Acta Cryst. (1980). B**36**, 2042–2046

Preparation, Structure, and Magnetic Properties of a Dodecanuclear Mixed-Valence Manganese Carboxylate

By T. Lis

Instytut Chemii Uniwersytetu Wrocławskiego, 50-383 *Wrocław, ul. Joliot-Curie* 14, *Poland*

(*Received* 29 *January* 1980; *accepted* 17 *March* 1980)

Abstract

This new type of dodecanuclear crystalline complex was obtained by reaction of Mn^{2+} with MnO_4^- in acetic and propionic acids. The reddish-black acetate complex has the formula $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$, established by chemical and single-crystal X-ray diffraction methods. This complex is tetragonal, space group $I\bar{4}$, with a = 17·319 (9), c = 12·388 (7) Å, V = 3716 Å^3, Z = 2, M_r = 2060·3, D_c = 1·84, D_m = 1·83 Mg m^{-3}. The final R and R_w were 0·045 and 0·034 for 1172 non-zero reflexions. The crystals are built up of $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}]$ molecules, waters of crystallization and disordered acetic acid molecules. In the dodecanuclear molecules, which have $\bar{4}$ (S_4) crystallographic symmetry, the Mn atoms are linked by triply bridging oxo O atoms and by carboxylate bridges from acetate anions. The occurrence of a strong Jahn–Teller effect in Mn^{3+} ions differentiates the Mn^{3+} and Mn^{4+} ions. The interesting magnetic properties (the magnetic moment increases from 30·9 × 10^{-24} J T^{-1} at 3·3 K to a maximum of 56·5 × 10^{-24} J T^{-1} in the range 17–31 K and then decreases to 33·4 × 10^{-24} J T^{-1} at 280K per Mn atom) may be interpreted in terms of the Mn—Mn distances and superexchange *via* bridge O atoms.

Introduction

It is known that the reaction of Mn^{2+} with MnO_4^- ions can produce a variety of complex compounds with a given oxidation number of Mn, with variations of the molar ratio of both ions and modification of the ligating species. To date, many papers describing the crystal structures of trivalent Mn complexes have been published. Furthermore, three crystal structures containing Mn atoms in mixed-valence states, *i.e.* $[Mn_2(2,2'\text{-bipyridine})_4O_2](ClO_4)_3.3H_2O$ (Plaksin, Stoufer, Mathew & Palenik, 1972), $(K_2\{Mn(H_2O)_2[Mn_3(HCOO)_9O]_2\})_n$ (Lis & Jeżowska-Trzebiatowska, 1977), $[Mn_3O(O_2CMe)_6(py)_3]$ (Baikie, Hursthouse, New & Thornton, 1978), have been investigated. In continuation of our previous studies on the crystal structures of Mn carboxylates (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977; Lis & Jeżowska-Trzebiatowska, 1977; Lis, 1977) we have started an examination of the mixed-valence Mn^{3+}/Mn^{4+} carboxylate complexes. The strong Jahn–Teller effect in the Mn^{3+} ions allowed the identification of the Mn^{3+} and Mn^{4+} ions. Propionic and acetic acids were used as the reaction media and as the ligating species. As a result, a new type of dodecanuclear complex was obtained, and the structure determined chemically and by X-ray diffraction. The present paper is a report of the synthesis, isolation and structural determination of $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$.

The possibility of the formation of Mn dodecanuclear acetate complexes had been suggested by Weinland & Fischer (1921).

Experimental

Preparation

4 g of powdered $Mn(CH_3COO)_2.4H_2O$ in 40 ml 60% CH_3COOH were heated until dissolution. 1 g of powdered $KMnO_4$ was added to the cooled solution dropwise, and the reaction mixture slowly heated to 333 K. The red-brown mixture was allowed to stand at room temperature in air. After two days reddish-black crystals were filtered through a Büchner funnel and dried in a stream of air. Analysis: calculated for $C_{36}H_{72}Mn_{12}O_{56}$: C 21·0; H 3·5; O 43·5; Mn 32·0%; found: C 20·8; H 3·4; O 43·9; Mn 31·9%. C and H were determined microanalytically and Mn gravimetrically as $Mn_2P_2O_7$.

Oxidation-state determination

The oxidation-state determination was made by dissolving the compound in 0·5 M H_2SO_4 with excess KI, and titrating the liberated iodine with 0·05 M $Na_2S_2O_3$. The compound investigated has an oxidation state of 3·34 per Mn atom.

0567-7408/80/092042-05$01.00

Physical measurements

Magnetic susceptibilities were obtained over the range 3·3–67 K with a Foner-type vibrating-sample magnetometer (50A PAR) and in the range 78–300 K with a sensitive Gouy balance. All magnetic-susceptibility data were corrected for diamagnetism. Thermogravimetric results were obtained on a Paulik–Paulik–Erdey-type OD-102 derivatograph in the range 293–523 K.

Crystal data

Systematic absences were observed for *hkl* when $h + k + l = 2n + 1$. Since the Laue symmetry is $4/m$ the space group is $I4$, $I4/m$ or $I\bar{4}$. A crystal 0·09 × 0·09 × 0·10 mm was selected for data collection. A Syntex $P2_1$ diffractometer with a graphite monochromator and Cu $K\alpha$ radiation were used for lattice-parameter and intensity measurements. The crystal data are: $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$, $M_r = 2060·3$, tetragonal, space group $I\bar{4}$, $a = 17·319\ (9)$, $c = 12·388\ (7)$ Å, $Z = 2$, $D_m = 1·83$, $D_c = 1·84$ Mg m^{-3}, μ(Cu $K\alpha$, $\lambda = 1·54018$ Å) = 17·89 mm^{-1}.

The intensities were measured by the 2θ–ω scan technique. After each group of 15 reflexions the intensity of a standard was measured and no significant change observed. The data were corrected for Lorentz and polarization effects only. Of 1428 accessible reflexions below $2\theta \simeq 114·5°$, 1172 with $I > 1·96\sigma(I)$ were used. The calculations (except *MULTAN*) were performed on the Nova mini-computer with programs supplied by Syntex. Neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for Mn, O and C.

Table 1. *The final positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

Atoms marked with an asterisk were included with an occupancy factor of 0·5.

	x	y	z	B_{eq} (Å^2)
Mn(1)	0·4170 (2)	−0·0180 (2)	0·1732 (2)	1·51
Mn(2)	0·2597 (2)	−0·0463 (2)	0·1730 (2)	1·90
Mn(3)	0·3587 (2)	−0·1955 (2)	0·2709 (2)	1·90
O(1)	0·4312 (5)	−0·0152 (5)	0·3253 (7)	1·88
O(2)	0·3518 (4)	−0·1044 (5)	0·1870 (7)	1·79
O(3)	0·3265 (4)	0·0388 (5)	0·1836 (7)	2·17
O(4)	0·4147 (5)	−0·0216 (5)	0·0190 (7)	2·19
O(5)	0·2871 (5)	−0·0459 (5)	−0·0044 (7)	2·47
O(6)	0·2360 (5)	−0·0522 (6)	0·3462 (8)	4·35
O(7)	0·3098 (5)	−0·1453 (5)	0·4125 (7)	3·08
O(8)	0·1688 (5)	0·0160 (5)	0·1513 (7)	2·73
O(9)	0·3611 (5)	−0·2933 (5)	0·3533 (8)	3·15
O(10)	0·1932 (5)	−0·1341 (5)	0·1455 (8)	3·25
O(11)	0·2522 (5)	−0·2303 (5)	0·2284 (8)	3·03
O(12)	0·3939 (5)	−0·2636 (5)	0·1315 (8)	3·34
O(13)	0·3086 (7)	−0·2194 (7)	−0·0448 (8)	6·21
*O(14)	0·0752 (29)	0·0759 (28)	0·3753 (42)	18·39
*O(15)	0·0622 (33)	−0·0901 (37)	0·3579 (53)	24·53
C(1)	0·3549 (8)	−0·0367 (7)	−0·0397 (10)	2·07
C(2)	0·3707 (8)	−0·0450 (9)	−0·1581 (11)	4·07
C(3)	0·2701 (9)	−0·0865 (8)	0·4212 (12)	3·40
C(4)	0·2659 (19)	−0·0552 (11)	0·5347 (13)	15·06
C(5)	0·1578 (7)	0·0888 (8)	0·1357 (11)	2·55
C(6)	0·0799 (8)	0·1087 (9)	0·0975 (14)	4·38
C(7)	0·1983 (7)	−0·2031 (7)	0·1786 (11)	2·07
C(8)	0·1311 (8)	−0·2550 (8)	0·1488 (13)	4·12
*C(9)	0·0474 (20)	0·0090 (32)	0·3681 (31)	7·07
*C(10)	−0·0598 (21)	0·0412 (27)	0·3478 (31)	5·03
H(1)	0·437	−0·240	0·100	
H(2)	0·363	−0·250	0·075	
H(3)	0·335	−0·225	−0·124	
H(4)	0·263	−0·188	0·000	
H(21)	0·334	−0·034	−0·210	
H(22)	0·416	−0·093	−0·175	
H(23)	0·394	0·008	−0·184	
H(41)	0·227	−0·015	0·530	
H(42)	0·300	−0·020	0·500	
H(43)	0·266	−0·090	0·588	
H(61)	0·050	0·150	0·129	
H(62)	0·066	0·127	0·020	
H(63)	0·033	0·070	0·110	
H(81)	0·153	−0·309	0·106	
H(82)	0·088	−0·221	0·172	
H(83)	0·114	−0·288	0·195	

Structure determination and refinement

The structure was solved by direct methods. 220 E values > 1·40 were used in *MULTAN* of the XRAY system (1978) in all three space groups: $I4$, $I\bar{4}$ and $I4/m$. In each space group three E maps corresponding to the solution with the best figure of merit were computed. A satisfactory solution was obtained in $I\bar{4}$ for the third solution which proved to be the best when peaks 1, 2, 4 on the E map were assumed to be Mn atoms ($R = 0·30$). A series of difference syntheses yielded the positions of the non-H atoms; R then dropped to 0·095. The compound was identified as $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].4H_2O$. Full-matrix least-squares refinement of the parameters of the two enantiomers (with isotropic thermal parameters) gave $R = 0·086$ for one form and 0·110 for the inverted structure. Further refinement with anisotropic thermal parameters for the first enantiomer only gave $R = 0·069$ and $R_w = 0·082$. A difference synthesis at this stage revealed three relatively large peaks (~3 e Å^{-3}). From an examination of the distances between these peaks, the corresponding angles, and the peak electron densities, it was concluded that they corresponded to a disordered acetic acid molecule of solvation. From geometric and crystallographic principles it follows that the occupancy factors for the atoms from disordered acetic acid molecules could not be higher than 0·5. Further difference syntheses located all H atoms (except those belonging to the acetic acid molecules).

Further refinement with isotropic temperature factors for atoms from the disordered acetic acid molecules and fixed parameters for H atoms ($B = 4{\cdot}0$ Å^2) gave a final $R = 0{\cdot}045$ and $R_w = 0{\cdot}034$. A final difference synthesis was featureless. The final atomic coordinates are listed in Table 1.*

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

Symmetry code: (i) $\frac{1}{2} - y, -\frac{1}{2} + x, \frac{1}{2} - z$; (ii) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$; (iii) $1 - x, -y, z$.

Mn(1)···Mn(1^{i})	2·820 (3)	Mn(1)···Mn(1^{iii})	2·943 (3)
Mn(1)···Mn(2)	2·767 (3)	Mn(1)···Mn(3)	3·455 (3)
Mn(1)···Mn(3^{ii})	3·447 (3)	Mn(2)···Mn(3)	3·329 (3)
Mn(2)···Mn(3^{ii})	3·413 (3)		
Mn(1)—O(1)	1·901 (8)	Mn(1)—O(1^{i})	1·916 (7)
Mn(1)—O(1^{ii})	1·908 (8)	Mn(1)—O(2)	1·883 (7)
Mn(1)—O(3)	1·854 (7)	Mn(1)—O(4)	1·912 (8)
Mn(2)—O(2)	1·894 (7)	Mn(2)—O(3)	1·878 (7)
Mn(2)—O(5)	2·248 (8)	Mn(2)—O(6)	2·187 (10)
Mn(2)—O(8)	1·928 (8)	Mn(2)—O(10)	1·939 (8)
Mn(3)—O(2)	1·892 (7)	Mn(3)—O(3^{i})	1·902 (8)
Mn(3)—O(7)	2·132 (8)	Mn(3)—O(9)	1·978 (8)
Mn(3)—O(11)	2·011 (8)	Mn(3)—O(12)	2·178 (9)
C(1)—O(4)	1·292 (14)	C(1)—O(5)	1·264 (15)
C(3)—O(6)	1·251 (17)	C(3)—O(7)	1·234 (17)
C(5)—O(8)	1·289 (15)	C(5)—O(9^{ii})	1·221 (15)
C(7)—O(10)	1·266 (14)	C(7)—O(11)	1·215 (14)
C(1)—C(2)	1·498 (18)	C(3)—C(4)	1·508 (22)
C(5)—C(6)	1·471 (18)	C(7)—C(8)	1·516 (18)
O(12)···O(6^{i})	2·756 (12)	O(12)···O(13)	2·745 (13)
O(12)—H(1)	0·93	O(12)—H(2)	0·92
H(1)···O(6^{i})	2·15	H(2)···O(13)	1·83
[C(9)—O(14)	1·26 (8)]	[C(9)—O(15)	1·74 (9)]
[C(9)—C(10)	1·95 (6)]		

Description of the structure and discussion

Fig. 1 shows the arrangement of the molecules in projection on the (001) plane with the numbering scheme. Interatomic distances and angles are given in Table 2.

The crystals are composed of discrete dodecanuclear $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}]$ molecules, waters of hydration and disordered acetic acid molecules. The overall structure of the molecule is quite unusual, resembling a snow-flake. The Mn atoms are linked by triply bridging oxo O atoms and by carboxylate bridges from acetate anions. Since the centers of the molecules occupy the points of $\bar{4}$ symmetry the molecules as a whole have $\bar{4}$ (S_4) point symmetry, and therefore there are only three crystallographically independent Mn atoms in one molecule. All Mn atoms have a distorted octahedral coordination. Because the experimentally found oxidation state was 3·34 per Mn atom, eight Mn atoms must be in oxidation state +3 and four in oxidation state +4. It is known that the trivalent octahedral Mn complexes

Table 2 (*cont.*)

O(1)—Mn(1)—O(1^{i})	83·5 (4)	O(1)—Mn(1)—O(1^{ii})	83·7 (4)	O(1^{i})—Mn(1)—O(1^{ii})	79·3 (4)
O(1)—Mn(1)—O(2)	90·4 (4)	O(1)—Mn(1)—O(3)	91·6 (4)	O(1)—Mn(I)—O(4)	173·7 (4)
O(1^{i})—Mn(1)—O(2)	99·5 (4)	O(1^{i})—Mn(1)—O(3)	173·5 (4)	O(1^{i})—Mn(1)—O(4)	90·7 (4)
O(1^{ii})—Mn(1)—O(2)	174·1 (4)	O(1^{ii})—Mn(1)—O(3)	95·9 (4)	O(1^{ii})—Mn(1)—O(4)	92·8 (4)
O(2)—Mn(1)—O(3)	84·7 (4)	O(2)—Mn(1)—O(4)	93·0 (4)	O(3)—Mn(1)—O(4)	94·0 (4)
O(2)—Mn(2)—O(3)	83·8 (4)	O(2)—Mn(2)—O(5)	85·1 (4)	O(2)—Mn(2)—O(6)	92·5 (4)
O(2)—Mn(2)—O(8)	176·5 (4)	O(2)—Mn(2)—O(10)	95·7 (4)	O(3)—Mn(2)—O(5)	86·3 (4)
O(3)—Mn(2)—O(6)	94·8 (4)	O(3)—Mn(2)—O(8)	94·2 (4)	O(3)—Mn(2)—O(10)	173·8 (4)
O(5)—Mn(2)—O(6)	177·2 (4)	O(5)—Mn(2)—O(8)	91·9 (4)	O(5)—Mn(2)—O(10)	87·5 (4)
O(6)—Mn(2)—O(8)	90·6 (4)	O(6)—Mn(2)—O(10)	91·4 (4)	O(8)—Mn(2)—O(10)	85·9 (4)
O(2)—Mn(3)—O(3^{i})	93·2 (4)	O(2)—Mn(3)—O(7)	95·0 (4)	O(2)—Mn(3)—O(9)	176·7 (4)
O(2)—Mn(3)—O(11)	92·8 (4)	O(2)—Mn(3)—O(12)	91·9 (4)	O(3^{i})—Mn(3)—O(7)	92·6 (4)
O(3^{i})—Mn(3)—O(9)	89·9 (4)	O(3^{i})—Mn(3)—O(11)	173·8 (4)	O(3^{i})—Mn(3)—O(12)	94·7 (4)
O(7)—Mn(3)—O(9)	86·1 (4)	O(7)—Mn(3)—O(11)	88·5 (4)	O(7)—Mn(3)—O(12)	169·7 (4)
O(9)—Mn(3)—O(11)	84·1 (4)	O(9)—Mn(3)—O(12)	86·6 (4)	O(11)—Mn(3)—O(12)	83·5 (4)
Mn(1)—O(1)—Mn(1^{i})	95·5 (4)	Mn(1)—O(1)—Mn(1^{ii})	95·3 (4)	Mn(1^{i})—O(1)—Mn(1^{ii})	100·6 (4)
Mn(1)—O(2)—Mn(2)	94·2 (4)	Mn(1)—O(2)—Mn(3)	132·5 (4)	Mn(2)—O(2)—Mn(3)	123·1 (4)
Mn(1)—O(3)—Mn(2)	95·7 (4)	Mn(1)—O(3)—Mn(3^{ii})	133·2 (5)	Mn(2)—O(3)—Mn(3^{ii})	129·1 (5)
Mn(1)—O(4)—C(1)	125·8 (8)	Mn(2)—O(5)—C(1)	122·4 (8)	Mn(2)—O(6)—C(3)	131·5 (9)
Mn(2)—O(8)—C(5)	133·5 (8)	Mn(2)—O(10)—C(7)	129·9 (8)	Mn(3)—O(7)—C(3)	129·1 (9)
Mn(3)—O(9)—C(5^{i})	131·8 (9)	Mn(3)—O(11)—C(7)	136·2 (9)	O(4)—C(1)—O(5)	125·1 (11)
C(2)—C(1)—O(4)	115·1 (11)	C(2)—C(1)—O(5)	119·8 (11)	O(6)—C(3)—O(7)	126·2 (14)
C(4)—C(3)—O(6)	119·9 (15)	C(4)—C(3)—O(7)	113·9 (15)	O(8)—C(5)—O(9^{ii})	125·2 (12)
C(6)—C(5)—O(8)	114·4 (12)	C(6)—C(5)—O(9^{ii})	120·4 (12)	O(10)—C(7)—O(11)	125·8 (12)
C(8)—C(7)—O(10)	115·3 (11)	C(8)—C(7)—O(11)	118·9 (12)		
[O(14)—C(9)—O(15)	149 (5)]	[C(10)—C(9)—O(14)	96 (4)]	[C(10)—C(9)—O(15)	114 (4)]
O(12)—H(1)···O(6^{i})	121·7	O(12)—H(2)···O(13)	174·3		

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35276 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

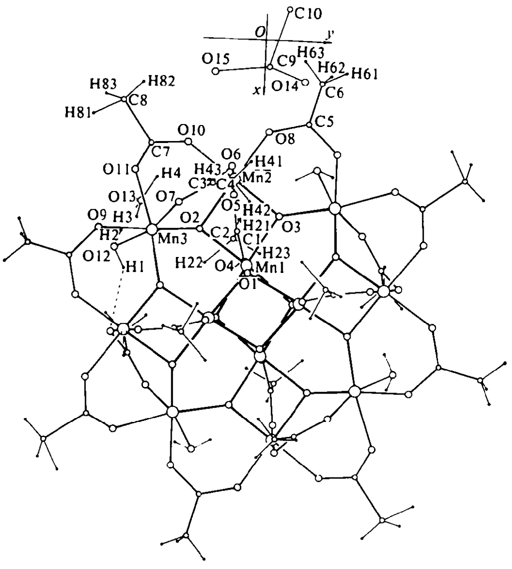

Fig. 1. The crystal structure of $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$: projection on the (001) plane.

should be subject to strong Jahn–Teller distortions. Since the Mn—O distances vary between 1·85 (1)–1·92 (1), 1·88 (1)–2·25 (1), and 1·89 (1)–2·18 (1) Å for Mn(1), Mn(2), and Mn(3) respectively, they support the hypothesis that Mn(1) is the Mn^{4+} ion and Mn(2) and Mn(3) are the Mn^{3+} ions.

Each Mn(1) atom is bridged with three symmetry-equivalent Mn(1) atoms through O(1) atoms and each O(1) atom is linked with three Mn(1) atoms. In this way four Mn(1) and four O(1) atoms form an almost ideal cubane structure.

The Mn(1) atoms are linked with Mn(2) and Mn(3) atoms as well as the Mn(2) atoms with Mn(3) atoms by triply bridging oxo O(2) and O(3) atoms. In this way there are two crystallographically independent triangles formed of one Mn(1), one Mn(2) and one Mn(3) atom. The bridging μ_3-oxo O(2) and O(3) atoms are, however, displaced by 0·34 (1) and 0·15 (1) Å, respectively, from the planes formed by the three-coordinated metal atoms. Furthermore, the Mn(1) atoms are linked with Mn(2) atoms by one carboxylate bridge, and the Mn(2) atoms are linked with the Mn(3) atoms through three independent carboxylate bridges. One water molecule completes the octahedral environment of the Mn(3) atom.

The Mn—O(oxo) distances are in the range 1·85 (1)–1·92 (1) Å and are similar to metal—O(oxo) distances in other μ_3-oxo trinuclear Mn, Rh, Cr, Fe, and V complexes. The Jahn–Teller effect which occurs in the Mn^{3+} ions differentiates the Mn—O distances. For Mn(2) there are two long [2·25 (1) and 2·19 (1) Å] and four short [1·88 (1)–1·94 (1) Å] Mn—O distances and the Jahn–Teller distortion may be classified as tetragonal elongation. The most probable description of Mn(3) is that there are three pairs of different Mn—O *cis* distances: two long [2·18 (1) and 2·13 (1) Å], two intermediate [1·98 (1) and 2·01 (1) Å] and two short [1·89 (1) and 1·90 (1) Å] and thus the Jahn–Teller distortion may be classified as orthorhombic. Both kinds of distortion were earlier observed in other Mn^{III} carboxylate complexes (Lis & Jeżowska-Trzebiatowska, 1977; Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977).

The Mn–water distances of 2·18 (1) Å are shorter than those in the monoclinic and orthorhombic modifications of $K[Mn(H_2O)_2(mal)_2].2H_2O$ of 2·29 (2) A (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977; Lis & Matuszewski, 1980) and a little shorter than those in $CsMnF_4.2H_2O$ of 2·21 (1) Å (Bukovec & Kaučič, 1977). The H atoms from coordinated [O(12)] water molecules form one intramolecular [with O(6)] hydrogen bond and one intermolecular [with O(13)] hydrogen bond. The parameters of these hydrogen bonds are summarized in Table 2. The H atoms from O(13) water molecules are not involved in hydrogen bonds.

The compound contains two types of acetate groups with different structural functions: bridging acetate ligands and the acetate group from the acetic acid molecules of solvation. The bridging acetate groups are almost planar. All distances and angles are similar to those found in other acetate complexes. The acetic acid molecules of solvation are located between the adjacent complex molecules. There is half a molecule of acetic acid in the crystallographic asymmetric unit. The molecules are situated around twofold axes and are statistically distributed between symmetry-equivalent positions. The positions of the O(15) and C(10) atoms from symmetry-equivalent acetic acid molecules are similar and therefore the coordinates and the bond lengths and angles are probably subject to more uncertainty than is indicated by the e.s.d.'s (Tables 1 and 2). The shortest interatomic distances O(14)···O(12) of 2·84 (5) and O(15)···O(6) of 3·08 (6) Å suggest that the hydrogen bonds are not strong.

The Mn···Mn distances are summarized in Table 2. The Mn(1)···Mn(3) and Mn(2)···Mn(3) distances are in the range 3·33 (1)–3·45 (1) Å and are comparable with the metal–metal distances found in μ_3-oxo trinuclear complexes of Fe, Cr, Mn and others (Głowiak, Kubiak, Szymańska-Buzar & Jeżowska-Trzebiatowska, 1977). The values of these distances are rather too large to allow a direct metal–metal magnetic interaction. The Mn(1)···Mn(2) distance of 2·767 (3) Å is relatively short and comparable with that of 2·716 Å found in $[Mn_2(2,2'\text{-bipyridine})_4O_2](ClO_4)_3.3H_2O$ (Plaksin *et al.*, 1972). In both complexes the structural unit $Mn^{IV}\langle{}^{O}_{O}\rangle Mn^{III}$ may be distinguished although the Mn—O distances are longer in the compound under investigation. Plaksin *et al.* (1972)

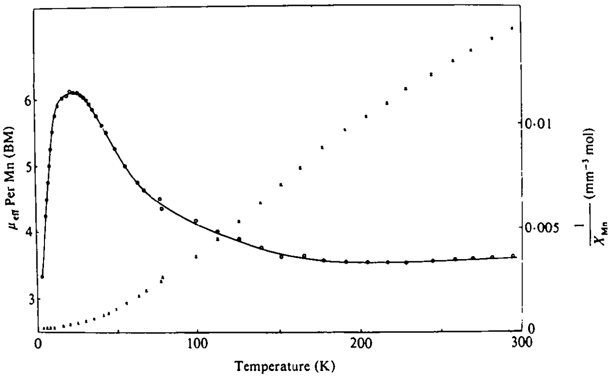

Fig. 2. Magnetic moment (continuous curve) and inverse of the magnetic susceptibility (broken curve) (both per one Mn atom) for $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$. [1 BM ≡ $9{\cdot}27 \times 10^{-24}$ J T^{-1}.]

and Cooper (1976) determined the temperature dependence of the magnetic susceptibility of $[Mn_2$-(2,2′-bipyridine)$_4O_2](ClO_4)_3.3H_2O$ and concluded that Mn^{3+} and Mn^{4+} are high spin and antiferromagnetically coupled.

The Mn(1)···Mn(1) symmetry-equivalent distances are 2·820 (3) (two) and 2·943 (3) Å. If exchange between all twelve Mn(1), Mn(2) and Mn(3) high-spin atoms is assumed to be *via* O atoms, such a complicated dodecameric unit should have interesting magnetic properties. The magnetic measurements are given in Fig. 2. The magnetic moment increases from $30{\cdot}9 \times 10^{-24}$ J T^{-1} at 3·3 K to a maximum of $56{\cdot}5 \times 10^{-24}$ J T^{-1} in the range of 17–31 K and then decreases to $33{\cdot}4 \times 10^{-24}$ J T^{-1} at 280 K per Mn atom.

Since slow decomposition was sometimes oberved at room temperature, to obtain more information about the stability of the compound thermogravimetric measurements were made. It was found that decomposition started at 308 K. Above 308 K, up to 463 K, it follows the endothermic splitting off of water and acetic acid molecules of solvation. Next, at 468 K it follows the rapid exothermic decomposition of a complex.

The author thanks Mr Trúóng Xuân Mâo (Vietnam) and Mr Edward Haraszkiewicz who participated in the early stage of this research for their MSc degrees.

References

Baikie, A. R. E., Hursthouse, M. B., New, D. B. & Thornton, P. (1978). *J. Chem. Soc. Chem. Commun.* pp. 62–63.

Bukovec, P. & Kaučič, V. (1977). *J. Chem. Soc. Dalton Trans.* pp. 945–947.

Cooper, S. R. (1976). PhD thesis, Univ. of California, Berkeley, California, USA.

Głowiak, T., Kubiak, M., Szymańska-Buzar, T. & Jeżowska-Trzebiatowska, B. (1977). *Acta Cryst.* B**33**, 3106–3109.

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

Lis, T. (1977). *Acta Cryst.* B**33**, 2964–2966.

Lis, T. & Jeżowska-Trzebiatowska, B. (1977). *Acta Cryst.* B**33**, 2112–2116.

Lis, T. & Matuszewski, J. (1980). *Pol. J. Chem.* **54**, 163–169.

Lis, T., Matuszewski, J. & Jeżowska-Trzebiatowska, B. (1977). *Acta Cryst.* B**33**, 1943–1946.

Plaksin, P. M., Stoufer, R. C., Mathew, M. & Palenik, G. J. (1972). *J. Am. Chem. Soc.* **94**, 2121–2122.

Weinland, R. F. & Fischer, G. (1921). *Z. Anorg. Allg. Chem.* **120**, 161–180.

XRAY system (1978). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1980). B**36**, 2046–2050

Tetrameric Methylzinc Methoxide

By H. M. M. Shearer† and C. B. Spencer*

The Chemistry Department, The University, Durham, England

(*Received* 5 *March* 1980; *accepted* 16 *April* 1980)

Abstract

Methylzinc methoxide is orthorhombic with a = 7·481 (15), b = 7·673 (15), c = 29·42 (5) Å, space group $P2_12_12_1$, $Z = 4$ units of $(CH_3ZnOCH_3)_4$. Final $R = 0{\cdot}087$ for 1287 observed reflections. Methylzinc methoxide is tetrameric in the crystal, as was found in solution in benzene. The Zn and O atoms occupy the corners of two regular interpenetrating tetrahedra of different sizes, so that these atoms are four-coordinate and are situated on alternate corners of a distorted

---

† Deceased.

* Present address: ICI Ltd, PO Box 54, Wilton Works, Middlesbrough, Cleveland TS6 8JB, England.

0567-7408/80/092046-05$01.00