be compared with the 2·14 (2) Å for the corresponding distances in $PhCCo_3(CO)_6(\pi\text{-}C_6H_3Me_3)$ (Dellaca & Penfold, 1972) where all three carbonyls from a single Co atom have been replaced by a six-electron donor. The structures of these two compounds may be contrasted with those of $PhCCo_3(CO)_6(\pi\text{-}C_8H_8)$ (Brice, Dellaca, Penfold & Spencer, 1971) and $PhCCo_3(CO)_6(\pi\text{-}C_7H_8)$ (Holloway & Penfold, 1977) in each of which a polyene ligand has replaced the axial carbonyls of three different Co atoms while still leaving the basic Co_3C core and the remaining terminal carbonyls unchanged.

While the lengths of the coordinated double bonds of norbornadiene [mean 1·36 (2) Å] do not differ significantly (1·5σ) from the value of 1·333 Å observed in the free ligand (Wilcox, Winstein & McMillan, 1960), the observed lengthening is certainly expected (Stephens, 1972). Corresponding values for the coordinated double bonds in other Co carbonyl norbornadiene complexes, *e.g.* $Co_2(CO)_5(\pi\text{-}C_7H_8)$, $Ph_2Sn[Co(CO)_2(\pi\text{-}C_7H_8)]_2$ and $Cl_2Sn[Co(CO)_2(\pi\text{-}C_7H_8)]_2$, are 1·37 (1), 1·40 (2) and 1·40 (1) Å with Co—C distances of 2·16, 2·18 and 2·17 Å respectively (Stephens, 1972; Boer & Flynn, 1971).

The orientation of the norbornadiene molecule may be conveniently described in terms of the planar group C(4)C(5)C(7)C(8) which makes an angle of 67·5° with the Co_3 plane. An alternative description is in terms of the orientation of the π bonds to Co(1); there is an angle of 22·7° between the Co_3 plane and the Co(1)-C(4–5)C(7–8) plane, where C(4–5) and C(7–8) are the mid-points of the double bonds C(4)—C(5) and C(7)—C(8). This is to be compared with angles of 31·2 and 32·7° between the Co_3 plane and planes formed by Co(2)C(22)C(23) and Co(3)C(32)C(33) respectively. This orientation of the norbornadiene achieves a balance between non-bonded repulsions with the apical C atom [minimum C(1)···C(4)/C(8) = 2·91 Å] and the axial carbonyl bonded to Co(1) [minimum C(11)···C(5)/C(7) = 2·70 Å].

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Two Crystal Structures of Polymorphic Bis(glycine)manganese(II) Bromide Dihydrate

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Abstract. Two crystal structures of the polymorphic compound $[Mn(^-OOCCH_2NH_3^+)_2(OH_2)_2]Br_2$ (M_r = 400·9) have been determined: (I) monoclinic, $P2_1/c$, $Z = 2$, a = 11·943 (3), b = 6·060 (2), c = 8·979 (2) Å, β = 111·65 (3)°, V = 604·06 Å^3, D_m = 2·21, D_x = 2·20 g cm^{-3}, μ(Cu $K\alpha$) = 182·1 cm^{-1}; (II) orthorhombic, *Pbca*, Z = 8, a = 21·613 (5), b = 12·649 (3), c = 8·990 (2) Å, V = 2457·7 Å^3, D_m = 2·15, D_x = 2·17 g cm^{-3}, μ(Cu $K\alpha$) = 197·0 cm^{-1}. All measurements were made on a computer-controlled four-circle diffractometer with Cu $K\alpha$ radiation. The final R_1 values for 722 (I) and 1398 (II) reflections were 0·040 and 0·047 respectively. The title compound has a polymeric nature. In both types of crystals different arrangements of the polymeric chains were found. Mn—O bonds lie in the range 2·169–2·183 Å (I) and 2·137–2·255 Å (II). N, O(water) and Br atoms form weak hydrogen bonds.

Introduction. Berezina & Pozigun (1967) prepared crystalline anhydrous manganous complexes with amino acids of the $MnCl_2(aa)_n$, $MnBr_2(aa)_n$ and $MnSO_4(Gly)_n$ types, where $n = 2, 4, 6$, aa = glycine (Gly) or α-alanine (α-Ala). They have also made IR spectroscopic studies of the crystalline $Mn(NO_3)_2(Gly)_n$ and $MnCl_2(\alpha\text{-Ala})_n$ complexes (Berezina & Pozigun, 1970) and found that the amino acid molecules do not appear as zwitterions and are bidentate (O, N donor atoms). An X-ray examination of only one of these compounds has been carried out: $[Mn(Gly)_2Cl_2]$ (Narayanan & Venkataraman, 1975), which is an addition compound with a chain-like Mn—$(Gly)_2$—Mn structure. Other X-ray-examined Mn^{2+} and glycine compounds are: $[Mn(Gly)_2(OH_2)_2Cl_2]$ (Głowiak & Sawka-Dobrowolska, 1976) and $[Mn(Gly)(OH_2)_2Br_2]$ (Głowiak & Ciunik, 1977*a*) with a chain-like Gly—Mn—Gly—Mn— structure. In all these compounds glycine appears as a zwitterion and there are no Mn—N bonds. In the present paper two structures of a new polymorphic addition compound belonging to this group of compounds are presented.

Both types of crystals were grown from the same aqueous solution of glycine and manganese(II) bromide (2:1) at room temperature. All measurements for crystals of approximate dimensions 0·1 × 0·1 × 0·15 mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator using Cu $K\alpha$ radiation (λ = 1·5418 Å). The cell parameters were determined from a least-squares refinement of setting angles of 15 reflections given by the automatic centering program. The systematic absences for (I) ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) and (II) ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) indicated space groups $P2_1/c$ and *Pbca* respectively. Intensities of 768 (I) and 1648 (II) independent reflections were measured up to 2θ = 114·0° with the variable θ–2θ scan technique. After each group of 15 reflections the intensity of a standard reflection was measured and no significant change in intensity was observed. The scan rate varied from 3·8 to 20·0° min^{-1}, depending on the intensity of reflection. 722 (I) and 1398 (II) reflections with $I > 1{\cdot}96(I)$ were used in the analysis. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The densities of the crystals were measured by flotation in a mixture of $CHCl_3$ and $CHBr_3$.

Both crystal structures were solved by the heavy-atom method. Positions of Mn and Br atoms were determined from three-dimensional Patterson syntheses. Coordinates of other non-hydrogen atoms were determined from Fourier difference syntheses. The full-matrix least-squares refinement with isotropic thermal parameters yielded R_1 ($= \sum||F_o| - |F_c||/\sum|F_o|$) values of 0·083 (I) and 0·107 (II). The final values of R_1 after refinement with anisotropic thermal parameters were 0·040 (I) and 0·047 (II); $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ was 0·046 (I) and 0·053 (II).* The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F)$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional parameters are given in Table 1.

Table 1. *The positional parameters* (×10⁴) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Monoclinic crystals (I)			
Mn	0	0	5000
O(1)	1513 (4)	−1342 (8)	4510 (5)
O(2)	581 (4)	−3403 (9)	2335 (6)
C(1)	1504 (6)	−2554 (10)	3370 (8)
C(2)	1698 (6)	−2992 (13)	3171 (9)
N	3735 (5)	−2176 (10)	4616 (7)
O(*W*)	1036 (4)	2948 (9)	6066 (7)
Br	3901 (1)	3013 (1)	6541 (1)
Orthorhombic crystals (II)			
Mn	3234 (1)	1329 (1)	3775 (2)
O(1)	3509 (3)	2815 (6)	714 (8)
O(2)	4000 (3)	1953 (5)	2516 (8)
C(1)	3994 (4)	2449 (8)	1330 (11)
C(2)	4597 (4)	2584 (9)	479 (11)
N(1)	5138 (3)	2358 (7)	1494 (9)
O(3)	2602 (3)	627 (6)	5318 (8)
O(4)	2262 (3)	−499 (6)	7032 (8)
C(3)	2201 (5)	−14 (9)	5826 (13)
C(4)	1629 (5)	−239 (9)	4941 (12)
N(2)	1603 (4)	471 (7)	3565 (9)
O(1*W*)	3851 (3)	−5 (6)	4118 (9)
O(2*W*)	2617 (3)	2720 (6)	3263 (9)
Br(1)	1339 (1)	2351 (1)	783 (1)
Br(2)	4848 (1)	4777 (1)	2765 (2)

Table 2. *Symmetry operations used in all tables, figures and in the text*

Monoclinic crystals (I)				Orthorhombic crystals (II)			
None	x,	y,	z	None	x,	y,	z
(i)	$1 - x$,	$-y$,	$1 - z$	(i)	x,	$\frac{1}{2} - y$,	$\frac{1}{2} + z$
(ii)	x,	$-\frac{1}{2} + y$,	$-\frac{1}{2} + z$	(ii)	$\frac{1}{2} - x$,	$\frac{1}{2} - y$,	$-\frac{1}{2} + z$
(iii)	x,	$\frac{1}{2} - y$,	$-\frac{1}{2} + z$	(iii)	$\frac{1}{2} - x$,	$\frac{1}{2} - y$,	z
(iv)	$1 - x$,	$-\frac{1}{2} + y$,	$\frac{1}{2} - z$	(iv)	$\frac{1}{2} - x$,	$-y$,	$\frac{1}{2} + z$
(v)	x,	$\frac{1}{2} + y$,	$\frac{1}{2} + z$	(v)	$I - x$,	$-\frac{1}{2} - y$,	$\frac{1}{2} - z$
(vi)	x,	$-\frac{1}{2} - y$,	$\frac{1}{2} + z$	(vi)	$\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$-z$

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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 33405 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

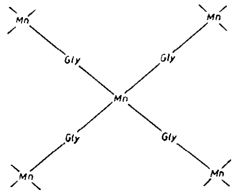
All calculations were performed with the Syntex XTL structure determination system (NOVA 1200 computer and additional external disc memory).

Discussion. In both types of crystals the Mn atoms have coordination number 6. Slightly distorted coordination octahedra are formed by two water molecules in *trans* positions and by the O atoms derived from the carboxylic groups of the glycine molecules which coordinate simultaneously with the two adjacent Mn atoms. The Mn—O bond lengths range from 2·169 to 2·183 Å (I) and from 2·137 to 2·255 Å (II) and are consistent with those found in other manganese(II) and glycine compounds and in MnBr$_2$.4H$_2$O (Sudarsanan, 1975). The O(Gly)—Mn—OH$_2$ angles differ from 90° by 0·9° (I) and 6·5° (II) (max.), the O(Gly)—Mn—O(Gly) angles by 2·0° (I) and 10·2° (II). The symmetry operations are given in Table 2, the bond distances and angles are presented in Table 3.

In the coordination octahedron in orthorhombic crystals (II) the O(Gly) atoms were found to deviate considerably from the O(1$^{\rm i}$)O(2)O(3)O(4$^{\rm ii}$) plane (equation: $-0{\cdot}5644X + 0{\cdot}7846Y - 0{\cdot}2071Z + 3{\cdot}4727 = 0$): Mn 0·005, O(1$^{\rm i}$) 0·146, O(2) −0·110, O(3) −0·181, O(4$^{\rm ii}$) 0·132 Å. Owing to the presence of the Mn—O—C—O—Mn bridges both crystal structures have a chain-like nature. In monoclinic crystals (I) the Mn atoms situated on plane (100) are linked through the carboxylic groups. In the [011] and [01$\bar{1}$] directions determined by the Mn atom positions, intersecting chains are formed. A two-dimensional polymer lattice is formed where the Mn—Mn distance is 5·42 Å.

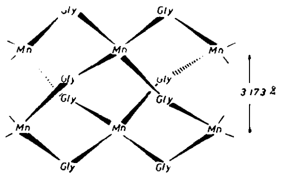
Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Monoclinic crystals (I)			
Mn—O(1)	2·169 (5)	O(1)—Mn—O(2$^{\rm vi}$)	92·0 (2)
Mn—O(2$^{\rm vi}$)	2·177 (5)	O(1)—Mn—O(*W*)	90·9 (2)
Mn—O(*W*)	2·183 (6)	O(*W*)—Mn—O(2$^{\rm vi}$)	90·8 (2)
C(1)—O(1)	1·257 (8)	O(1)—C(1)—O(2)	125·6 (7)
C(1)—O(2)	1·260 (9)	O(1)—C(1)—C(2)	118·0 (6)
C(1)—C(2)	1·524 (11)	O(2)—C(1)—C(2)	116·3 (6)
C(2)—N	1·509 (10)	C(1)—C(2)—N	110·4 (6)
Orthorhombic crystals (II)			
Mn—O(1$^{\rm i}$)	2·137 (7)	O(1$^{\rm i}$)—Mn—O(2*W*)	86·3 (3)
Mn—O(2)	2·155 (7)	O(2)—Mn—O(4$^{\rm ii}$)	100·2 (3)
Mn—O(3)	2·140 (8)	O(2)—Mn—O(1*W*)	83·5 (3)
Mn—O(4$^{\rm ii}$)	2·169 (7)	O(2)—Mn—O(2*W*)	93·6 (3)
Mn—O(1*W*)	2·173 (8)	O(3)—Mn—O(4$^{\rm ii}$)	87·2 (3)
Mn—O(2*W*)	2·255 (8)	O(3)—Mn—O(1*W*)	88·7 (3)
C(1)—O(1)	1·273 (12)	O(3)—Mn—O(2*W*)	94·5 (3)
C(1)—O(2)	1·238 (13)	O(4$^{\rm ii}$)—Mn—O(1*W*)	91·7 (3)
C(1)—C(2)	1·521 (14)	O(4$^{\rm ii}$)—Mn—O(2*W*)	86·5 (3)
C(2)—N(1)	1·510 (13)	O(1)—C(1)—O(2)	124 (1)
C(3)—O(3)	1·272 (14)	O(1)—C(1)—C(2)	116 (1)
C(3)—O(4)	1·253 (14)	O(2)—C(1)—C(2)	119 (1)
C(3)—C(4)	1·498 (15)	C(1)—C(2)—N(1)	110 (1)
C(4)—N(2)	1·530 (15)	O(3)—C(3)—O(4)	123 (1)
O(1$^{\rm i}$)—Mn—O(2)	91·7 (3)	O(3)—C(3)—C(4)	119 (1)
O(1$^{\rm i}$)—Mn—O(3)	81·9 (3)	O(4)—C(3)—C(4)	117 (1)
O(1$^{\rm i}$)—Mn—O(1*W*)	96·1 (3)	C(3)—C(4)—N(2)	110 (1)



(I)

The distance between the consecutive sites filled by the Mn atoms is equal to d_{100} and is 11·100 Å. In orthorhombic crystals (II) the Mn atoms are situated on the planes which are normal to the direction [100]. The Mn atoms situated in one plane are linked to one another by the carboxylic groups. At a distance of 3·173 Å from that plane is the next identical plane whose Mn atoms are displaced by $\frac{1}{2}b$ with respect to the former plane. The carboxylic groups also link the Mn atoms located on the two adjacent planes. Thus a 'packet' built from two planes is formed in which the Mn atoms linked by the carboxylic groups are situated.



(II)

The Mn—Mn distance in one plane is 5·39 Å and between two linked atoms from the adjacent planes is 6·45 Å. The distance between the centers of successive

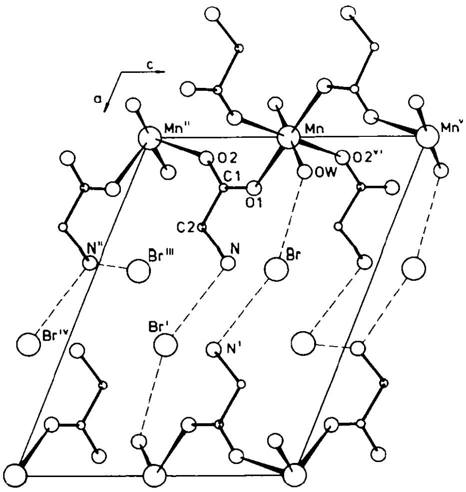


Fig. 1. The monoclinic (I) crystal structure viewed along **b**. The hydrogen bonds are represented by broken lines.

Table 4. *Hydrogen-bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Donor (*D*)···acceptor (*A*)	*D*···*A*	∠C–*D*···*A*	∠*A*(1)···*D*···*A*(2)	
Monoclinic crystals (I)				
C(2)–N···Br^{i}	3·387 (6)	101·5	Br^{iii}···N^{ii}···Br^{iv}	97·5
C(2^{ii})–N^{ii}···Br^{iii}	3·358 (6)	91·8		
O(*W*)···Br	3·288 (6)			
Orthorhombic crystals (II)				
C(2)–N(1)···Br(1^{vi})	3·326 (8)	102·2	Br(1^{vi})···N(1)···Br(2)	104·8
C(2)–N(1)···Br(2)	3·322 (9)	83·5	Br(1^{vi})···N(1)···Br(2^{v})	103·0
C(2)–N(1)···Br(2^{v})	3·334 (9)	108·4	Br(2)···N(1)···Br(2^{v})	146·3
C(4^{iii})–N(2^{iii})···Br(2)	3·338 (9)	93·2	Br(1^{iv})···O(1*W*)···Br(2^{v})	105·0
O(1*W*)···Br(1^{iv})	3·349 (8)			
O(1*W*)···Br(2^{v})	3·288 (8)			

'packets' is equal to $\frac{1}{2}a$ and is 10·806 Å. Figs. 1 and 2 give a more complete picture of both structures.

Although the H atom positions were not determined, the interatomic distances and angles summarized in Table 4 are evidence of weak hydrogen bonds. The donors are the coordinated H_2O molecules and NH_3 groups from glycine molecules. The acceptors are the Br^- ions which are involved in the formation of two or three hydrogen bonds simultaneously. Thus branched hydrogen bonds appear between the successive lattices (I) and 'packets' (II) of the polymer.

In the crystals under investigation the glycine molecules occur as zwitterions. The bond lengths and angles are presented in Table 3.

All the Mn^{2+}–amino acid addition compounds examined previously by X-ray methods may be divided into two groups:

- chain-like compounds which include the compound under investigation and $[Mn(Gly)(OH_2)_2Br_2]$, $[Mn(Pro)(OH_2)_4]SO_4$ (Głowiak & Ciunik, 1978) and $[Mn(Gly)_2Cl_2]$;
- monomeric compounds which include $[Mn(Pro)_2(OH_2)_2Br_2]$ (Głowiak & Ciunik, 1977*b*) and $[Mn(Gly)_2(OH_2)_2Cl_2]$ (where Pro = DL-proline).

In the crystalline state in all the compounds investigated the amino acids are bonded with Mn^{2+} through O atoms. They are bidentate in chain-like compounds and monodentate, in the *trans* position, in monomers. The Cl atoms appear in the inner coordination sphere whereas in $MnCl_2(aa)_6$ (obtained by Berezina and Pozigun) they should be in the outer sphere. The presence of the Br atoms in the inner coordination sphere depends on the number of amino acid molecules and the polymeric or monomeric nature. Similar effects were found in monomeric bis(α-aminomethylmethylphosphinic acid)manganese(II) dichloride dihydrate (Głowiak & Sawka-Dobrowolska, 1977*b*) and in polymeric diaquabis(α-aminomethylmethylphosphinic acid)manganese(II) dibromide dihydrate (Głowiak & Sawka-Dobrowolska, 1977*a*). In (proline)manganous sulphate tetrahydrate the SO_4^{2-} ion appears in the outer coordination sphere.

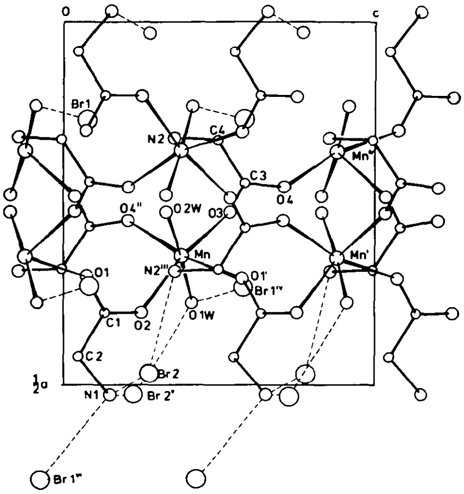


Fig. 2. The orthorhombic (II) crystal structure viewed along **b**. The hydrogen bonds are represented by broken lines.

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