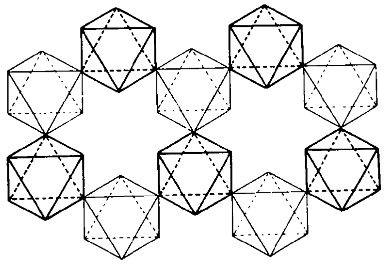

Fig. 2. A schematic representation of the corrugated Bi_2Br_9 layer.

(Fig. 2). Cs(1) lies inside the layer, Cs(2) outside the layer. The shorter Bi–Br(terminal) distances [2·713 (2) Å] and the longer Bi–Br(bridging) distances [2·979 (1) Å] are in reasonable agreement with the corresponding distances found in some other bromobismuthates(III): 2·65 to 2·88 Å and 3·02 to 3·13 Å in bispiperidinium pentabromobismuthate(III) (McPherson & Meyers, 1968), 2·64 Å and 2·97 to 3·27 Å in 2-picolinium tetrabromobismuthate(III) (Robertson, McPherson & Meyers, 1967) and 2·749 to 2·879 Å and 2·979 to 3·006 Å in potassium decabromodibismuthate(III) tetrahydrate (Lazarini, 1977*a*). The structure of $Cs_3Bi_2I_9$ is different (Lindqvist, 1968). Cs and I atoms are in the hexagonal close-packed structure with Bi atoms in pairs of adjacent octahedral holes, so that complex $Bi_2I_9^{3-}$ anions are present.

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Manganese(II) Propionate Dihydrate

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Abstract. $C_6H_{14}O_6Mn$, monoclinic, $C2/c$, a = 22·857 (9), b = 6·645 (3), c = 14·057 (6) Å, β = 114·28 (3)°, M_r = 237·12, V = 1946·2 Å^3, Z = 8, D_m = 1·61, D_x = 1·618 g cm^{-3}, μ(Mo $K\alpha$, λ = 0·71069 Å) = 14·2 cm^{-1}. The Mn atoms are linked by a bridging system that contains three types of bridges: a bidentate $C_2H_5COO^-$ group, one O atom from a second propionate group and one water molecule, to give infinite, almost linear, chains parallel to **b**, with a distorted octahedral Mn coordination and Mn–Mn distances of 3·350 (1) Å. The compound shows a temperature-independent magnetic moment very close to the value 5·9 BM (78–295 K). The structure was refined to an R of 0·037 for 1537 diffractometer data.

Introduction. As part of our continuing study on the stereochemistry of Mn–carboxylate complexes (Lis & Jeżowska-Trzebiatowska, 1977; Lis, Matuszewski &

Jeżowska-Trzebiatowska, 1977) our purpose is to establish the relative variability of the mode of Mn^{2+} coordination by propionate ligands in the crystalline state. Our study on propionate complexes of Mn in higher valence states will be published later.

Single crystals of the compound were prepared by evaporation of an aqueous mixture of freshly precipitated manganese(II) hydroxide and propionic acid. Weissenberg photographs showed that the crystals are monoclinic; the systematic absences were: hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$; space group $C2/c$ or Cc. An irregularly shaped crystal of approximate size 0·2 × 0·3 × 0·15 mm was selected for the data collection. A Syntex $P2_1$ diffractometer and Mo $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the θ–2θ scan technique. After each group of 40 reflexions the intensity of a standard reflexion was measured and no significant change in intensity was observed. The data were corrected for Lorentz and polarization effects. Of 1966 accessible reflexions in the range $7{\cdot}0 \le 2\theta \le 53°$, 1537 with $I > 1{\cdot}96\sigma(I)$ were used for the structure determination. All calculations were performed with the Syntex XTL structure-determination system (NOVA 1200 computer and additional external disc memory). Neutral-atom scattering factors used were those listed in *International Tables for X-ray Crystallography* (1974).

The heavy-atom method was employed for the phase determination. A satisfactory solution was obtained in space group $C2/c$ with the Mn atom in a general position with $x \sim \frac{1}{4}, y \sim 0, z \sim \frac{1}{4}$. All non-H atoms were found from several Fourier and difference-Fourier syntheses. Full-matrix least-squares refinement first with isotropic, then with anisotropic thermal parameters gave $R = 0{\cdot}083$ and $0{\cdot}047$ respectively. A difference-Fourier synthesis at this stage showed all H atoms. Further refinement with fixed parameters for H atoms (for all $B = 3{\cdot}5$ Å^2) reduced R to 0·037 and R_w to 0·036. The final atomic coordinates and their estimated standard deviations are listed in Table 1.* A final three-dimensional difference-Fourier synthesis was quite featureless.

The crystal structure is depicted in Fig. 1, which also gives the numbering scheme used in the text. The principal bond lengths and angles are presented in Table 2.

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

Positional parameters are given as fractions of cell edges $\times 10^5$. The hydrogen atom positions ($\times 10^3$) are unrefined.

	x	y	z
Mn	23987 (2)	1577 (7)	23995 (4)
$H_2O(1)$	30749 (11)	25379 (32)	36066 (16)
$H_2O(2)$	17225 (13)	25457 (36)	43938 (20)
O(1)	28406 (11)	9353 (32)	13519 (17)
O(2)	30125 (11)	42297 (33)	15638 (18)
O(3)	31670 (11)	−21175 (31)	30268 (17)
O(4)	39670 (10)	875 (36)	36273 (18)
C(1)	30922 (16)	25304 (50)	12252 (23)
C(2)	35344 (18)	24415 (52)	6685 (28)
C(3)	42124 (21)	20468 (77)	14344 (38)
C(4)	37708 (16)	−16515 (49)	34007 (25)
C(5)	42394 (18)	−33471 (57)	35668 (34)
C(6)	49326 (20)	−27526 (69)	40118 (42)
H(1)	341	182	364
H(2)	318	273	432
H(3)	193	364	432
H(4)	193	136	432
H(5)	352	370	23
H(6)	339	110	18
H(7)	410	−410	295
H(8)	412	−445	385
H(9)	420	90	205
H(10)	432	318	182
H(11)	455	182	114
H(12)	523	−410	409
H(13)	500	−182	477
H(14)	500	−182	341

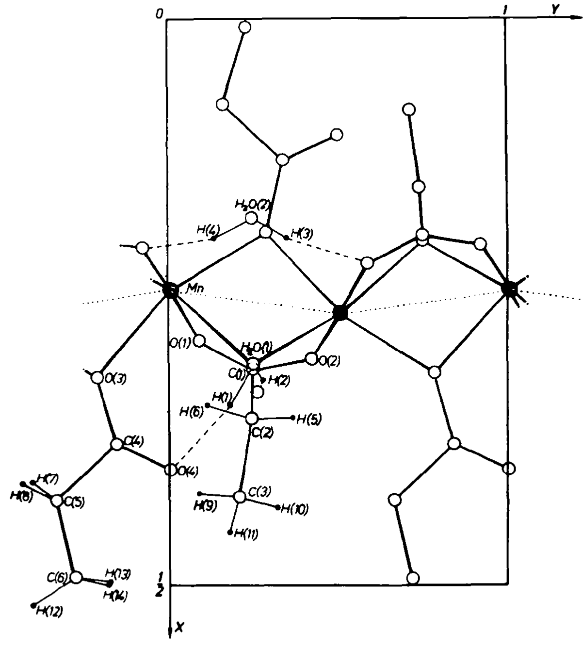

Fig. 1. The crystal structure projected on the (001) plane.

Discussion. The crystal structure, which is defined by the unit-cell dimensions, the positional parameters of Table 1, and the space-group symmetry operations, consists of infinite, almost linear chains of Mn ions

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32730 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

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

Mn—O(1)	2·163 (3)	Mn—O(2^{ii})	2·125 (3)
Mn—O(3)	2·208 (2)	Mn—O(3^{i})	2·162 (2)
Mn—H_2O(1)	2·369 (2)	Mn—H_2O(1^{ii})	2·223 (2)
O(1)—C(1)	1·253 (4)	O(2)—C(1)	1·267 (4)
C(1)—C(2)	1·512 (6)	C(2)—C(3)	1·502 (7)
O(3)—C(4)	1·296 (5)	O(4)—C(4)	1·233 (5)
C(4)—C(5)	1·505 (5)	C(5)—C(6)	1·498 (7)
O(1)—Mn—O(2^{ii})	176·8 (1)	O(1)—Mn—O(3)	85·3 (1)
O(1)—Mn—O(3^{i})	90·3 (1)	O(1)—Mn—H_2O(1)	88·8 (1)
O(1)—Mn—H_2O(1^{ii})	89·7 (1)	O(2^{ii})—Mn—O(3)	91·8 (1)
O(2^{ii})—Mn—O(3^{i})	92·9 (1)	O(2^{ii})—Mn—H_2O(1)	92·6 (1)
O(2^{ii})—Mn—H_2O(1^{ii})	88·4 (1)	O(3)—Mn—O(3^{i})	166·2 (1)
O(3)—Mn—H_2O(1)	89·6 (1)	O(3)—Mn—H_2O(1^{ii})	79·5 (1)
O(3^{i})—Mn—H_2O(1)	77·2 (1)	O(3^{i})—Mn—H_2O(1^{ii})	113·6 (1)
H_2O(1)—Mn—H_2O(1^{ii})	169·1 (1)		
O(1)—C(1)—O(2)	123·7 (4)	O(1)—C(1)—C(2)	119·0 (3)
O(2)—C(1)—C(2)	117·3 (3)	C(1)—C(2)—C(3)	110·4 (4)
O(3)—C(4)—O(4)	122·8 (4)	O(3)—C(4)—C(5)	117·1 (4)
O(4)—C(4)—C(5)	120·1 (4)	C(4)—C(5)—C(6)	115·5 (4)

Table 3. *Geometry of the hydrogen bonds* (*in* Å *and degrees*)

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

X—H···Y	X···Y	X—H	H···Y	∠X—H···Y
H_2O(1)—H(1)—O(4)	2·600 (3)	0·89	1·72	170·1
H_2O(1)—H(2)—H_2O(2^{iii})	2·655 (3)	0·94	1·79	164·5
H_2O(2)—H(3)—O(1^{i})	2·834 (4)	0·90	1·97	159·7
H_2O(2)—H(4)—O(2^{ii})	2·776 (3)	0·95	1·92	148·6

parallel to **b**. The Mn atoms have distorted octahedral geometry and are linked by three different kinds of bridges. It is apparent (Fig. 1) that there are two propionate bridges of different kinds. One type bridges Mn atoms as a bidentate ligand, and in the second propionate group only one O atom is the bridging atom. The Mn—O(propionate) distances vary from 2·125 (3) to 2·208 (2) Å. The third bridging group is the $H_2O(1)$ water molecule, giving one longer and one shorter Mn—O bond of 2·369 (2) and 2·223 (2) Å, respectively.

All bond lengths and angles in the $C_2H_5COO^-$ groups are unexceptional. The C—O bond lengths in the bidentate propionate group are equivalent [1·253 (4) and 1·267 (4) Å]. The monodentate carboxylate group appears to be unsymmetric, with a C(4)—O(4) bond of 1·233 (5) Å, close to the expected double-bond value.

In addition to the polymeric nature of the structure there is a network of hydrogen bonds utilizing the lone water of hydration, $H_2O(2)$, holding the polymeric units together. All four H atoms from two different water molecules are involved in hydrogen bonding and their parameters are summarized in Table 3.

It is noteworthy that the crystal structure of $Mn(C_2H_5COO)_2.2H_2O$ is quite different from the crystal structures of $Mn(CH_3COO)_2.4H_2O$ (Bertaut, Tranqui, Burlet, Burlet, Thomas & Moreau, 1974) and $Mn(HCOO)_2.2H_2O$ (Osaki, Nakai & Watanabé, 1964).

The Mn—Mn distances of 3·350 (1) Å indicate that no metal–metal interaction occurs. To investigate the effect of intra-chain superexchange interactions, we have measured the temperature variation of the magnetic susceptibility between 78 and 295 K. The investigated compound has a temperature-independent magnetic moment very close to the spin-only value (5·9 $\mp$ 0·1 BM), which suggests that there is no superexchange within this temperature range.

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