(DL-Proline)manganese(II) Sulphate Tetrahydrate [*catena*-Diaqua-μ-(DL-proline)-manganese(II) Sulphate]

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Abstract. $C_5H_{17}MnNO_{10}S$, monoclinic, Cc, $a = 8.165$ (2), $b = 16.857$ (5), $c = 9.222$ (2) Å, $\beta = 92.02$ (2)°, $M_r = 338.2$, $V = 1268.5$ Å^3, $Z = 4$, $D_m = 1.77$, $D_c = 1.76$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.30 mm^{-1}, $\lambda = 0.71069$ Å. Final $R = 0.038$ for 1515 diffractometer data. The compound is polymeric.

Introduction. Crystals of the title compound were grown as colourless plates from an aqueous solution of MnSO$_4$ and DL-proline. Weissenberg photographs indicated a monoclinic lattice with systematic absences hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$, consistent with the space groups Cc or $C2/c$. Determination of the chemical formula and the fact that $Z = 4$ eliminated the centrosymmetric space group $C2/c$.

All measurements for a crystal $0.10 \times 0.12 \times 0.20$ 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 from the setting angles of 15 reflections. Intensities of 1694 independent reflections were measured up to $2\theta = 60°$ with the variable θ–2θ scan technique. The scan rate varied from 2.0 to 20.0° min^{-1}, depending on the intensity. 1515 reflections with $I > 1.96\sigma(I)$ 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 least-squares refinement with isotropic thermal parameters to $R_1(= \sum ||F_o| - |F_c||/\sum |F_o|) = 0.061$ and with anisotropic thermal parameters to $R_1 = 0.045$ was performed. The positions of the H atoms in the pyrrolidine ring were calculated with C–H and N–H = 1.0 Å; eight other H atoms were included in the structure factor calculations with individual isotropic thermal parameters, but were not refined. The final $R_1 = 0.038$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.038$. The function minimized was $\sum w(F_o - F_c)^2$ 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* system (Nova 1200 computer and additional external disc memory).

The final atom parameters are given in Table 1.* Bond lengths and angles are in Table 2.

Table 1. *The final atomic parameters*

(a) Positional ($\times 10^4$, for Mn and S $\times 10^5$) and equivalent thermal parameters (Å^2) of the nonhydrogen atoms

The x and z parameters of Mn have fixed values.

	x	y	z	B_{eq}
Mn	18000	9001 (5)	14000	1.64
S	18673 (20)	22990 (8)	59644 (15)	1.54
O(1)	3666 (5)	734 (3)	−234 (4)	2.2
O(2)	2469 (5)	120 (3)	3240 (4)	2.5
O(3W)	−183 (5)	1288 (3)	2724 (4)	2.4
O(4W)	3563 (5)	1701 (3)	2466 (4)	2.8
O(5W)	781 (6)	1682 (3)	−206 (5)	3.6
O(6W)	532 (6)	−173 (2)	616 (4)	2.8
O(7)	3553 (5)	2159 (3)	5413 (4)	2.3
O(8)	1464 (6)	1626 (2)	6893 (4)	2.6
O(9)	705 (6)	2353 (3)	4740 (5)	3.0
O(10)	1858 (5)	3042 (2)	6797 (4)	2.6
N	5431 (6)	1386 (3)	−2390 (5)	2.1
C(1)	3525 (7)	373 (3)	−1423 (6)	1.8
C(2)	4805 (7)	545 (3)	−2526 (6)	2.0
C(3)	6338 (9)	21 (4)	−2295 (9)	3.8
C(4)	7710 (9)	588 (5)	−1870 (9)	4.2
C(5)	7242 (8)	1353 (5)	−2595 (8)	3.8

(b) Fixed positional ($\times 10^3$) and isotropic thermal parameters (Å^2) of the H atoms

	x	y	z	B_{iso}
H(1)	425	46	−351	2.1
H(2)	616	−38	−152	3.6
H(3)	659	−27	−322	3.6
H(4)	778	65	−78	4.4
H(5)	880	38	−219	4.4
H(6)	784	183	−215	3.9
H(7)	751	135	−368	3.9
H(8)	486	174	−315	2.1
H(9)	520	160	−141	2.1
H(10)	0	161	357	2.4
H(11)	−88	160	232	2.4
H(12)	354	180	336	2.7
H(13)	464	161	214	2.7
H(14)	103	170	−114	2.6
H(15)	500	286	500	2.6
H(16)	75	65	607	3.0
H(17)	79	23	474	3.0

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

Mn—O(1)	2·198 (4)	O(2)—Mn—O(6W)	82·1 (2)
Mn—O(2)	2·200 (4)	O(3W)—Mn—O(4W)	93·1 (2)
Mn—O(3W)	2·163 (4)	O(3W)—Mn—O(5W)	85·6 (2)
Mn—O(4W)	2·182 (4)	O(3W)—Mn—O(6W)	94·6 (2)
Mn—O(5W)	2·130 (5)	O(4W)—Mn—O(5W)	99·5 (2)
Mn—O(6W)	2·194 (4)	O(5W)—Mn—O(6W)	96·5 (2)
S—O(7)	1·503 (4)	C(1)—O(1)—Mn	128·0 (4)
S—O(8)	1·466 (4)	C(1)—O(2^{ii})—Mn^{ii}	138·7 (4)
S—O(9)	1·452 (5)	O(7)—S—O(8)	107·7 (2)
S—O(10)	1·469 (4)	O(7)—S—O(9)	109·2 (2)
C(1)—O(1)	1·256 (7)	O(7)—S—O(10)	109·4 (2)
C(1)—O(2^{ii})	1·229 (7)	O(8)—S—O(9)	110·4 (3)
C(1)—C(2)	1·512 (8)	O(8)—S—O(10)	110·4 (2)
C(2)—C(3)	1·540 (9)	O(9)—S—O(10)	109·7 (2)
C(3)—C(4)	1·514 (10)	O(1)—C(1)—O(2^{ii})	126·2 (5)
C(4)—C(5)	1·496 (11)	O(1)—C(1)—C(2)	116·7 (5)
C(5)—N	1·498 (8)	O(2^{ii})—C(1)—C(2)	117·0 (5)
N—C(2)	1·511 (7)	C(1)—C(2)—C(3)	112·0 (5)
O(1)—Mn—O(2)	107·1 (2)	C(1)—C(2)—N	111·3 (4)
O(1)—Mn—O(4W)	85·7 (2)	C(2)—C(3)—C(4)	105·3 (6)
O(1)—Mn—O(5W)	82·2 (2)	C(3)—C(4)—C(5)	104·6 (6)
O(1)—Mn—O(6W)	90·0 (1)	C(4)—C(5)—N	102·3 (6)
O(2)—Mn—O(3W)	85·2 (2)	C(2)—N—C(5)	106·7 (5)
O(2)—Mn—O(4W)	83·1 (2)	N—C(2)—C(3)	104·8 (5)

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

Symmetry code: None x, y, z; (i) $x, -y, \frac{1}{2} + z$; (ii) $x, -y, -\frac{1}{2} + z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (v) $x, y, -1 + z$.

D—H⋯A	D⋯A	H⋯A	∠D—H⋯A
O(3W)—H(10)⋯O(9)	2·667 (6)	1·74	162·3
O(3W)—H(11)⋯O(10^{iii})	2·774 (6)	1·99	153·6
O(4W)—H(12)⋯O(7)	2·826 (6)	1·99	173·5
O(4W)—H(13)⋯O(10^{iv})	2·815 (6)	1·94	151·7
O(5W)—H(14)⋯O(8^v)	2·753 (6)	1·86	173·8
O(5W)—H(15)⋯O(7^{iii})	2·743 (6)	1·72	174·2
O(6W)—H(16)⋯O(8^{ii})	2·812 (6)	1·90	172·7
O(6W)—H(17)⋯O(2)	2·887 (6)	1·99	148·5
N—H(8)⋯O(7^v)	2·817 (6)	1·82	166·5
N—H(9)⋯O(9^{iv})	2·898 (6)	2·09	136·7

Table 4. *Least-squares planes*

Values are given in the following order: atoms defining the plane, equation of plane, deviations of atoms from the plane (Å) with e.s.d.'s in parentheses.

Plane 1: O(1), O(2), O(3W), O(5W)

$$-0.5463X - 0.7359Y - 0.3999Z + 2.4257 = 0$$

O(1) −0·038 (4), O(2) 0·038 (4), O(3W) −0·046 (4),
O(5W) 0·063 (5), Mn 0·015 (1)

Plane 2: O(1), O(2^{ii}), C(1), C(2)

$$-0.5639X + 0.7334Y - 0.3796Z + 0.6992 = 0$$

O(1) −0·003 (4), O(2^{ii}) −0·003 (4), C(1) 0·009 (5),
C(2) −0·002 (5), N 0·704 (5), Mn 0·519 (1), Mn^{ii} −0·049 (1)

Plane 3: N, C(2), C(3), C(4)

$$0.2452X + 0.0273Y - 0.9691Z - 3.2917 = 0$$

O(1) −2·313 (4), O(2^{ii}) −1·217 (4), C(1) −1·287 (5),
C(2) −0·029 (5), C(3) 0·047 (8), C(4) −0·036 (8), C(5) 0·559 (7),
N 0·013 (5)

Plane 4: N, C(2), C(5)

$$-0.1205X + 0.1300Y - 0.9842Z - 1.9278 = 0$$

O(1) −1·916 (4), O(2^{ii}) −0·608 (4), C(1) −0·908 (5), C(2) 0,
C(3) −0·474 (8), C(4) −0·868 (8), C(5) 0, N 0

Plane 5: N, C(2), C(3), C(5)

$$-0.0103X - 0.0266Y - 0.9996Z - 2.1619 = 0$$

O(1) −2·010 (4), O(2^{ii}) −0·557 (4), C(1) −0·899 (5),
C(2) 0·099 (5), C(3) −0·102 (8), C(4) −0·531 (8), C(5) 0·106 (7),
N −0·069 (5)

Discussion. The crystals under investigation are built from alternate layers of D- and L-proline molecules and [Mn(H$_2$O)$_6^{2+}$] ions stacked in the z direction. The proline molecules link the closest Mn ions (Mn⋯Mn = 5·52 Å) by a carboxyl bridge system. Fig. 1 shows a fragment of the structure projected along c. The adjacent polymer chains [Mn(DL-proline)(H$_2$O)$_4$]$_n^{2+}$ are linked by a network of hydrogen bonds, O—H⋯O and N—H⋯O, in which all the H atoms directed towards the SO$_4^{2-}$ ions participate. Table 3 summarizes lengths and angles of the hydrogen bonds. One of these, O(6)—H(17)⋯O(2), seems to be uncertain since both the donor and acceptor belong to one octahedron although the parameters support its presence. The Mn atom exhibits the geometry of a slightly distorted octahedron. Mn—O(proline) bonds (average 2·199 ± 0·001 Å) are longer than Mn—H$_2$O bonds [2·130 (5)–2·194 (4) Å]. The most distorted angle of the octahedron is O(1)—Mn—O(2) of 107·1 (2)°. The least-squares planes are presented in Table 4.
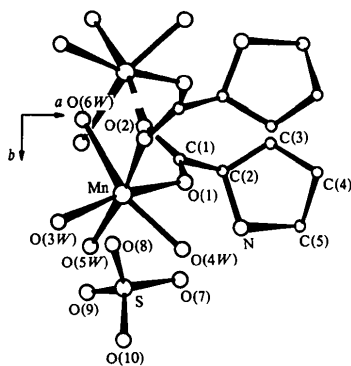

Fig. 1. Projection along c of part of the unit cell. H atoms have been omitted for clarity.

The proline molecules occur in the form of zwitterions. The bridging carboxyl groups form *syn* [O(1)—Mn], *anti* [O(2)—Mn] bonds. Bond lengths and angles in the proline molecule do not differ from the corresponding values found in the absence of any anomalies occurring in the pyrrolidine ring (Ashida & Kakudo, 1974). The most deflected atom from the best plane of the pyrrolidine ring is C(4) which is situated on the same side as C(1). The torsion angles in the proline molecule are listed in Table 5.

Table 5. *Torsion angles* (°)

Numbers in parentheses are e.s.d.'s.

O(1)–C(1)–C(2)–N	−31·1 (6)
O(2^{ii})–C(1)–C(2)–N	150·5 (6)
O(1)–C(1)–C(2)–C(3)	85·8 (6)
O(2^{ii})–C(1)–C(2)–C(3)	−92·5 (6)
C(1)–C(2)–C(3)–C(4)	−114·5 (7)
C(2)–C(3)–C(4)–C(5)	−29·0 (7)
C(3)–C(4)–C(5)–N	40·1 (7)
C(4)–C(5)–N–C(2)	−36·5 (7)
C(5)–N–C(2)–C(3)	18·5 (5)
N–C(2)–C(3)–C(4)	6·4 (6)

Bond lengths and angles in the tetrahedral SO_4^{2-} ion are normal.

A common property of polymeric Mn^{2+} complexes with α-amino acids with single carboxyl bridges (Głowiak & Ciunik, 1978; Ciunik & Głowiak, 1980) is the formation of *syn,anti* bonds by the bridging carboxyl groups. Only in one case were additional *anti,anti* bonds found (Głowiak & Ciunik, 1978).

$Mn\cdots Mn$ distances between the bridged atoms range from 5·36 to 5·52 Å. Distances of the Mn atoms from the $C^{\alpha}COO$ planes do not exceed 0·52 Å. In all cases the *syn* bonds are formed by the O atoms of carboxyl groups located closer to the N atoms (NH_3^+ or NH_2^+ groups). The C—O—Mn(*syn*) angles range from 126 to 131° (average 128·6 ± 2·7), C—O—Mn(*anti*) angles from 139 to 143° (average 140·6 ± 2·4°).

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The Symmetrical-Facial Isomer of Ammine(diethylenetriamine)dinitrocobalt(III) Chloride, s-fac-[Co(dien)(NH₃)(NO₂)₂]Cl

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Abstract. [Co($C_4H_{13}N_3$)(NH_3)(NO_2)$_2$]Cl, monoclinic, $P2_1/n$, $Z = 4$, $a = 7\cdot993$ (2), $b = 10\cdot893$ (2), $c = 12\cdot969$ (2) Å, $\beta = 102\cdot49$ (2)°, $V = 1102\cdot4$ (4) Å^3, $D_c = 1\cdot847$ Mg m^{-3}, $M_r = 306\cdot60$, μ(Mo $K\alpha$) = $1\cdot81$ mm^{-1}. Final $R_1 = 3\cdot9\%$ for 1821 data with $F_o > \sigma(F_o)$. The Co^{III} ion has a slightly distorted octahedral geometry; the dien ligand occupies facial sites with Co—N(4) = 1·985 (3), Co—N(5) = 1·950 (3), and Co—N(6) = 1·962 (3) Å. The Co—NH$_3$ bond length is Co—N(1) = 1·957 (3) Å, while Co—NO$_2$ linkages are Co—N(2) = 1·929 (3) Å and Co—N(3) = 1·932 (3) Å.

Introduction. There are five possible isomers of the [Co(dien)(NH$_3$)(NO$_2$)$_2$]$^+$ cation. The *trans* isomer (dien in meridional sites and NO$_2$ ligands mutually *trans*) is that whose synthesis in ~90% yield has been described in detail (Crayton, 1963). We are presently attempting to assign the stereochemistry to four isomers found in the filtrate from Crayton's procedure.

The *s-fac* (symmetrical facial) cation under study was isolated as the second of four bands from elution of the above filtrate with 0·15 *M* aqueous NaCl from an ion-exchange column (AG 50Wx8, 200–300 mesh, Na-type).

Cell dimensions and intensities were measured at 297 K with a Syntex $P2_1$ diffractometer (Churchill, Lashewycz & Rotella, 1977). The systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/n$. Data with $3\cdot5° < 2\theta < 50°$ (Mo $K\alpha$ radiation, $\lambda = 0\cdot71073$ Å) were collected from an orange crystal of size 0·25 × 0·30 × 0·30 mm using a θ–2θ scan and the structure was solved *via* Patterson and difference-Fourier techniques. Full-matrix least-squares refinement led to convergence with $R_1 = 3\cdot9\%$ and $R_2 = 3\cdot5\%$ for 1821 reflections with $F_o > \sigma(F_o)$. [$R_1 = 4\cdot4\%$ and $R_2 = 3\cdot5\%$ for all 1954 unique data, none being rejected.] The strongest feature on a final difference-Fourier map was a peak of height 0·53 e Å^{-3}