SILVIDI, A. A. & WORKMAN, D. T. (1971). *J. Chem. Phys.* **55**, 4672–4673.
SODA, G. & CHIBA, T. (1969). *J. Phys. Soc. Japan*, **26**, 723–732.
TELLGREN, R. & LIMINGA, R. (1972). *J. Solid State Chem.* **4**, 255–261.
TELLGREN, R. & LIMINGA, R. (1974*a*). *Acta Cryst.* **B30**, 2497–2499.
TELLGREN, R. & LIMINGA, R. (1974*b*). *Ferroelectrics*, **8**, 629–635.
TELLGREN, R. & LIMINGA, R. (1977). *Ferroelectrics*. In the press.
TELLGREN, R., RAMANUJAM, P. S. & LIMINGA, R. (1974). *Ferroelectrics*, **6**, 191–196.
THOMAS, J. O. & LIMINGA, R. (1977). To be published.

Acta Cryst. (1977). **B33**, 2112–2116

The Reaction between Potassium Permanganate and Formic Acid. Structural Characterization of the Polymeric Compound $(K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\})_n$

BY T. LIS AND B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, 50-383 *Wrocław, ul. Joliots-Curie* 14, *Poland*

(*Received* 12 *July* 1976; *accepted* 21 *December* 1976)

When potassium permanganate and concentrated formic acid solutions are mixed, a red–brown solution is formed. From this solution various crystalline compounds precipitated, depending on the HCOOH concentrations and temperatures used. One of these compounds is a red–brown, paramagnetic complex with the formula $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]^2\}$, as established by a single-crystal X-ray diffraction study. This complex crystallizes in the triclinic space group $P\bar{1}$, with $a = 6{\cdot}884$ (4), $b = 12{\cdot}440$ (6), $c = 15{\cdot}414$ (8) Å, $\alpha = 97{\cdot}59$ (6), $\beta = 108{\cdot}72$ (6), $\gamma = 120{\cdot}88$ (6)°. Data to $2\theta \sim 114°$ (Cu $K\alpha$ radiation) for 2498 reflexions were measured on a Syntex $P2_1$ four-circle diffractometer. The structure was solved by the heavy-atom technique and refined by the full-matrix least-squares method. The final R and R_w were 0·054 and 0·056 for 1815 non-zero reflexions. The structure consists of the $\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}^{2-}$ polymeric anion and potassium cations. In the complex anion, the Mn^{2+} ions (which lie on the symmetry points of the crystal) coordinate two water molecules and are bonded with the Mn_3O groups through the four formate groups. The equilateral triangle of the Mn^{3+} ions is bridged by the six formate groups and the central O atom, which lies essentially in the Mn_3 plane. All Mn atoms have distorted octahedral coordination; the Mn—O distances vary between 1·87 and 2·21 Å.

Introduction

The overall reaction between permanganate and formic acid is expressed by the equation

$$6H^+ + 2MnO_4^- + 5HCOOH \rightarrow 2Mn^{2+} + 5CO_2 + 8H_2O.$$

This reaction has not, until recently, been systematically investigated. The well known interaction between $KMnO_4$ and oxalic or malonic acid suggested that this process would also be complicated.

Solutions of freshly prepared MnO_2 in formic acid are known to form a red Mn^{III} formate complex with the formula $Mn_3(form)_6(form)_3.2H_2O$ (Weinland & Stark, 1926). It was observed by us that this compound can also be obtained from the reaction of 100% HCOOH with solid $KMnO_4$ at room temperature. However, if a diluted solution of HCOOH was used, the brown MnO_2 precipitated and the reaction stopped. When the concentration of HCOOH varies in the range 70–95% and reaction proceeds at 0°C, a few different products may be obtained.

In this work a compound was isolated which was shown by X-ray diffraction to contain the novel $\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}^{2-}$ anion. In order to obtain more information and a better understanding of this and related anions, an extensive study involving the methods of synthesis, the properties, and the molecular and crystal structures was undertaken.

Experimental

Materials

$KMnO_4$ (POCh or Analar), 98–100% HCOOH (Merck) or 99·5% HCOOH (Fluka AG) without further purification and distilled water were used.

Preparation

To a mixture of 8 ml of formic acid and 0·9 ml of water, 0·25 g of non-powdered $KMnO_4$ was slowly added at 0°C with continual stirring. After 10–20 min, the reaction mixture was allowed to stand at room temperature in air. After two or three days the compound precipitated as pure, small, red–brown crystals. These were filtered through a Büchner funnel, and dried in a stream of air. The compound decomposed a little after some weeks. Analysis: calculated for $C_{18}H_{22}O_{40}Mn_7K_2$: C 16·12; H 1·65; O 47·72; Mn 28·67; K 5·83%; found: C 16·1; H 1·8; O 49·2; Mn 27·6; K 5·3%. C and H were determined microanalytically, Mn gravimetrically as $Mn_2P_2O_7$, and K with a flame photometer calibrated with $KMnO_4$.

Oxidation-state determination

The oxidation-state determination was made by dissolving the compound in $1N$ H_2SO_4 with excess KI, and titrating the liberated iodine with $0·1N$ $Na_2S_2O_3$. The compound investigated has an oxidation state of 2·86 per Mn atom. To test the generality of this procedure, the oxidation state of the $KMnO_4$ standard compound was also determined; this was found to be 7·00.

Physical measurements

The infrared spectra were measured in the region 4000–200 cm^{-1}, as Nujol and hexachlorobutadiene mulls on a Perkin–Elmer 621 spectrophotometer. Magnetic susceptibilities were measured by the Gouy method within the range 78–300 K.

Crystal data

$C_{18}H_{22}O_{40}Mn_7K_2$, $M_r = 1341·2$, triclinic, a = 6·884 (4), b = 12·440 (6), c = 15·414 (8) Å, α = 97·59 (6), β = 108·72 (6), γ = 120·88 (6)°, V = 998·9 Å^3, D_m = 2·20, Z = 1, D_c = 2·23 g cm^{-3}, μ(Cu $K\alpha$, λ = 1·5418 Å) = 214·7 cm^{-1}. Space group $P1$ from diffraction symmetry, lack of systematic absences, and equality of Friedel pairs.

Data collection

An irregularly shaped crystal (approximately 0·09 × 0·08 × 0·06 mm) was selected for the data collection. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the 2θ–ω scan technique. The intensity of a standard reflexion, which was monitored after every 15 intensity scans, decreased approximately 3% over the period of data collection. Scans of other reflexions indicated that decomposition was essentially isotropic. Decomposition of crystals appeared to be caused in part by the X-ray radiation and was accompanied by a slight darkening of the crystal. The data were corrected for Lorentz and polarization effects only. Of 2498 accessible reflexions below $2\theta \sim 114°$, 1815 with $I > 3·0\,\sigma(I)$ were used. All calculations were performed with the Syntex XTL structure determination system (NOVA 1200 computer and additional external disc memory).

Table 1. *The final atom parameters with standard deviations in parentheses*

Positional parameters are given as fractions of cell edges × 10^4. The hydrogen atom positions (× 10^3) are unrefined and these atoms have the same numbers as the parent carbon atoms.

	x	y	z
Mn(0)	0	5000	0
Mn(1)	4616 (4)	2001 (2)	4282 (2)
Mn(2)	1878 (4)	2511 (2)	2359 (2)
Mn(3)	739 (4)	−451 (2)	2119 (2)
K	6270 (6)	5313 (3)	1687 (3)
O(1)	−1647 (16)	3914 (8)	856 (6)
O(2)	−1785 (15)	−4018 (7)	266 (6)
O(3)	3478 (15)	6515 (7)	1381 (5)
O(4)	1250 (18)	3640 (7)	1697 (6)
O(5)	−1156 (16)	−2317 (7)	1264 (6)
O(6)	2362 (15)	1327 (7)	2912 (5)
O(7)	3139 (17)	2312 (8)	1408 (6)
O(8)	−2045 (16)	955 (8)	1277 (6)
O(9)	5688 (17)	4314 (8)	3184 (6)
O(10)	755 (17)	2940 (9)	3256 (6)
O(11)	1649 (17)	151 (8)	999 (6)
O(12)	−2816 (16)	−896 (8)	1554 (6)
O(13)	−193 (17)	−1301 (8)	3154 (6)
O(14)	3805 (18)	−414 (9)	2507 (6)
O(15)	2203 (18)	511 (8)	4538 (6)
O(16)	6363 (19)	1071 (10)	4067 (6)
O(17)	7387 (17)	3582 (8)	4208 (6)
O(18)	3277 (20)	3099 (10)	4691 (6)
O(19)	7060 (16)	2749 (8)	5667 (6)
O(20)	8232 (19)	3452 (9)	7253 (6)
C(1)	−762 (28)	3552 (12)	1491 (9)
C(2)	−563 (25)	−2787 (12)	689 (10)
C(3)	2828 (24)	1284 (12)	959 (9)
C(4)	−3450 (24)	−205 (12)	1191 (8)
C(5)	572 (26)	−726 (14)	4055 (11)
C(6)	5844 (30)	254 (15)	3332 (12)
C(7)	7544 (28)	4397 (13)	3785 (9)
C(8)	1657 (31)	3235 (13)	4180 (11)
C(9)	6584 (29)	2889 (14)	6393 (11)
H(1)	−177	315	188
H(2)	93	−214	56
H(3)	365	139	50
H(4)	−537	−67	78
H(5)	−25	−132	442
H(6)	719	8	338
H(7)	934	520	394
H(8)	96	361	453
H(9)	472	251	625

Determination of the structure

The heavy-atom method was employed for the phase determination. A satisfactory solution was obtained in space group $P\bar{1}$ for two trinuclear Mn_3 units per cell in general positions; the derived coordinates for the three Mn atoms indicated a roughly equilateral-triangular arrangement with a Mn–Mn separation of 3·3 Å. Three cycles of least-squares refinement of these coordinates gave $R = 0{\cdot}47$. A difference Fourier synthesis was computed, from which were obtained the positions of the remaining Mn and K atoms. A refinement, with full-matrix least-squares methods, lowered the residual R to 0·36. A difference Fourier map at this point revealed the positions of 29 peaks with similar density. All these peaks were used for the determination of the light-atom positions, and R then dropped to 0·078. The structure was then refined with anisotropic temperature factors to $R = 0{\cdot}058$. The nine independent H atoms (from formate groups) were placed in geometrically calculated positions with a distance of 1·0 Å. Further refinement reduced R and R_w to 0·054 and 0·056 respectively. A final three-dimensional difference synthesis was essentially flat. No attempt was made to locate the H atoms of the water molecules. Scattering factors for Mn, K^+, O, C and H atoms were those listed in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for all atoms. The final atomic coordinates and their estimated standard deviations are listed in Table 1.*

Description of the structure and discussion

Fig. 1 shows the arrangement of the molecules in projection on the (100) plane and includes the numbering scheme used in the text. Interatomic distances and angles are given in Table 2.

In one unit cell there are seven Mn atoms. Because the experimentally found oxidation state was 2·86 per Mn atom, six Mn atoms must be in oxidation state +3 and one in oxidation state +2, giving an average formal oxidation state of 2·857. This situation is possible only if the Mn^{2+} ion [Mn(0)] lies on the centre of symmetry at $0,\frac{1}{2},0$, so that the $\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}^2$ anions possess C_i crystallographic symmetry.

All Mn atoms have a distorted octahedral coordination. The Mn^{2+} ion is coordinated by four O atoms from the formate groups [mean Mn(0)–O 2·19 (3) Å], and two water molecules [Mn(0)–O(3) 2·20 (1) Å, where O(3) denotes the water molecule]. A similar octahedral arrangement for the Mn^{2+} ion was found by Osaki, Nakai & Watanabé (1964) in $Mn(HCOO)_2.2H_2O$. However, in the monoclinic unit cell of $Mn(HCOO)_2.2H_2O$ four Mn^{2+} are present, and are distributed equally between two kinds of non-equivalent sites; the Mn^{2+} ions on the first site are surrounded by six O atoms belonging to the formate groups, and on the second site by four water molecules and two O atoms (which belong to the formate groups).

In $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}$, the Mn^{2+} ion is bonded to Mn^{3+} ions through four formate groups. The equilateral triangle of Mn^{III} atoms is bridged by the six formate groups and the central O atom, which lies essentially in the Mn_3 plane. The Mn–Mn distances in this triangle are 3·29 (1) Å, and the molecular symmetry is similar to that found in the corresponding Fe, Cr, Rh, Ru and Mn complexes. However,

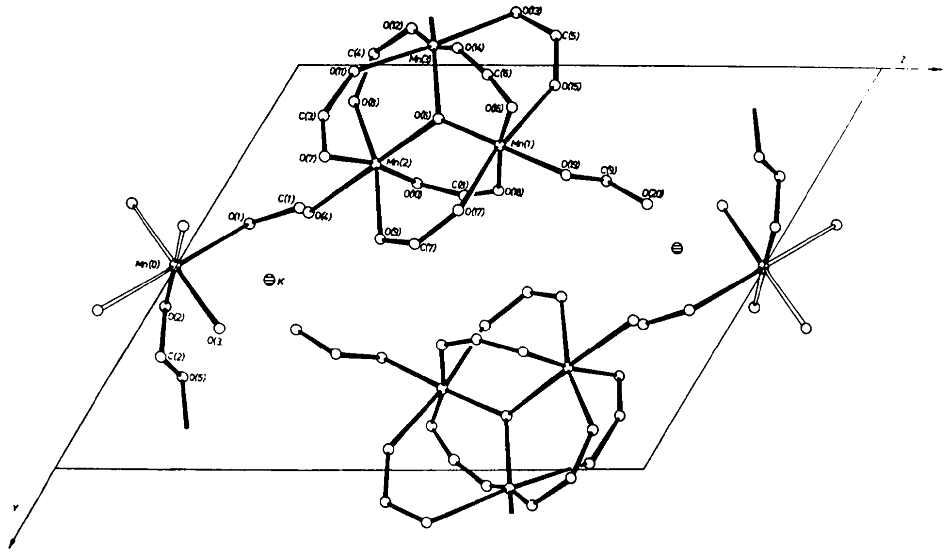

Fig. 1. The crystal structure of $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}$: projection on the (100) plane.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32414 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the only known trinuclear Mn complex, $[Mn_3O(OAc)_6.AcOH.OAc]_n$ (Hessel & Romers, 1969), has a relatively low precision for the atomic parameters and does not warrant detailed conclusions.

The average Mn–O(central) distance [1·90 (2) Å] is the shortest of all Mn–O distances in the present compound. The four formate O atoms [*cis* to central O(6) atom] surrounding each Mn^{3+} ion are essentially coplanar, but the Mn–O distances vary between 1·93 and 2·17 Å. Each Mn^{III} atom is displaced from these planes towards the central O atom. It is interesting to note that each carboxyl group forms one longer and one shorter Mn–O bond, and the longer-with-longer and the shorter-with-shorter bonds are in mutually *trans* positions, whereas in all previously investigated carboxyl trimeric oxo compounds the Me–O(carboxyl) bond distances were similar. However, the C–O distances and O–C–O angles (mean 1·252 Å and 125·3°) are equal within experimental error (3σ), and are similar to those found in NaHCOO [1·246 (1) Å and 126·3 (2)°] (Markila, Rettig & Trotter, 1975). Hence, these values are typical for those bonds in the formate anion.

Each Mn^{III} atom has a formate ion coordinated opposite to the central oxygen. The Mn–O[*trans* to O(central)] bonds are similar [average value found: 1·96 (2) Å] and may be classified as rather strong bonds with one group of 'longer' Mn–O[*cis* to O(central)] distances. The formate ions bonded to Mn(2) and Mn(3) are the bridging groups between these and the Mn(0) atoms. The third formate group [bonded to Mn(1)] is not a bridging group; its second O atom, not bonded directly to Mn, forms a hydrogen bond with the water molecule.

In the crystal structure, two hydrogen bonds of lengths 2·73 (2) and 2·8 (2) Å, linking O(3) to O(20) and O(12) respectively, can be distinguished. The existence of hydrogen-bonded water is confirmed by a broad band at 3470 cm^{-1} in the infrared spectrum (Fig. 2) of the complex. These hydrogen bonds stabilize the crystal structure.

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* $\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}^{2-}$ *anion*

See Fig. 1 for numbering.

Mn(0)–O(1)	2·171 (9)	Mn(0)–O(2)	2·214 (11)
Mn(0)–O(3)	2·203 (8)	Mn(1)–O(6)	1·913 (7)
Mn(1)–O(15)	1·951 (11)	Mn(1)–O(16)	2·116 (14)
Mn(1)–O(17)	1·967 (11)	Mn(1)–O(18)	2·133 (18)
Mn(1)–O(19)	1·954 (9)	Mn(2)–O(6)	1·913 (9)
Mn(2)–O(4)	1·979 (10)	Mn(2)–O(7)	1·977 (11)
Mn(2)–O(8)	2·170 (10)	Mn(2)–O(9)	2·143 (10)
Mn(2)–O(10)	1·926 (12)	Mn(3)–O(6)	1·874 (8)
Mn(3)–O(5)	1·951 (9)	Mn(3)–O(11)	2·119 (11)
Mn(3)–O(12)	2·041 (12)	Mn(3)–O(13)	2·117 (10)
Mn(3)–O(14)	1·974 (14)	C(1)–O(1)	1·244 (17)
C(1)–O(4)	1·259 (25)	C(2)–O(2)	1·240 (16)
C(2)–O(5)	1·278 (20)	C(3)–O(7)	1·245 (18)
C(3)–O(11)	1·236 (17)	C(4)–O(8)	1·212 (16)
C(4)–O(12)	1·265 (18)	C(5)–O(13)	1·265 (17)
C(5)–O(15)	1·253 (18)	C(6)–O(14)	1·287 (21)
C(6)–O(16)	1·227 (21)	C(7)–O(9)	1·257 (21)
C(7)–O(17)	1·253 (17)	C(8)–O(10)	1·269 (17)
C(8)–O(18)	1·248 (24)	C(9)–O(19)	1·276 (20)
C(9)–O(20)	1·228 (18)		

Table 2 (*cont.*)

O(6)–Mn(1)–O(15)	94·6 (5)	Mn(1)–O(6)–Mn(2)	119·1 (5)	O(7)–Mn(2)–O(9)	82·6 (5)
O(6)–Mn(1)–O(17)	93·2 (5)	Mn(2)–O(6)–Mn(3)	120·6 (5)	O(7)–Mn(2)–O(4)	84·0 (5)
O(6)–Mn(1)–O(19)	177·1 (5)	Mn(0)–O(2)–C(2)	123·1 (10)	O(8)–Mn(2)–O(10)	90·3 (5)
O(15)–Mn(1)–O(17)	172·2 (5)	Mn(1)–O(16)–C(6)	131·5 (12)	O(9)–Mn(2)–O(10)	93·5 (5)
O(15)–Mn(1)–O(19)	88·2 (5)	Mn(1)–O(18)–C(8)	131·0 (12)	O(10)–Mn(2)–O(4)	88·4 (5)
O(16)–Mn(1)–O(18)	172·3 (5)	Mn(2)–O(4)–C(1)	121·2 (10)	O(6)–Mn(3)–O(12)	94·7 (4)
O(17)–Mn(1)–O(18)	91·5 (5)	Mn(2)–O(8)–C(4)	129·7 (10)	O(6)–Mn(3)–O(14)	97·1 (5)
O(18)–Mn(1)–O(19)	87·8 (5)	Mn(2)–O(10)–C(8)	130·0 (11)	O(11)–Mn(3)–O(12)	97·3 (4)
O(6)–Mn(2)–O(8)	95·1 (4)	Mn(3)–O(11)–C(3)	130·3 (10)	O(11)–Mn(3)–O(14)	83·2 (5)
O(6)–Mn(2)–O(10)	94·2 (5)	Mn(3)–O(13)–C(5)	129·5 (11)	O(12)–Mn(3)–O(13)	85·7 (4)
O(7)–Mn(2)–O(8)	91·8 (4)	O(1)–C(1)–O(4)	125·1 (15)	O(12)–Mn(3)–O(5)	81·7 (4)
O(7)–Mn(2)–O(10)	171·8 (5)	O(7)–C(3)–O(11)	128·2 (14)	O(13)–Mn(3)–O(5)	84·2 (5)
O(8)–Mn(2)–O(9)	165·6 (4)	O(13)–C(5)–O(15)	125·4 (16)	O(1)–Mn(0)–O(2)	82·0 (4)
O(8)–Mn(2)–O(4)	82·0 (4)	O(9)–C(7)–O(17)	125·2 (15)	O(2)–Mn(0)–O(3)	90·0 (4)
O(9)–Mn(2)–O(4)	84·2 (5)	O(19)–C(9)–O(20)	122·7 (16)	Mn(1)–O(6)–Mn(3)	120·3 (5)
O(6)–Mn(3)–O(11)	92·0 (4)	O(6)–Mn(1)–O(16)	94·4 (5)	Mn(0)–O(1)–C(1)	129·6 (10)
O(6)–Mn(3)–O(13)	95·6 (5)	O(6)–Mn(1)–O(18)	93·0 (5)	Mn(1)–O(15)–C(5)	133·6 (11)
O(6)–Mn(3)–O(5)	176·4 (5)	O(15)–Mn(1)–O(16)	92·5 (5)	Mn(1)–O(17)–C(7)	135·6 (11)
O(11)–Mn(3)–O(13)	171·6 (5)	O(15)–Mn(1)–O(18)	89·0 (5)	Mn(1)–O(19)–C(9)	125·3 (11)
O(11)–Mn(3)–O(5)	88·5 (5)	O(16)–Mn(1)–O(17)	86·0 (5)	Mn(2)–O(7)–C(3)	127·8 (10)
O(12)–Mn(3)–O(14)	168·2 (5)	O(16)–Mn(1)–O(19)	84·7 (5)	Mn(2)–O(9)–C(7)	125·4 (10)
O(13)–Mn(3)–O(14)	92·3 (5)	O(17)–Mn(1)–O(19)	84·0 (5)	Mn(3)–O(5)–C(2)	127·4 (10)
O(14)–Mn(3)–O(5)	86·6 (5)	O(6)–Mn(2)–O(7)	93·6 (5)	Mn(3)–O(12)–C(4)	126·4 (10)
O(1)–Mn(0)–O(3)	88·6 (4)	O(6)–Mn(2)–O(9)	98·5 (4)	Mn(3)–O(14)–C(6)	129·8 (12)
		O(6)–Mn(2)–O(4)	176·2 (5)	O(2)–C(2)–O(5)	120·9 (14)
				O(8)–C(4)–O(12)	127·1 (14)
				O(14)–C(6)–O(16)	127·0 (17)
				O(10)–C(8)–O(18)	125·7 (17)

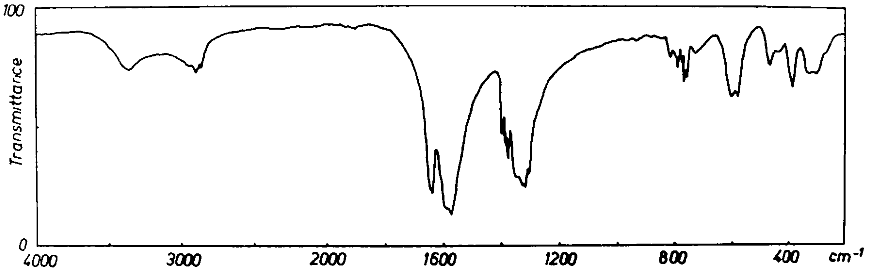

Fig. 2. The infrared spectrum of $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}$ (combined from spectra in Ñujol and hexachlorobutadiene mulls).

The potassium ion has an irregular coordination sphere, and attempts to classify it as a distorted form of an idealized polyhedron failed.

The magnetic properties of the present compound differ from those of mononuclear high-spin compounds of Mn^{2+} and Mn^{3+} in which their temperature-independent $\mu_{\text{eff.}}$ are 54·9 and 4·9 BM respectively. In $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}$ the effective magnetic moment is temperature-dependent, and increases from 11·7 BM per molecule at 78 K to 13·0 BM at 298 K. These results show that there exist some weak exchange interactions between Mn ions. The Mn^{2+}–Mn^{3+} distances greater than 5·3 Å suggest that the interactions between these ions in the temperature range studied are excluded, and that the Mn^{2+} ion should be in a ground state, $S = \frac{5}{2}$, *i.e.* 5·92 BM. Schriempf & Friedberg (1964) suggested that in $Mn(HCOO)_2.2H_2O$, where the Mn^{2+}–Mn^{2+} distances are similar, the interaction between these ions may be observed at liquid helium temperature only. The distances between Mn^{3+} ions [3·29 (1) Å] are rather too large to allow a direct metal–metal exchange. It could be supposed that superexchange interactions occur *via* bridge O atoms. In the other compounds of Cr, Fe and Ru, the M_3O groups may even exhibit diamagnetism or weak paramagnetism.

The authors wish to express their gratitude to Mr Trúóng Xuân Mão (Vietnam) who participated in the early stage of research for his MSc degree.

References

Hessel, L. W. & Romers, C. (1969). *Rec. Trav. Chim. Pays-Bas*, **88**, 545–552.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Markila, P. L., Rettig, S. J. & Trotter, J. (1975). *Acta Cryst.* B**31**, 2927–2928.

Osaki, K., Nakai, Y. & Watanabé, T. (1964). *J. Phys. Soc. Japan*, **19**, 717–723.

Schriempf, J. T. & Friedberg, S. A. (1964). *J. Chem. Phys.* **40**, 296–302.

Weinland, R. & Stark, A. (1926). *Ber. dtsch. chem. Ges.* **59**, 471–479.