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The Structure of *catena*-Octakis-μ-(β-alanine)-trimanganese(II) Hexaperchlorate Dihydrate

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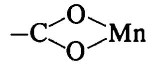
Abstract

$[Mn_3(C_3H_7NO_2)_8](ClO_4)_6.2H_2O$ is orthorhombic, space group *Pbca*, with $a = 23{\cdot}455$ (5), $b = 21{\cdot}159$ (5), $c = 11{\cdot}187$ (3) Å, $Z = 4$. The structure was refined with 1919 Cu $K\alpha$ diffractometer data to $R_1 = 0{\cdot}082$. The Mn atoms form infinite, almost linear chains along **c**. The molecules of β-alanine link these atoms by *syn, syn* and *syn,anti* carboxyl bridges. One molecule of β-alanine is tridentate, forming  $-C\langle^{O}_{O}\rangle Mn(2)$ chelate bonds and a third bond with Mn(1).

Introduction

Previous crystallographic studies of Mn^{2+} complexes with carboxylic acids (Kay, Almodovar & Kaplan, 1968; Tranqui, Burlet, Filhol & Thomas, 1977; Lis, 1977; Carrell & Glusker, 1973; Schultz, 1974; Karipides & Reed, 1976) and amino acids (Narayanan & Venkataraman, 1975; Głowiak & Ciunik, 1978; Ciunik & Głowiak, 1978, 1980*a*,*b*) showed that a typical feature is their polymeric nature. In polymeric Mn^{2+} amino acid complexes the amino acid molecules occur as zwitterions and are bidentate, linking adjacent Mn^{2+} ions. Infinite chains with single (Mn—Mn distance > 5·3 Å) or double (Mn—Mn distance from 4·8 to 5·0 Å) carboxyl bridges are thereby formed. The title compound also is a polymer but one of the amino acid molecules is tridentate and the Mn—Mn distances are shorter than those found previously.

Experimental

Colourless crystals were grown from an aqueous solution of β-alanine and manganous perchlorate (2 : 1) at room temperature. Preliminary Weissenberg photographs indicated an orthorhombic lattice with systematic absences $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$, consistent with the space group *Pbca*. All measurements for a crystal 0·08 × 0·12 × 0·25 mm 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 from the setting angles of 15 reflections given by the automatic centring program. Intensities of 2865 independent reflections were measured up to $2\theta = 135°$ with the variable θ–2θ scan technique. The scan rate varied from 2·0 to 20·0° min^{-1} depending on the intensity. 1919 reflections 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 crystal data are presented in Table 1.

Table 1. *Crystal data*

$C_{24}H_{56}Mn_3N_8O_{16}^{6+}.6ClO_4^-.2H_2O$
$a = 23{\cdot}455$ (5) Å
$b = 21{\cdot}159$ (5)
$c = 11{\cdot}187$ (3)
$V = 5551{\cdot}9$ Å^3
$M_r = 1510{\cdot}45$

Pbca
$D_m = 1{\cdot}82$ Mg m^{-3}
$D_c = 1{\cdot}81$
μ(Cu $K\alpha$) = 9·50 mm^{-1}
$\lambda = 1{\cdot}5418$ Å

The heavy-atom method was employed for the phase determination. A satisfactory solution of the Patterson synthesis was $x \sim 0{\cdot}03$, $y \sim 0$, $z = 0{\cdot}32$ and $x = 0$, $y = 0$, $z = 0$ for two Mn atoms. All non-H atoms were found from Fourier and difference syntheses. Full-matrix least-squares refinement first with isotropic then anisotropic thermal parameters gave R_1 $(= \sum ||F_o| - |F_c|| / \sum |F_o|) = 0{\cdot}115$ and 0·085, respectively. At this stage, sixteen H atoms from β-alanine molecules with calculated positions (C—H = 1·0 Å and $B_{iso} = 3{\cdot}0$ Å^2) were included but not refined. Refinement reduced R_1 to 0·082 and R_2 $[= \sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ to 0·067.* A final difference synthesis did not show the H atoms from the NH_3 group and H_2O molecule. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F)$. Scattering factors for neutral atoms were

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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 35244 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Mn(1)	0	0	0
Mn(2)	−357 (1)	−45 (1)	−3202 (2)
Cl(1)	2522 (2)	−6 (3)	4494 (4)
Cl(2)	2521 (2)	2600 (2)	4071 (4)
Cl(3)	4767 (2)	2547 (2)	3876 (5)
O(*W*)	726 (5)	2198 (5)	3486 (11)
O(11)	3086 (6)	−186 (6)	4665 (16)
O(21)	2474 (5)	676 (5)	4699 (11)
O(31)	2382 (10)	−92 (8)	3299 (13)
O(41)	2138 (6)	−329 (6)	5254 (17)
O(12)	2191 (6)	2340 (6)	4997 (12)
O(22)	2148 (6)	2844 (6)	3190 (13)
O(32)	2866 (6)	2123 (7)	3577 (15)
O(42)	2873 (7)	3076 (7)	4492 (13)
O(13)	4565 (7)	2919 (7)	2966 (19)
O(23)	5359 (7)	2743 (6)	4066 (13)
O(33)	4802 (7)	1936 (6)	3482 (18)
O(43)	4405 (10)	2579 (8)	4765 (22)
β-Alanine, molecule *A*			
O(1)	349 (4)	−563 (4)	1502 (8)
O(2)	1032 (5)	−720 (5)	2844 (9)
C(1)	832 (7)	−819 (7)	1777 (16)
C(2)	1124 (7)	−1235 (8)	946 (15)
C(3)	1605 (8)	−1616 (7)	1492 (15)
N(1)	2087 (5)	−1212 (6)	1900 (13)
β-Alanine, molecule *B*			
O(3)	606 (4)	771 (5)	220 (9)
O(4)	878 (5)	649 (5)	2135 (11)
C(4)	905 (7)	896 (7)	1083 (17)
C(5)	1369 (7)	1424 (8)	974 (17)
C(6)	1860 (7)	1348 (7)	1881 (20)
N(2)	1679 (5)	1364 (6)	3149 (12)
β-Alanine, molecule *C*			
O(5)	615 (5)	−402 (5)	−1270 (10)
O(6)	360 (5)	−650 (5)	−3115 (10)
C(7)	699 (8)	−657 (7)	−2244 (17)
C(8)	1268 (7)	−980 (8)	−2430 (17)
C(9)	1270 (7)	−1427 (9)	−3499 (16)
N(3)	1132 (6)	−1128 (6)	−4700 (11)
β-Alanine, molecule *D*			
O(7)	226 (5)	673 (4)	−3921 (9)
O(8)	829 (5)	409 (5)	−5362 (10)
C(10)	709 (7)	673 (7)	−4387 (16)
C(11)	1177 (7)	1023 (8)	−3768 (17)
C(12)	1134 (8)	1061 (8)	−2416 (17)
N(4)	636 (5)	1392 (6)	−1953 (12)
H(1)	131	−98	28
H(2)	84	−153	56
H(3)	174	−196	91
H(4)	144	−187	221
H(5)	118	186	114
H(6)	152	146	12
H(7)	216	169	170
H(8)	205	93	166
H(9)	139	−121	−167
H(10)	159	−65	−259
H(11)	97	−178	−331
H(12)	165	−167	−353
H(13)	119	147	−405
H(14)	156	82	−398
H(15)	151	126	−209
H(16)	115	60	−209

taken from Cromer & Waber (1974). All calculations were performed with the Syntex *XTL* structure determination system (Nova 1200 computer and additional external disc memory).

Results and discussion

The crystal structure, which is defined by the cell dimensions, the positional parameters of Table 2 and the space-group symmetry, consists of infinite, almost linear chains of Mn^{2+} ions parallel to *z*. The molecules of *β*-alanine situated along these chains form layers which are stacked in the *y* direction. Each layer consists of parallel polymeric chains of formula $[Mn_{1.5}(\beta\text{-ala})_4]_n^{3n+}$. A fragment of a single chain is presented in Fig. 1.

The ClO_4^- ions and H_2O molecules located between adjacent polymer chains are acceptors of most hydrogen bonds in the crystal, in which the NH_3 groups of the *β*-alanine molecules and the water molecule are donors. Since in the last difference synthesis no H atoms were located, the lengths and angles summarized in Table 3 correspond to probable hydrogen bonds.

The Mn atoms have an octahedral coordination forming six bonds each with the O atoms of the *β*-alanine carboxyl groups. The coordination polyhedron around Mn(1) formed by the O atoms from six *β*-alanine molecules is almost an ideal octahedron. The average length of Mn(1)—O is 2·20 ± 0·02 Å (e.s.d.'s for Mn—O bonds are 0·01 Å) and deviations of valency angles from 90° range from 2 to 4°. The lengths of all bonds and angles in the crystal are summarized in Tables 4 and 5. The coordination octahedron around Mn(2) formed by the atoms from five *β*-alanine molecules is very distorted. The lengths of Mn(2)—O range from 2·10 (1) to 2·30 (1) Å and deviations of valency angles from 90° are considerable (32·3° maximum). The best planes are presented in Table 6

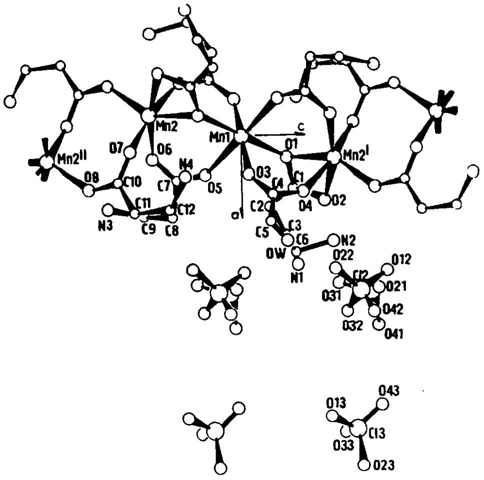

Fig. 1. A fragment of the structure viewed down **b**.

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

Symmetry code superscript: none x,y,z; (i) $-x,-y,-z$; (ii) $-x, -y, -1-z$; (iii) $x, y, 1+z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (v) $-\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (vii) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (viii) $x, y, -1+z$; (ix) $\frac{1}{2}-x, -\frac{1}{2}+y, -1+z$; (x) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (xi) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$.

Donor	Acceptor	$D\cdots A$	C—N$\cdots A$
O(*W*)	O(23^{iv})	2·87 (2)	
O(*W*)	O(23^{v})	3·20 (2)	
O(*W*)	O(33^{v})	3·14 (2)	
C(3)—N(1)	O(21^{vi})	2·90 (2)	103·5 (9)
C(3)—N(1)	O(31)	2·92 (2)	144·0 (10)
C(3)—N(1)	O(22^{vii})	3·05 (2)	102·5 (9)
C(6)—N(2)	O(*W*)	2·88 (2)	111·2 (10)
C(6)—N(2)	O(21)	2·93 (2)	112·0 (10)
C(6)—N(2)	O(12)	3·16 (2)	122·1 (10)
C(9)—N(3)	O(41^{viii})	2·90 (2)	94·9 (9)
C(9)—N(3)	O(42^{ix})	3·02 (2)	82·4 (9)
C(9)—N(3)	O(43^{ix})	3·07 (2)	83·6 (9)
C(12)—N(4)	O(W^{x})	3·03 (2)	118·3 (10)
C(12)—N(4)	O(3)	2·76 (2)	96·0 (10)
C(12)—N(4)	O(1^{i})	2·95 (2)	113·8 (10)
C(12)—N(4)	O(13^{xi})	3·12 (2)	137·8 (10)
C(12)—N(4)	O(23^{xi})	3·06 (2)	100·5 (10)

Acceptor(1)	Donor	Acceptor(2)	$A(1)\cdots D\cdots A(2)$
O(23^{iv})	O(*W*)	O(23^{v})	139·0 (6)
O(23^{iv})	O(*W*)	O(33^{v})	118·0 (6)
O(23^{iv})	O(*W*)	O(33^{v})	41·5 (4)
O(21)	N(1)	O(31)	93·1 (6)
O(21)	N(1)	O(22^{vii})	116·7 (6)
O(31)	N(1)	O(22^{vii})	98·0 (6)
O(*W*)	N(2)	O(21)	136·2 (6)
O(*W*)	N(2)	O(12)	78·9 (5)
O(21)	N(2)	O(12)	72·3 (4)
O(41^{viii})	N(3)	O(42^{ix})	72·0 (5)
O(41^{viii})	N(3)	O(43^{ix})	148·1 (7)
O(42^{ix})	N(3)	O(43^{ix})	76·2 (6)
O(W^{x})	N(4)	O(3)	109·1 (5)
O(W^{x})	N(4)	O(1^{i})	127·8 (5)
O(W^{x})	N(4)	O(13^{xi})	69·8 (5)
O(W^{x})	N(4)	O(23^{xi})	63·3 (4)
O(3)	N(4)	O(1^{i})	63·0 (4)
O(3)	N(4)	O(13^{xi})	121·4 (6)
O(3)	N(4)	O(23^{xi})	163·4 (6)
O(1^{i})	N(4)	O(13^{xi})	73·0 (5)
O(1^{i})	N(4)	O(23^{xi})	108·8 (5)
O(13^{xi})	N(4)	O(23^{xi})	43·0 (5)

Table 4. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Mn(1)—O(1)	2·217 (9)	C(7)—C(8)	1·51 (3)
Mn(1)—O(3)	2·18 (1)	C(8)—C(9)	1·53 (3)
Mn(1)—O(5)	2·20 (1)	C(9)—N(3)	1·52 (2)
Mn(2)—O(1^{i})	2·30 (1)	C(10)—O(7)	1·25 (2)
Mn(2)—O(2^{i})	2·30 (1)	C(10)—O(8)	1·26 (2)
Mn(2)—O(4^{i})	2·13 (1)	C(10)—C(11)	1·49 (2)
Mn(2)—O(6)	2·11 (1)	C(11)—C(12)	1·52 (3)
Mn(2)—O(7)	2·20 (1)	C(12)—N(4)	1·46 (2)
Mn(2)—O(8^{ii})	2·10 (1)	Cl(1)—O(11)	1·39 (1)
C(1)—O(1)	1·29 (2)	Cl(1)—O(21)	1·46 (1)
C(1)—O(2)	1·30 (2)	Cl(1)—O(31)	1·39 (2)
C(1)—C(2)	1·45 (2)	Cl(1)—O(41)	1·42 (2)
C(2)—C(3)	1·52 (2)	Cl(2)—O(12)	1·40 (1)
C(3)—N(1)	1·49 (2)	Cl(2)—O(22)	1·42 (2)
C(4)—O(3)	1·22 (2)	Cl(2)—O(32)	1·41 (2)
C(4)—O(4)	1·29 (2)	Cl(2)—O(42)	1·39 (2)
C(4)—C(5)	1·57 (2)	Cl(3)—O(13)	1·37 (2)
C(5)—C(6)	1·54 (3)	Cl(3)—O(23)	1·47 (2)
C(6)—N(2)	1·48 (3)	Cl(3)—O(33)	1·31 (3)
C(7)—O(5)	1·23 (2)	Cl(3)—O(43)	1·37 (2)
C(7)—O(6)	1·26 (2)		

Table 5. *Valency angles* (°) *with e.s.d.'s in parentheses*

O(1)—Mn(1)—O(3)	94·3 (3)	O(1)—C(1)—O(2)	117·8 (14)
O(1)—Mn(1)—O(5)	92·3 (4)	O(1)—C(1)—C(2)	121·0 (14)
O(3)—Mn(1)—O(5)	86·3 (4)	O(2)—C(1)—C(2)	121·0 (15)
O(1^{i})—Mn(2)—O(2^{i})	57·7 (3)	C(1)—C(2)—C(3)	114·6 (14)
O(1^{i})—Mn(2)—O(4^{i})	82·9 (4)	C(2)—C(3)—N(1)	112·6 (14)
O(1^{i})—Mn(2)—O(6)	107·1 (4)	O(3)—C(4)—O(4)	127·3 (16)
O(1^{i})—Mn(2)—O(7)	84·9 (4)	O(3)—C(4)—C(5)	119·5 (15)
O(2^{i})—Mn(2)—O(4^{i})	85·9 (4)	O(4)—C(4)—C(5)	113·2 (14)
O(2^{i})—Mn(2)—O(7)	90·3 (4)	C(4)—C(5)—C(6)	113·1 (14)
O(2^{i})—Mn(2)—O(8^{ii})	91·6 (4)	C(5)—C(6)—N(2)	114·5 (14)
O(4^{ii})—Mn(2)—O(6)	93·9 (4)	O(5)—C(7)—O(6)	125·3 (16)
O(4^{ii})—Mn(2)—O(8^{ii})	84·6 (4)	O(5)—C(7)—C(8)	117·4 (15)
O(6)—Mn(2)—O(7)	86·6 (4)	O(6)—C(7)—C(8)	117·2 (15)
O(6)—Mn(2)—O(8^{ii})	103·5 (4)	C(7)—C(8)—C(9)	112·9 (15)
O(7)—Mn(2)—O(8^{ii})	107·6 (4)	C(8)—C(9)—N(3)	115·8 (14)
Mn(1)—O(1)—Mn(2^{i})	109·2 (4)	O(7)—C(10)—O(8)	124·4 (15)
C(1)—O(1)—Mn(1)	136·9 (10)	O(7)—C(10)—C(11)	118·3 (15)
C(1)—O(1)—Mn(2^{i})	91·8 (9)	O(8)—C(10)—C(11)	117·3 (15)
C(1)—O(2)—Mn(2^{i})	91·4 (9)	C(10)—C(11)—C(12)	116·0 (15)
C(4)—O(3)—Mn(1)	128·7 (10)	C(11)—C(12)—N(4)	115·7 (15)
C(4)—O(4)—Mn(2^{i})	141·4 (11)	O(11)—Cl(1)—O(21)	108·7 (8)
C(7)—O(5)—Mn(1)	147·9 (11)	O(11)—Cl(1)—O(31)	108·7 (10)
C(7)—O(6)—Mn(2)	123·1 (11)	O(11)—Cl(1)—O(41)	112·9 (10)
C(10)—O(7)—Mn(2)	135·9 (10)	O(21)—Cl(1)—O(31)	105·2 (9)
C(10)—O(8)—Mn(2^{ii})	135·2 (11)	O(21)—Cl(1)—O(41)	109·5 (9)
O(31)—Cl(1)—O(41)	111·4 (10)	O(13)—Cl(3)—O(23)	105·8 (10)
O(12)—Cl(2)—O(22)	108·4 (8)	O(13)—Cl(3)—O(33)	109·0 (11)
O(12)—Cl(2)—O(32)	109·0 (9)	O(13)—Cl(3)—O(43)	108·1 (13)
O(12)—Cl(2)—O(42)	111·2 (9)	O(23)—Cl(3)—O(33)	104·8 (10)
O(22)—Cl(2)—O(32)	110·1 (9)	O(23)—Cl(3)—O(43)	119·4 (12)
O(22)—Cl(2)—O(42)	109·9 (9)	O(33)—Cl(3)—O(43)	109·4 (12)
O(32)—Cl(2)—O(42)	108·1 (9)		

(planes 1, 2). O···O contacts in the Mn(2) polyhedron range from [O(4)···O(8)] 2·85 to [O(7)···O(8)] 3·47 Å. The main reason for such large distortions is the chelated coordination of Mn(2) by the carboxyl group of *β*-alanine molecule *A*, being, to our knowledge, the first case of this type of Mn^{2+} coordination. Similar coordination is frequently found in calcium compounds where the metal ions exhibit a coordination number higher than 6 (Einspahr & Bugg, 1977). The lengths Mn(2^{i})—O(1) 2·30 (1) and Mn(2^{i})—O(2) 2·30 (1) Å are longer than the Mn—O(carboxyl) lengths (2·23 Å maximum). Mn(2^{i}) is located precisely midway between the two O atoms of the chelating carboxyl group [C(1)—O(1)—Mn(2^{i}) = 91·8 (9)°, C(1)—O(2)—Mn(2^{i}) = 91·4 (9)°] and lies near the plane of C(2)C(1)O(1)O(2) (Table 6, plane 3).

O(1) forms another short bond with Mn(1). Mn(1) and Mn(2) are connected additionally by two *syn,syn* carboxyl bridges from two *β*-alanine molecules, *B* and *C*. Deviations of the Mn atoms from the best planes of these bridging carboxyl groups do not exceed 0·5 Å (Table 6, planes 4, 5). The Mn(1)—Mn(2) distance is

Table 6. *Least-squares planes*

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

Plane 1: O(1), O(2), O(6$^{\rm i}$), O(8$^{\rm iii}$)

$$0{\cdot}5175X + 0{\cdot}6563Y - 0{\cdot}5490Z + 1{\cdot}3692 = 0$$

O(1) 0·089 (9), O(2) −0·125 (10), O(6$^{\rm i}$) −0·078 (11), O(8$^{\rm iii}$) 0·095 (11), Mn(2$^{\rm i}$) −0·101 (2)

Plane 2: O(1), O(4), O(7$^{\rm i}$), O(8$^{\rm iii}$)

$$-0{\cdot}7547X + 0{\cdot}6386Y - 0{\cdot}1505Z + 1{\cdot}4045 = 0$$

O(1) −0·227 (9), O(4) 0·367 (11), O(7$^{\rm i}$) 0·235 (11), O(8$^{\rm iii}$) −0·290 (11), Mn(2$^{\rm i}$) 0·295 (2)

Plane 3: O(1), O(2), C(1), C(2)

$$0{\cdot}4965X + 0{\cdot}7923Y - 0{\cdot}3545Z + 1{\cdot}1300 = 0$$

O(1) −0·002 (9), O(2) −0·003 (10), C(1) 0·021 (16), C(2) −0·007 (17), C(3) −0·301 (17), N(1) 0·775 (13), Mn(1) 1·130, Mn(2$^{\rm i}$) 0·352 (2)

Plane 4: O(3), O(4), C(4), C(5)

$$0{\cdot}6651X - 0{\cdot}6914Y - 0{\cdot}2821Z + 0{\cdot}2512 = 0$$

O(3) −0·001 (10), O(4) −0·002 (11), C(4) 0·012 (16), C(5) −0·003 (17), C(6) 0·588 (16), N(2) −0·116 (13), Mn(1) 0·251, Mn(2$^{\rm i}$) −0·269 (2)

Plane 5: O(5), O(6), C(7), C(8)

$$0{\cdot}4011X + 0{\cdot}8535Y - 0{\cdot}3326Z - 0{\cdot}3222 = 0$$

O(5) 0·002 (10), O(6) 0·002 (10), C(7) −0·016 (17), C(8) 0·004 (17), C(9) −0·403 (18), N(3) 0·455 (13), Mn(1) −0·322, Mn(2) 0·452 (2)

Plane 6: O(7), O(8), C(10), C(11)

$$-0{\cdot}2377X + 0{\cdot}8342Y - 0{\cdot}4977Z - 3{\cdot}2439 = 0$$

O(7) 0·001 (10), O(8) 0·001 (11), C(10) −0·009 (16), C(11) 0·003 (18), C(12) −0·659 (18), N(4) −0·054 (12), Mn(2) −1·342 (2), Mn(2$^{\rm ii}$) 0·422 (2)

Table 7. *Torsion angles* (°) *in β-alanine molecules with e.s.d.'s in parentheses*

O(1)—C(1)—C(2)—C(3)	ξ_A^1	−166 (2)
O(2)—C(1)—C(2)—C(3)	ξ_A^2	10 (2)
C(1)—C(2)—C(3)—N(1)	ξ_A^3	−66 (2)
O(3)—C(4)—C(5)—C(6)	ξ_A^4	−156 (2)
O(4)—C(4)—C(5)—C(6)	ξ_B^1	26 (2)
C(4)—C(5)—C(6)—N(2)	ξ_B^2	−60 (2)
O(5)—C(7)—C(8)—C(9)	ξ_B^3	164 (2)
O(6)—C(7)—C(8)—C(9)	ξ_B^4	−19 (2)
C(7)—C(8)—C(9)—N(3)	ξ_C^1	59 (2)
O(8)—C(10)—C(11)—C(12)	ξ_C^2	−152 (2)
O(7)—C(10)—C(11)—C(12)	ξ_C^3	30 (2)
C(10)—C(11)—C(12)—N(4)	ξ_C^4	−62 (2)

3·68 Å. A similar bridging group was found in manganese acetate tetrahydrate (Tranqui, Burlet, Filhol & Thomas, 1977), where the Mn—Mn distance is 3·6 Å. In both cases the Mn—Mn distances are longer than those usually found between metal atoms linked by *syn,syn* carboxyl bridges and longer than those expected for Mn compounds (3·2 Å maximum). In the presence of two bridging O atoms and a bridging *syn, syn* carboxyl group the Mn—Mn distance is 3·35 Å (Lis, 1977).

Mn(2) and Mn(2$^{\rm ii}$) are linked by two *syn,anti* carboxyl bridges formed by two, crystallographically equivalent, *D* molecules of *β*-alanine. The Mn(2)—Mn(2$^{\rm ii}$) distance of 4·33 Å is shorter by about 0·5 Å than the values found in analogous groups with Mn atoms (Narayanan & Venkataraman, 1975; Ciunik & Głowiak, 1980*b*; Głowiak, 1980).

The reasons for the deformation of the Mn(2) octahedron are (*a*) chelated coordination of *β*-alanine molecule *A* and (*b*) decrease in the Mn(2)—Mn(2$^{\rm ii}$) distance resulting in an increase of O(7)—Mn(2)—O(8$^{\rm ii}$) by about 14° compared with the corresponding angles in double carboxyl bridges between Mn atoms. It seems that both disturbances (*a*) and (*b*) could not occur independently but are coupled to each other in this case. Deviations of Mn(2) and Mn(2$^{\rm ii}$) from the best plane of the *D* molecule carboxyl group are −1·342 (2) and 0·422 (2) Å, respectively (Table 6, plane 6). Similar deviations of the Mn atoms were found only in polymeric Mn^{2+} amino acid complexes with double carboxyl bridges (Ciunik & Głowiak, 1980*b*).

Four crystallographically independent *β*-alanine molecules, *A*, *B*, *C* and *D*, occur in the crystals under investigation as zwitterions. Bond lengths and angles in the *B*, *C* and *D* molecules do not differ (within the limits of 3σ) from the corresponding values found for *β*-alanine (Jose & Pant, 1965), except for the C—C—N angles which on average are larger by about 7°.

The geometry of the carboxyl group in the chelating *A* molecules is slightly different. O(1)—C(1)—O(2) is smaller by about 9° than the corresponding value in *β*-alanine, resulting in an increase of the other C—C—O angles. Torsion angles inside the *β*-alanine molecules are presented in Table 7.

If the conformation of the *β*-alanine molecule determined by angles $-\xi^1$, ξ^2, $-\xi^3$ is denoted as *d* and that determined by angles ξ^1, $-\xi^2$, ξ^3 is denoted as *l*, a single chain of the described polymer has a sequence *-ddd,lll,dl,dl,ddd,lll,dl-*, where commas denote successive Mn atoms. With the nomenclature of organic polymer chemistry (Saunders, 1973) the chain described has a syndiotactic nature. In the group of polymeric Mn^{2+} amino acid complexes the crystal structure of only one complex built of isotactic chains has been investigated until now (Ciunik & Głowiak, 1978).

Bond lengths and angles in the ClO_4^- ions correspond to the values in other crystal structures.

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The Crystal and Absolute Molecular Structure of $(+)_{546}$-*cis*-α-Sodium Carbonato[(2*S*,2′*S*)-1,1′-ethylenedi-2-pyrrolidinecarboxylato(2−)]cobaltate(III) Trihydrate

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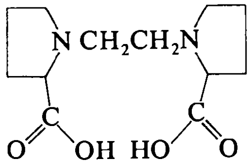
Abstract

Monoclinic crystals of the title compound, $Na[Co(C_{12}H_{18}N_2O_4)(CO_3)].3H_2O$, $C_{13}H_{18}CoN_2O_7^-.Na^+.3H_2O$, space group $P2_1$, have a = 7·845 (4), b = 7·760 (2), c = 14·922 (10) Å, β = 106·51 (3)° and Z = 2. Refinement with 2463 diffractometer data measured with Mo $K\alpha$ radiation converged at R = 0·059. The structure consists of $[Co(pren)(CO_3)]^-$ complex anions linked into double layers parallel to the (001) planes by O—Na—O and $O—H_2O—H_2O—O$ bridges. The distorted octahedral complex anion has the *cis*-α geometrical arrangement and its absolute configuration is Δ(OC−6−13−C). The Na^+ ions have approximate NaO_6 octahedral coordination.

Introduction

The quadridentate ligand (2*S*,2′*S*)-1,1′-ethylenedi-2-pyrrolidinecarboxylic acid (1), abbreviated as H_2-pren, has been used recently to prepare a series of cobalt(III) complexes including $Na[Co(pren)(CO_3)].3H_2O$ (Woon & O'Connor, 1979).



(1)

^{13}C NMR and absorption spectral measurements indicated that this and related compounds have the symmetrical *cis*-α structure in aqueous solution. A strong negative circular dichroism band under the $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic absorption band and the presence of a negative Cotton effect in the visible region of the optical rotatory dispersion spectrum in aqueous solution were used to predict that the complex anion $[Co(pren)(CO_3)]^-$ has the Δ absolute configuration (IUPAC Commission on Inorganic Chemical Nomenclature, 1971). The present study was carried out to confirm these predictions.

Experimental

The title compound was prepared by the method of Woon & O'Connor (1979), and purple tabular crystals

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