *C2cm*, or *Cmcm*. Data were collected on a Syntex P2₁ diffractometer with Nb-filtered Mo *Kα* radiation. Reflections were measured in two quadrants ($-h, k, \pm l$ and $h, k, \pm l$) up to $\sin \theta/\lambda = 0.90$ and 0.97 Å⁻¹ respectively, yielding 2789 reflections. Coinci-