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Diaquabis(α-aminomethylmethylphosphinic acid)manganese(II) Dibromide Dihydrate

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Abstract. $(C_2H_8NO_2P)_2Mn(H_2O)_2.Br_2.2H_2O$, M_r = 505·0, triclinic, $P\bar{1}$, a = 10·183 (2), b = 9·676 (2), c = 11·056 (3) Å, α = 112·69 (2), β = 93·74 (1), γ = 117·75 (2)°, D_m = 1·99 (by flotation), D_x = 1·98 g cm^{-3}, Z = 2, $F(000)$ = 502. Refinement yielded a final R = 0·055. The Mn atom is octahedrally coordinated by four O atoms from four phosphinic groups and two water O atoms in *cis* positions. Mn–O distances range between 2·129 (7) and 2·261 (7) Å.

Introduction. Crystals suitable for X-ray analysis were colourless prisms. Weissenberg photographs showed that the crystals were triclinic. The centrosymmetric space group $P\bar{1}$ was assumed. The subsequent refinement confirmed this choice. All measurements were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and a graphite monochromator. The cell parameters were determined by least-squares refinement of the setting angles of 15 reflexions given by the automatic centring program [λ(Cu $K\alpha$) = 1·5418 Å]. 2280 independent reflexions were measured up to 2θ = 114·0° with the variable θ–2θ scan technique. The scan rate varied from 3·8 to 20·0° min^{-1}, depending on the intensity. After each group of 15 reflexions the intensity of a standard was measured; no significant change was observed. The intensities were corrected for Lorentz and polarization factors, but not for absorption [μ(Cu $K\alpha$) = 149 cm^{-1}].

The structure was solved by the heavy-atom technique and refined anisotropically by full-matrix least squares. The final R_1 = 0·055 and R_2 = 0·059 for

Table 1. *Atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
Mn	1909 (1)	3615 (1)	4963 (1)
Br(1)	0	0	0
Br(2)	5000	0	5000
Br(3)	4959 (1)	2392 (1)	8956 (1)
O(W1)	2127 (8)	2485 (8)	6278 (6)
O(W2)	119 (7)	835 (8)	3305 (6)
O(W3)	8495 (8)	648 (8)	5823 (7)
O(W4)	2085 (10)	3497 (10)	8918 (7)
Molecule I			
P(1)	72 (3)	4648 (3)	3033 (2)
O(1)	1351 (6)	4515 (7)	3635 (6)
O(2)	−201 (7)	5995 (7)	4053 (6)
C(1)	−1740 (11)	2459 (12)	2216 (9)
C(2)	428 (14)	5078 (15)	1599 (10)
N(1)	−2412 (9)	1884 (9)	3247 (8)
Molecule II			
P(2)	4431 (3)	2969 (3)	3107 (3)
O(3)	3559 (7)	2994 (7)	4149 (6)
O(4)	6144 (7)	3797 (7)	3684 (6)
C(3)	4143 (11)	4111 (12)	2227 (9)
C(4)	3639 (11)	750 (11)	1759 (9)
N(2)	−5611 (9)	−4122 (9)	−6766 (9)

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

(*a*) Coordination polyhedron

Mn–O(1)	2·137 (7)	Mn–O(4)	2·129 (7)
Mn–O(2)	2·213 (8)	Mn–O(W1)	2·184 (7)
Mn–O(3)	2·170 (8)	Mn–O(W2)	2·213 (8)
O(2′)–Mn–O(1)	87·0 (3)	O(3)–Mn–O(W1)	84·8 (3)
O(3)–Mn–O(1)	101·3 (3)	O(4′)–Mn–O(W1)	94·4 (3)
O(3)–Mn–O(2′)	171·3 (3)	O(1)–Mn–O(W2)	86·9 (3)
O(4′)–Mn–O(1)	91·5 (3)	O(2′)–Mn–O(W2)	94·3 (3)
O(4′)–Mn–O(2′)	95·2 (3)	O(3)–Mn–O(W2)	83·8 (3)
O(4′)–Mn–O(3)	87·1 (3)	O(4′)–Mn–O(W2)	170·2 (3)
O(1)–Mn–O(W1)	171·9 (3)	O(W2)–Mn–O(W1)	88·2 (3)
O(2′)–Mn–O(W1)	86·9 (3)		

(*b*) The ligand molecules

Molecule I

P(1)–O(1)	1·505 (8)	P(1)–C(1)	1·837 (8)
P(1)–O(2)	1·514 (8)	C(1)–N(1)	1·519 (14)
P(1)–C(2)	1·805 (12)		
O(2)–P(1)–O(1)	114·6 (4)	C(2)–P(1)–O(2)	110·3 (5)
C(1)–P(1)–O(1)	109·0 (5)	C(2)–P(1)–C(2)	102·7 (6)
C(1)–P(1)–O(2)	109·4 (5)	P(1)–C(1)–N(1)	113·1 (7)
C(2)–P(1)–O(1)	110·1 (5)		

Molecule II

P(2)–O(3)	1·500 (7)	P(2)–C(3)	1·829 (12)
P(2)–O(4)	1·504 (8)	C(3)–N(2)	1·524 (14)
P(2)–C(4)	1·801 (10)		
O(4)–P(2)–O(3)	114·7 (4)	C(4)–P(2)–O(4)	108·0 (5)
C(3)–P(2)–O(3)	108·9 (5)	C(4)–P(2)–C(3)	104·3 (5)
C(3)–P(2)–O(4)	108·8 (5)	P(2)–C(3)–N(2)	111·9 (7)
C(4)–P(2)–O(3)	111·5 (5)		

2000 observed reflexions for which $F > 3.92\sigma(F)$. For all 2280 reflexions R_1 and R_2 are 0·062 and 0·059. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the Syntex XTL structure determination system (Nova 1200 computer and additional external disc memory). The atomic coordinates are listed in Table 1 and the interatomic distances and angles in Table 2.*

Discussion. The molecular structure and atom numbering are shown in Fig. 1, in which the structure is projected down **c**. O(1), O(2′), O(3), and O(4′) from the four phosphinic groups and O(W1) and O(W2) from the water molecules form a distorted octahedron around the Mn atom, similar to those observed in other octahedral Mn^{II} complexes containing O as ligand atoms. The Br^- ions do not enter the coordination sphere. Each O atom forms only one bond with the metal atom. The phosphinic O atoms are bonded to different Mn atoms, forming Mn—O—P—O—Mn bridges. Similar Mn—O—C—O—Mn bridges were found in $MnCl_2(glyH)_2$ (Narayanan & Venkataraman, 1975) and $MnBr_2(glyH).2H_2O$ (Głowiak[l] & Ciunik, 1977). Mn—O distances vary from 2·129 to 2·261 Å, and the average (2·183 Å) is quite close to the 2·20 Å in $MnBr_2(glyH).2H_2O$ (Głowiak & Ciunik, 1977), the 2·189 Å in $MnCl_2(glyH)_2.2H_2O$ (Głowiak & Sawka-Dobrowolska, 1976), the 2·185 Å in $MnCl_2(glyH)_2$ (Narayanan & Venkataraman, 1975) and the 2·168 Å in $MnCl_2(AMMPh)_2.2H_2O$ (Głowiak & Sawka-Dobrowolska, 1977*b*).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32605 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

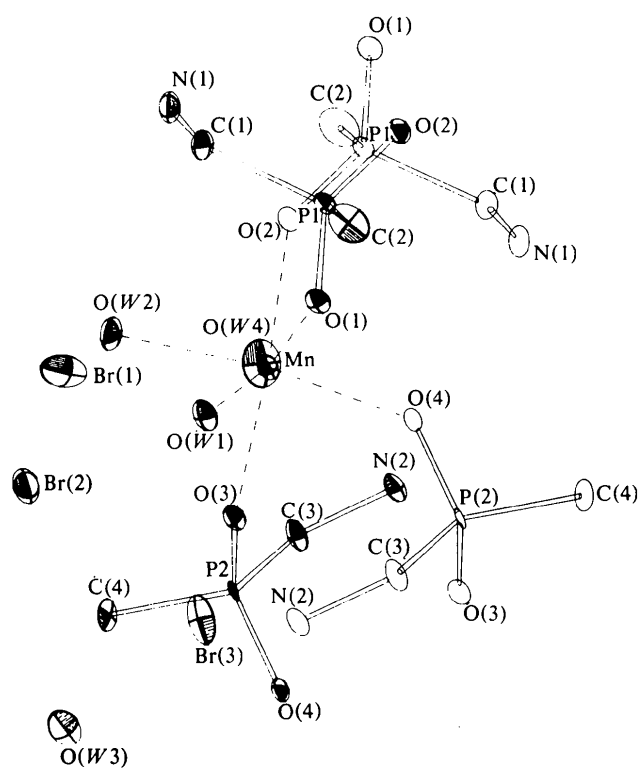

Fig. 1. A drawing of the molecule viewed along **c**. The atomic numbering is also shown.

Table 3. *Intermolecular distances* (Å)

For each pair of atoms, the coordinates of the second atom are transformed as shown.

Hydrogen-bond distances				
N(2)···O(1)	x,	y,	z	2·89 (1)
N(2)···O(3′)	$-x$,	$-y$,	$-z$	2·93 (1)
N(2)···Br(3′)	$-x$,	$-y$,	$-z$	3·38 (1)
N(1)···O(4)	x,	y,	z	2·78 (1)
N(1)···Br(3)	x,	y,	$z-1$	3·35 (1)
O(W3)···Br(2)	x,	y,	z	3·31 (1)
O(W3)···O(2′)	$-x$,	$1-y$,	$1-z$	2·82 (1)
O(W2)···O(W3′)	$1-x$,	$-y$,	$1-z$	2·79 (1)
O(W1)···O(W3′)	$1-x$,	$-y$,	$1-z$	2·75 (1)
O(W4)···Br(3)	x,	y,	z	3·34 (1)
O(W4)···O(W1)	x,	y,	z	2·71 (1)
Other important non-bonded distances less than 3·5 Å				
O(3)···O(W3′)	$1-x$,	$-y$,	$1-z$	3·17 (1)
O(W3)···O(W1)	x,	y,	z	3·17 (1)
O(W3)···O(W2)	x,	y,	z	3·35 (1)
O(W4)···O(W2′)	$-x$,	$-y$,	$1-z$	3·35 (1)
O(W1)···O(W2)	$-x$,	$-y$,	$1-z$	3·19 (1)
O(W1)···N(2)	$1+x$,	$1+y$,	z	3·04 (1)
N(1)···O(1)	x,	y,	z	3·35 (1)
N(1)···O(2)	x,	y,	z	3·05 (1)
N(1)···O(2′)	$-x$,	$-y$,	$1-z$	3·22 (1)
N(1)···O(W2)	x,	y,	z	3·18 (1)
N(2)···O(3)	x,	y,	z	3·10 (1)
N(2)···O(4)	x,	y,	z	3·39 (1)

The Mn coordination octahedron is moderately distorted (Table 2*a*). The O—Mn—O angles for pairs of contiguous O atoms range from 83·8 (3) to 101·3 (3)°, while those involving pairs of opposite O atoms range from 170·2 (3) to 171·9 (3)°. O(1), O(2′), O(3) and O(W1) lie almost in a plane [equation: $(-0.6258)X + (-0.7265)Y + (-0.2838)Z - (-3.5672) = 0$]; the largest distance from this plane is 0·04 Å. The Mn atom lies only −0·071 Å away from this plane. As can be seen in Table 2(b), corresponding bond distances and angles in the two aminomethylmethylphosphinic molecules (zwitterions) do not differ significantly and agree well with those found in α-aminomethylmethylphosphinic acid (AMMPh) (Głowiak & Sawka-Dobrowolska, 1977*a*) and in $MnCl_2(AMMPh)_2.2H_2O$ (Głowiak & Sawka-Dobrowolska, 1977*b*). The atoms defined by C(2), P(1), C(1) and N(1), and C(4), P(2), C(3) and N(2) are non-planar, as in $MnCl_2(AMMPh)_2.2H_2O$. Although the positions of the H

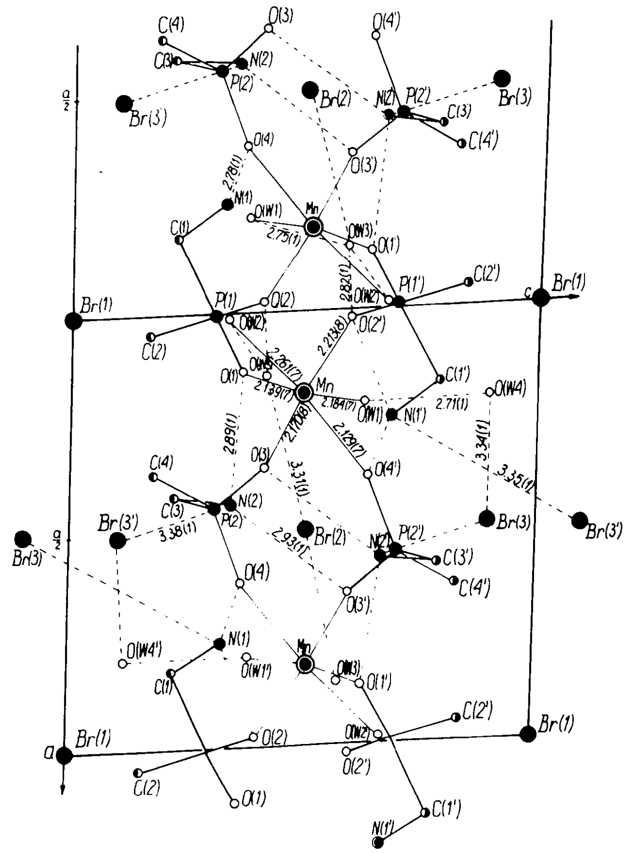

Fig. 2. The crystal structure viewed along **b**. The possible hydrogen bonds are represented by broken lines.

atoms have not been determined, some of the interatomic distances may be considered as hydrogen bonds. The structure viewed down **b** is shown in Fig. 2. The various hydrogen-bond distances are presented in Table 3. All four water molecules enter into hydrogen-bond formation. O(*W*1) and O(*W*2), and O(1), O(2), O(3) and O(4) of the phosphinic groups are coordinated to Mn and also form hydrogen bonds. Uncoordinated O(*W*3) and O(*W*4) take part in the hydrogen bonds with Br and the O atoms of other water molecules and the phosphinic group. The amino group in molecules I and II is also involved in hydrogen-bond formation. Short intermolecular contacts are listed in Table 3.

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Racemic *O*-Methylphenylphosphinylacetic Acid

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Abstract. (±)-Ph(MeO)P(O)CH_2COOH, monoclinic, $P2_1/c$, $a = 9{\cdot}552$ (5), $b = 9{\cdot}072$ (5), $c = 11{\cdot}882$ (6) Å, $\beta = 92{\cdot}25$ (8)°, $D_o = 1{\cdot}37$, D_c(for $Z = 4$) $= 1{\cdot}374$ g cm^{-3}, μ(Cu $K\alpha$) = 22·6 cm^{-1}. The symbolic addition procedure and full-matrix least-squares refinement led to the final R of 0·058 for 1473 independent reflexions (Weissenberg photographs, Ni-filtered Cu $K\alpha$ radiation). The molecules form dimers utilizing the O atom of the phosphoryl group.

Introduction. The structure of the title compound has been solved as part of the programme on the X-ray study of phosphinylacetic acid derivatives. These optically active compounds, obtained and resolved by Michalski & Musierowicz (1967), are particularly interesting for explaining the mechanism of stereospecific synthesis. The (−) enantiomer is at present under examination.

Colourless, transparent crystals were obtained from an acetone–water solution as thick needles, elongated along [010]. The systematic absences, $h0l$ with l odd and $0k0$ with k odd, indicated the space group explicitly. The unit-cell parameters were first calculated from high-order reflexions on Weissenberg and KFOR