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Bis(DL-proline)manganese(II) Dibromide Dihydrate

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Abstract. $C_{10}H_{22}N_2O_6Br_2Mn$, monoclinic, $P2_1/c$, a = 9·375 (1), b = 9·195 (2), c = 10·122 (2) Å, β = 106·38 (2)°, M_r = 481·1, V = 837·1 Å^3, Z = 2, D_m = 1·91, D_x = 1·91 g cm^{-3}, μ(Cu $K\alpha$) = 132·7 cm^{-1}, λ = 1·5418 Å. The proline molecule is a monodentate O-donor ligand. C^γ of the pyrrolidine ring is statistically situated on both sides of the $NC^\alpha C^\beta C^\delta$ plane. The structure was refined to an R of 0·038 for 1006 diffractometer data.

Introduction. The crystals grew as colourless plates from an aqueous solution of $MnBr_2$ and DL-proline in a molar ratio 1:2. All measurements for a crystal 0·12 × 0·14 × 0·15 mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator. The cell parameters were determined by least-squares refinement of the setting angles of 15 reflexions given by the automatic centring program. Intensities of 1127 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. 1006 reflexions with $I > 1{\cdot}96\sigma(I)$ were used in the analysis. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the heavy-atom method. Full-matrix refinement with isotropic thermal parameters to $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}096$ and anisotropic thermal parameters to R_1 = 0·050 was performed. Deviations from the expected geometry of the pyrrolidine ring (C^β–C^γ was 1·407 Å) and very large thermal parameters of C^γ were found. A difference synthesis, excluding C^γ, showed two new maxima consistent with the pyrrolidine ring. The structure was again refined with isotropic thermal parameters to R_1 = 0·092 and with anisotropic parameters to R_1 = 0·048. The occupancy factors, G, calculated for the new atoms were 0·60 and 0·40. The positions of the H atoms in the pyrrolidine ring were

Table 1. *The occupancy and positional* (×10^4) *parameters with e.s.d.'s in parentheses*

	G	x	y	z
Mn	1·0	0	0	0
Br	1·0	2156 (1)	1712 (1)	−566 (1)
O(1)	1·0	1505 (5)	−1830 (5)	636 (5)
O(2)	1·0	1195 (7)	−3382 (5)	−1101 (5)
O(W)	1·0	697 (6)	633 (5)	2161 (4)
N	1·0	2434 (6)	−3814 (6)	2596 (6)
C′	1·0	1571 (7)	−3052 (8)	142 (7)
C^α	1·0	2191 (7)	−4296 (7)	1146 (7)
C^β	1·0	3714 (10)	−4787 (11)	1085 (9)
$C^{\gamma 1}$	0·6	4744 (19)	−3863 (21)	2014 (17)
$C^{\gamma 2}$	0·4	4844 (27)	−4725 (43)	2564 (26)
C^δ	1·0	4032 (9)	−3482 (11)	3178 (9)

	Atom bearing	G	x	y	z
H(1)*	C^α	1·0	1435	−5114	879
H(2)	C^β	0·6	3821	−4678	120
H(3)	C^β	0·6	3921	−5830	1370
H(4)	C^β	0·4	3699	−5823	752
H(5)	C^β	0·4	4082	−4148	435
H(6)	$C^{\gamma 1}$	0·6	4916	−2957	1513
H(7)	$C^{\gamma 1}$	0·6	5726	−4371	2384
H(8)	$C^{\gamma 2}$	0·4	5812	−4361	2538
H(9)	$C^{\gamma 2}$	0·4	4850	−5599	3067
H(10)	C^δ	0·6	4496	−4075	4029
H(11)	C^δ	0·6	4192	−2416	3438
H(12)	C^δ	0·4	4285	−2480	2907
H(13)	C^δ	0·4	4357	−3536	4221
H(14)	N	1·0	2129	−4605	3159
H(15)	N	1·0	1813	−2927	2631
H(16)	O(W)	1·0	1300	−60	2870
H(17)	O(W)	1·0	940	1620	2520

* B = 4·8 Å^2 for the H atoms.

calculated with C–H and N–H = 1·00 Å and with the two conformations taken into account; two other H atoms were located from the difference synthesis. The H atoms were included in the structure factor calculations with $B = 4{\cdot}8$ Å^2, but were not refined. The final $R_1 = 0{\cdot}038$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0{\cdot}045$. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/\sigma^2(F)$. Scattering factors 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 final atomic parameters are given in Table 1.*

Discussion. The compound is a monomer. The coordination of the Mn atom is distorted octahedral with two Br atoms, two H_2O molecules and two O atoms from two proline molecules at the corners. The bond distances and angles are presented in Table 2. The lengths C^β–$C^{\gamma 1}$, 1·423, and C^β–$C^{\gamma 2}$, 1·537 (mean 1·480), $C^{\gamma 1}$–C^δ, 1·541, and $C^{\gamma 2}$–C^δ, 1·549 (mean 1·545), C^δ–N, 1·479 Å, in the pyrrolidine ring differ from the expected values, but these deviations do not affect the C^β–$C^{\gamma 1}$–C^δ and C^β–$C^{\gamma 2}$–C^δ angles. During refinement a partly disordered state was found. The pyrrolidine rings exhibit two conformations which occur in a ratio of 3:2. In the first conformation C′ and $C^{\gamma 1}$ are on the same side of the $NC^\alpha C^\beta C^\delta$ plane (equation: $-0{\cdot}0185X + 0{\cdot}9033Y - 0{\cdot}4285Z + 3{\cdot}9184 = 0$) and deviate from it by 1·49 and 0·37 Å respectively. In the second they are on opposite sides and $C^{\gamma 2}$ deviates from it by −0·57 Å. The distance between the $C^{\gamma 1}$ and $C^{\gamma 2}$ positions is 0·97 Å. Since the average C^β and C^δ positions were refined, their thermal parameters increased and certain disturbances in bond lengths occur. A similarly abnormal behaviour of C^γ in the proline residues in Leu-Pro-Gly was found by Leung & Marsh (1958). A more complete description of this phenomenon in peptides was presented by Ashida & Kakudo (1974).

There are two hydrogen bonds: N–H(14)···Br^{i} and O(*W*)–H(16)···O(2^{i}), whose lengths and angles are presented in Table 3.

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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 32777 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Mn–Br	2·746 (1)	O(1)–Mn–O(*W*)	94·4 (2)
Mn–O(1)	2·174 (5)	O(1)–C′–O(2)	126·6 (7)
Mn–O(*W*)	2·178 (4)	O(1)–C′–C^α	117·5 (6)
C′–O(1)	1·239 (8)	O(2)–C′–C^α	115·8 (6)
C′–O(2)	1·245 (8)	C′–C^α–N	110·9 (5)
C′–C^α	1·532 (10)	C′–C^α–C^β	112·4 (6)
C^α–N	1·488 (9)	C^α–C^β–$C^{\gamma 1}$	105·5 (10)
C^α–C^β	1·515 (12)	C^α–C^β–$C^{\gamma 2}$	106·9 (13)
C^β–$C^{\gamma 1}$	1·423 (20)	C^β–$C^{\gamma 1}$–C^δ	106·3 (12)
C^β–$C^{\gamma 2}$	1·537 (27)	C^β–$C^{\gamma 2}$–C^δ	101·3 (19)
$C^{\gamma 1}$–C^δ	1·549 (20)	$C^{\gamma 1}$–C^δ–N	104·8 (9)
$C^{\gamma 2}$–C^δ	1·541 (36)	$C^{\gamma 2}$–C^δ–N	101·1 (13)
C^δ–N	1·479 (11)	C^δ–N–C^α	108·1 (6)
Br–Mn–O(1)	92·9 (1)	N–C^α–C^β	104·2 (6)
Br–Mn–O(*W*)	91·5 (1)		

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code None x,y,z	(i) $x, -\frac{1}{2}-y, \frac{1}{2}+z$		
D–H···*A*	*D*···*A*	H···*A*	∠*D*–H···*A*
N–H(14)···Br^{i}	3·301 (6)	2·323	161·9
O(*W*)–H(16)···O(2^{i})	2·671 (7)	1·790	144

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