

The Crystal and Molecular Structure of Bis(α -aminomethylmethylphosphinic acid)-manganese(II) Dichloride Dihydrate

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The structure of $\text{MnCl}_2(\text{C}_2\text{H}_8\text{NO}_2\text{P})_2 \cdot 2\text{H}_2\text{O}$ has been determined from Cu $K\alpha$ diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with $a = 6.045$ (1), $b = 7.302$ (1), $c = 17.044$ (3) Å, $\beta = 104.53$ (1)°, $Z = 2$. The structure was solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.044$ for 919 counter reflexions for which $F > 3.92 \sigma(F)$. The Mn atom lies on a centre of symmetry and is surrounded octahedrally by two Cl and four O atoms: two of the latter are from α -aminomethylmethylphosphinic acid ligands, the other two from the water molecules. Mn–Cl, Mn–O and Mn–O(*W*) lengths are 2.569 (2), 2.141 (4) and 2.195 (4) Å respectively. The ligand exists as a zwitterion.

Introduction

Amino acids play a vital role in many body functions and readily coordinate to certain transition metals forming a wide variety of complexes. Although α -aminophosphinic acids may be considered to be P analogues of amino acids, the origin and function of these compounds in the human body have not been determined. In transition-metal chemistry only the interactions of aminoalkylphosphonic acids with labile metal ions have been investigated (Wozniak, Nicole, Tridot & Verbert, 1972; Rajan, Murase & Martell, 1969). A study of the metal complexes of an aminomethylmethylphosphinic acid has been undertaken to determine the influence of metal ions on the conformation of the acid and to provide structural data for the elucidation of their role in biological systems.

Experimental

The crystals were obtained from an aqueous solution of α -aminomethylmethylphosphinic acid and manganese chloride in a stoichiometric ratio. Weissenberg photographs showed the crystals to be monoclinic. The systematic absences ($h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$) uniquely determine the space group as $P2_1/c$. The cell parameters were determined by least-squares refinement of the setting angles of 15 reflexions given by the automatic centring program [$\lambda(\text{Cu } K\alpha) = 1.5418$ Å]. The density was measured by flotation in a mixture of $\text{C}_2\text{H}_4\text{Br}_2$ and CHCl_3 .

Crystal data

$\text{MnCl}_2(\text{C}_2\text{H}_8\text{NO}_2\text{P})_2 \cdot 2\text{H}_2\text{O}$, monoclinic $a = 6.045$ (1), $b = 7.302$ (1), $c = 17.044$ (3) Å, $\beta = 104.53$ (1)°;

space group $P2_1/c$; $Z = 2$, $M_r = 380$, $D_r = 1.73$, $D_c = 1.733$ g cm $^{-3}$.

All measurements for a crystal $0.2 \times 0.2 \times 0.25$ mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and a graphite monochromator. Intensities of 984 independent reflexions were measured up to $2\theta = 114^\circ$ with the variable θ - 2θ scan technique. The scan rate varied from 2.0 to 20.0° min $^{-1}$, depending on the intensity. After each group of 15 reflexions, the intensity of a standard was measured and no significant change observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure determination

The coordinates of the Mn atom were derived from a Patterson synthesis. The positions of the other non-hydrogen atoms were found from a Fourier synthesis. Full-matrix least-squares refinement with isotropic thermal parameters for all non hydrogen atoms reduced $R_1 = (\sum |F_o| - |F_c|) / \sum |F_o|$ to 0.09. Full-matrix refinement with anisotropic thermal parameters yielded a final $R_1 = 0.054$. A difference synthesis revealed the positions of all H atoms. In subsequent full-matrix refinement the coordinates of the H atoms and their isotropic thermal factor ($B = 4.5$ Å 2) were not refined. The final $R_1 = 0.044$ and the final $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.053$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Scattering factors for neutral atoms corrected for anomalous dispersion (Templeton, 1962) were taken from Cromer & Waber (1974). All calculations were performed with the Syntex XTL system (Nova 1200 computer and additional external disc memory). The

Table 1. *Positional parameters with estimated standard deviations in parentheses*

	x	y	z
Mn	0	0	0
Cl	-0.1514 (3)	0.0577 (2)	0.1258 (1)
P	-0.2274 (2)	0.3608 (2)	0.1231 (1)
O(1)	-0.1389 (7)	0.2608 (6)	-0.0442 (2)
O(2)	-0.3741 (7)	0.5244 (6)	-0.1167 (3)
O(W)	0.3213 (7)	0.1444 (6)	0.0529 (3)
N	0.2097 (8)	0.4863 (10)	0.0826 (3)
C(1)	-0.0251 (10)	0.4392 (9)	-0.1548 (4)
C(2)	-0.3736 (10)	0.2137 (10)	-0.2024 (4)
H(1)	0.079	0.338	0.186
H(2)	-0.015	0.549	-0.191
H(3)	-0.400	0.300	-0.250
H(4)	-0.300	0.099	-0.250
H(5)	-0.500	0.200	-0.200
H(6)	0.182	0.600	-0.055
H(7)	0.229	0.384	-0.041
H(8)	0.357	0.502	-0.099
H(9)	0.350	0.250	0.082
H(10)	0.471	0.068	0.062

final parameters are listed in Table 1. Table 2 gives the bond distances and angles.*

Discussion

The complex is centrosymmetric and the Mn atom is coordinated to two O atoms from the phosphinic groups, two water molecules and two Cl atoms (Fig. 1). The coordination forms a slightly distorted *trans, trans, trans* octahedron. Bond distances and angles in the coordination polyhedron agree well with those

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32560 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

found in $MnCl_2(gly)_2$ (Narayanan & Venkataraman, 1975) and $MnCl_2(gly)_2(H_2O)_2$ (Głowiak & Sawka-Dobrowolska, 1976). This type of coordination is rarely encountered in the complexes of amino acids. Fig. 2(a-e) shows five types of metal-O(carboxyl) interactions which can be distinguished in amino-acid complexes. Transition metals coordinate to the amino acids most frequently through the O atom from the carboxyl group and through the N atom from the amino group. The following are exceptions: $AgNO_3(gly)$ (Rao & Viswamitra, 1972), $MnBr_2(gly)(H_2O)_2$ (Głowiak & Ciunik, 1977), $MnCl_2(gly)_2(H_2O)_2$ (Głowiak & Sawka-Dobrowolska, 1976), $MnCl_2(gly)_2$

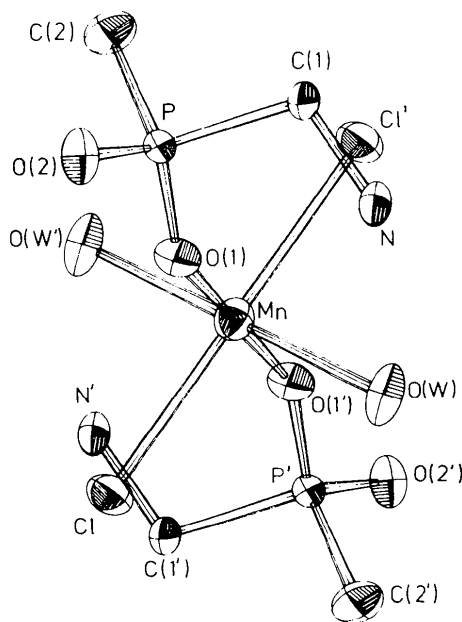


Fig. 1. The coordination geometry about the Mn atom, viewed along *b*.

Table 2. *Interatomic distances (Å) and bond angles (°)*

Mn-Cl	2.569 (2)	Mn-O(1)	2.141 (4)	Mn-O(W)	2.195 (4)
P-O(1)	1.505 (4)	P-O(2)	1.507 (4)	P-C(2)	1.778 (7)
P-C(1)	1.834 (6)	C(1)-N	1.479 (8)	O(1)-O(2)	2.523 (6)
O(1)-C(1)	2.678 (7)	O(1)-C(2)	2.735 (7)	C(1)-H(1)	1.01
C(1)-H(2)	1.00*	C(2)-H(3)	1.01	C(2)-H(4)	0.98
C(2)-H(5)	0.78	N-H(6)	0.99	N-H(7)	1.01
N-H(8)	1.01	O(W)-H(9)	0.92	O(W)-H(10)	1.04
O(1)-Mn-Cl	92.5 (1)	O(1)-Mn-Cl'	87.5 (1)	O(W)-Mn-Cl	92.5 (1)
O(W)-Mn-Cl'	87.5 (1)	O(W)-Mn-O(1)	93.1 (2)	O(W)-Mn-O(1')	86.9 (2)
N-C(1)-P	109.7 (4)	O(1)-P-O(2)	113.8 (2)	C(1)-P-O(1)	106.2 (3)
C(1)-P-O(2)	108.8 (3)	C(2)-P-O(1)	112.5 (3)	C(2)-P-O(2)	110.1 (3)
C(2)-P-C(1)	104.8 (3)	P-C(2)-H(3)	100.5	P-C(2)-H(4)	118.8
P-C(2)-H(5)	110.1	H(3)-C(2)-H(4)	112.6	H(4)-C(2)-H(5)	113.1
H(5)-C(2)-H(3)	99.4	P-C(1)-H(1)	109.4	P-C(1)-H(2)	110.0
H(1)-C(1)-H(2)	108.4	C(1)-N-H(6)	114.1	C(1)-N-H(7)	109.8
C(1)-N-H(8)	109.7	H(6)-N-H(7)	107.0	H(6)-N-H(8)	107.5
H(7)-N-H(8)	108.7	H(9)-O(W)-H(10)	109.3		

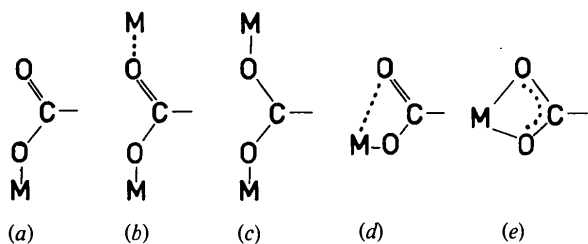
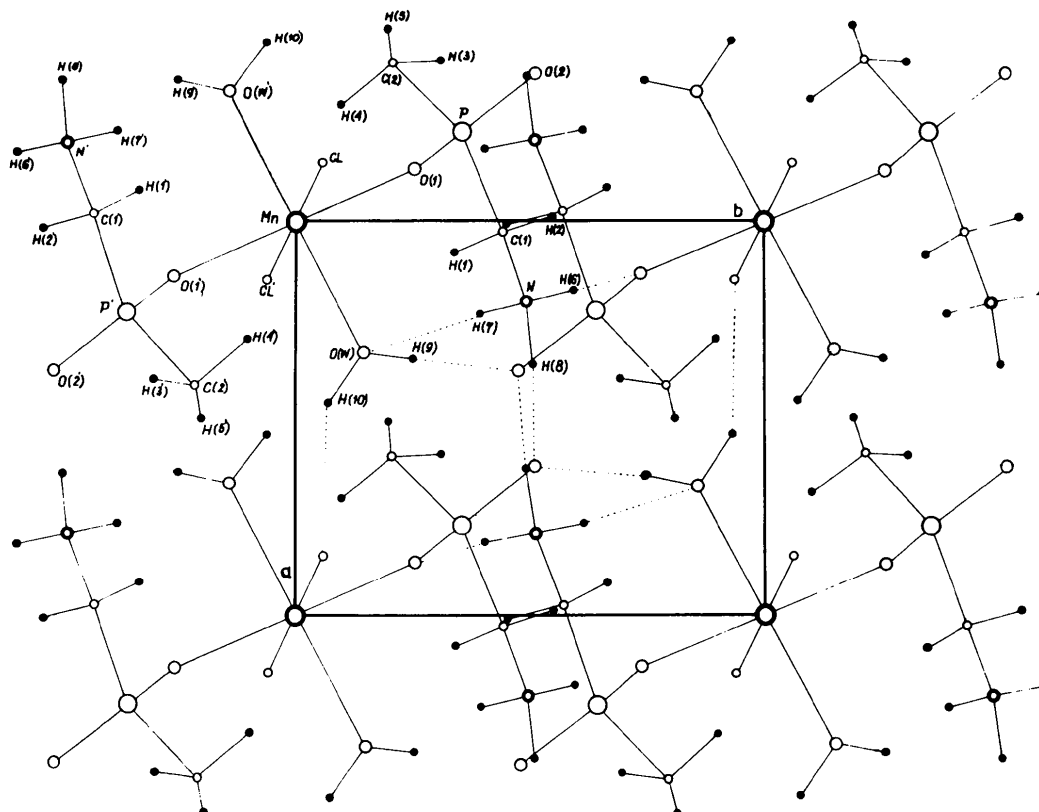


Fig. 2. O(carboxyl)-metal interactions (Freeman, 1973).

(Narayanan & Venkataraman, 1975). In these compounds the amino acid appears as a zwitterion. The type of coordination in these compounds is similar to that occurring in the compounds of amino acids with non-transition metals. In $\text{AgNO}_3(\text{gly})$ the coordination of the Ag atoms is approximately digonal. The carboxyl groups form a bridge between the two Ag atoms. This compound may be considered a dimer with a direct metal-metal bond. In $\text{MnBr}_2(\text{gly})(\text{H}_2\text{O})_2$ and $\text{MnCl}_2(\text{gly})_2$ the carboxyl O atoms are bonded to

Table 3. Hydrogen-bond lengths (\AA) and angles ($^\circ$) and angles around N ($^\circ$)

$D-H\cdots A$	Position of acceptor atom	$D\cdots A$	$H\cdots A$	$\angle D-H\cdots A$
$N-H(6)\cdots O(1')$	$-x, 1-y, -z$	2.955 (7)	2.05	151.9
$N-H(7)\cdots O(W)$	x, y, z	3.352 (7)	2.35	172.7
$N-H(8)\cdots O(2)$	$1-x, y, z$	2.735 (7)	1.74	174.4
$O(W)-H(9)\cdots O(2')$	$-x, 1-y, -z$	2.638 (6)	1.74	165.6
$O(W)-H(10)\cdots Cl$	$1-x, y, z$	3.180 (5)	2.27	145.2
$C(1)-N\cdots O(W)$	112.4	$O(W)\cdots N\cdots O(2)$	100.6	
$C(1)-N\cdots O(1')$	122.4	$O(W)\cdots N\cdots O(1')$	90.3	
$C(1)-N\cdots O(2)$	112.9	$O(1')\cdots N\cdots O(2)$	113.7	

Fig. 3. Projection of the structure down c . For clarity only half the molecules are shown. Hydrogen bonds are represented by broken lines.

different Mn atoms, each O atom forming only one coordination bond with the Mn atom. In contrast to $AgNO_3(gly)$ these complexes have a chain structure. The only known example where the carboxyl group is linked to the transition metal through one O atom only is $[Fe(OH_2)_6][Fe(gly)_2(OH_2)_4](SO_4)_2$ (Lindqvist & Rosenstein, 1960). In this compound the glycine ligands in the octahedral $[Fe(gly)_2(OH_2)_4]^{2+}$ ions are *trans* to each other. Lindqvist & Rosenstein maintain that the coordination of the Fe atom is still an open question, but we consider that this type of coordination is possible since it has been recently found in $MnCl_2(gly)_2(H_2O)_2$, which has a similar *trans,trans,trans* structure to that of the present complex.

The bond lengths and angles in the ligand are similar to those found in free α -aminomethylmethylphosphinic acid (Głowiak & Sawka-Dobrowolska, 1977), α -aminomethylphosphonic acid (Darriet, Darriet, Cassaigne & Neuzil, 1975) and 2-aminoethylphosphonic acid (Okaya, 1966). The P—O lengths of 1.505 (4) and 1.507 (4) Å are equal within experimental error. The angles at the P atom vary from 104.8 [C(2)—P—C(1)] to 112.5° [C(2)—P—O(1)]. In free α -aminomethylmethylphosphinic acid, C(2), P, C(1) and N lie practically in one plane. In the present compound this plane is given by $(-0.4960)X + (0.7958)Y + (-0.3474)Z - (-3.1394) = 0$. Distances of the C(2), P, C(1) and N atoms from the plane are 0.1721, -0.0067, -0.2618 and 0.1581 Å respectively.

The three H atoms of the NH_3^+ group are involved in intermolecular hydrogen bonds (Table 3). As shown in Fig. 3, the N atom has three nearest neighbours [O(1), O(2) and O(W)] for favourable hydrogen bonds at distances of 2.955, 2.735 and 3.352 Å respectively. A distorted tetrahedron is formed around the N atom by these three O atoms and C(1). The angles involving C(1) are greater than the usual tetrahedral angle; two of the three angles between hydrogen bonds are larger than ideal and one is smaller (Table 3). We include in the hydrogen-bond list $NH \cdots O(W)$, 2.35 Å, which is

less than the sum of the van der Waals radii for H and O (Pauling, 1960). Furthermore, the position of O(W) is compatible with tetrahedral bonding geometry about N (Table 3); the $NH \cdots O(W)$ angle is 172.7°. O(W) of the water molecule is coordinated to Mn and also forms two hydrogen bonds with O(2) (2.638 Å) and with Cl (3.180 Å). Three H positions have been located around N and this, coupled with the observation that the two P—O lengths are very nearly equal, establishes that in this complex the ligand occurs in the zwitterionic form.

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