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## Structure of Di- $\mu$ -hydroxo-bis{bis(*S*)-alaninato}chromium(III) Trihydrate

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### Abstract

The title compound,  $C_{12}H_{26}Cr_2N_4O_{10} \cdot 3H_2O$ , belongs to the triclinic space group  $P1$ , with  $a = 5.369$  (4),  $b = 9.994$  (3),  $c = 11.209$  (2) Å,  $\alpha = 72.65$  (2),  $\beta = 74.76$  (3),  $\gamma = 77.27$  (3)°,  $Z = 1$ ,  $D_c = 1.65$ ,  $D_o = 1.64$  (1) Mg m<sup>-3</sup>. The structure was refined on 2073 independent nonzero reflections to a conventional  $R$  factor of 0.031. The crystal consists of individual dihydroxo-bridged molecules in which each Cr atom is surrounded by a *cis-cis-cis* arrangement of two hydroxo O atoms, and two O and two N atoms of alanine. The molecules are held together by an intricate network of hydrogen bonds involving amino groups, free and coordinated O atoms of carbonyl groups and water molecules.

### Introduction

Chromium(III) forms two common types of complexes with simple bidentate amino acids (HL): monomeric  $CrL_3$  chelates and dihydroxo-bridged dimers of the formula  $Cr_2(OH)_2L_4$ . The tris-chelates can exist either as *facial* or as *meridional* isomers. The glycine complex studied by Bryan, Greene, Stokely & Wilson (1971) was found to be the *fac* isomer. For the dihydroxo-bridged molecules, 24 stereoisomers are theoretically possible, *i.e.* 10 pairs of enantiomers and 4 inactive diastereoisomers. The glycine compound examined by Veal, Hatfield, Jeter, Hempel & Hodgson (1973) had a *cis-cis-cis* distribution of donor atoms in the  $CrN_2O_2O_2$  coordination sphere. For an amino acid

with an asymmetric C atom, like (*S*)-alanine (HAla), the 24 stereoisomers above are all diastereoisomers. As part of an investigation of Cr complexes with amino acids, we have prepared crystals of  $Cr_2(OH)_2(S-Ala)_4$  and a crystallographic study was undertaken in order to determine the stereochemistry around Cr.

(*S*)-Alanine (0.4 g) and  $[Cr(NH_3)_6](NO_3)_3$  (0.5 g) were dissolved in water (15 ml). While the mixture was heated on a steam bath (1 h), pink needles of  $Cr(S-Ala)_3$  formed. After 3 d at room temperature, a small amount of burgundy crystals of  $Cr_2(OH)_2(S-Ala)_4$  had also appeared. The solid was filtered and the burgundy crystals were separated by hand. A similar compound had been prepared by Oki & Otsuka (1976) from racemic alanine, but Oki (1977) failed to obtain the analog with (*S*)-alanine.

A well formed crystal of dimensions  $0.35 \times 0.15 \times 0.11$  mm was used for X-ray work. Triclinic Laue symmetry was observed on a set of precession and cone-axis photographs. A cell-reduction calculation using program *TRACER* II (Lawton & Jacobson, 1965) showed that the lattice cannot be described with a cell of higher symmetry. The preparation of the compound from (*S*)-alanine unambiguously ruled out the centrosymmetric  $P\bar{1}$  group, leaving  $P1$  as the only acceptable space group.

The crystal was mounted on an Enraf-Nonius CAD-4 diffractometer. The cell parameters were obtained by least-squares refinement on the setting angles of 25 reflections ( $12^\circ < 2\theta < 24^\circ$ ). The cell used in this report is non-conventional. It can be transformed into a conventional Niggli reduced cell of type II (*International Tables for X-ray Crystallography*, 1969) using  $a_r = -a$ ,  $b_r = b$ ,  $c_r = a - c$ . The parameters of the reduced cell are:  $a_r = 5.369$ ,  $b_r =$

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9.994,  $c_r = 11.083$  Å,  $\alpha_r = 101.24$ ,  $\beta_r = 102.63$ ,  $\gamma_r = 102.73^\circ$ .

Intensity data were collected using the  $\omega/2\theta$  scan technique. The scan range was  $\omega = (0.80 + 0.35 \times \tan \theta)$ , extended 25% on each side for background measurements. The counter slit width was fixed at 2.0 mm. A fast prescan at  $6.7^\circ \text{ min}^{-1}$  was made and all the data for which  $I < \sigma(I)$  were labeled 'weak' and not remeasured at slower speed. For the others, a scan speed between  $6.7$  and  $0.40^\circ \text{ min}^{-1}$  was automatically selected to make the  $I/\sigma(I)$  ratio equal to 100, but a maximum scan time of 180 s was imposed. Three standard reflections were measured every hour as a check on crystal and instrument stability. They showed random fluctuations  $< \pm 2\%$  about their respective means.

A set of 2756 independent  $hkl$ ,  $hk\bar{l}$ ,  $h\bar{k}l$  and  $h\bar{k}\bar{l}$  reflections within a sphere  $2\theta \leq 57^\circ$  were measured using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71068$  Å). Net intensity  $I$  and standard deviation  $\sigma(I)$  were calculated as described elsewhere (Hubert & Beauchamp, 1980). A total of 683 reflections with  $I < 3\sigma(I)$  were assigned zero weight and the set of 2073 nonzero reflections was used to solve the structure. The data were corrected for Lp. No absorption correction was applied, since preliminary calculations ( $\mu = 1.03 \text{ mm}^{-1}$ ) showed that the transmission factor was in the narrow range  $0.78 \pm 0.05$ .

### Structure determination

The cell origin was defined by arbitrarily positioning Cr(1) at 0,0,0. The coordinates of Cr(2) were determined from a Patterson synthesis. A difference Fourier ( $\Delta F$ ) synthesis phased on Cr clearly revealed the positions of the nonhydrogen atoms in the four alanine ligands, except the methyl groups. At this stage, the known portion of the structure was still nearly centrosymmetric and the next  $\Delta F$  map had approximate  $P\bar{1}$  symmetry, two overlapping centrosymmetrically related images being present. Thus, two peaks were consistent with the methyl C on each asymmetric C of alanine; one peak was selected to obtain the *S* configuration. The structure was refined isotropically by full-matrix least squares on  $\sum w(|F_o| - |F_c|)^2$  with weights  $w = 1$ , and the  $R$  factor  $= \sum ||F_o| - |F_c|| / \sum |F_o|$  was stabilized at 0.125. The subsequent  $\Delta F$  map showed two residual peaks of  $\sim 4.3 \text{ e } \text{Å}^{-3}$  and four of  $\sim 2.5 \text{ e } \text{Å}^{-3}$  which were assumed to correspond to water molecules. The two highest peaks were introduced in the least-squares calculations and refined isotropically. The remaining four residual peaks were still present at the same positions in the next  $\Delta F$  map and they were also introduced as water O atoms. Isotropic refinement of all known atoms was continued and a large increase was noted on the temperature factors of all the water O atoms. Inspection of

interatomic distances and angles revealed that the six water molecules could not exist simultaneously in the structure, but that they had to be subdivided into two sets of three molecules. The distances between water molecules of the same set and with the rest of the structure were consistent with hydrogen bonding, but there were very short contacts between O atoms belonging to different sets. This was interpreted in terms of a twofold disorder and these O atoms were assigned occupancy factors of 0.50, which were kept constant at this point. Refinement was continued, first isotropically, then anisotropically, using block-diagonal least squares. The  $R$  factor was reduced to 0.054. Most of the H atoms of the alanine moieties were visible on the next  $\Delta F$  map. They were added to the list of atoms and refined isotropically, reducing the  $R$  factor to 0.039.

Although the structure was geometrically reasonable, some of the water O atoms still had high thermal motion. With the remaining atoms fixed, the parameters (including occupancy factors) of the six half-oxygens were refined by full-matrix least squares. Thermal motion became more reasonable and the occupancy factors for one set of three O atoms progressively increased to 0.8–1.0, while the others decreased to  $\leq 0.1$ . This clearly showed that three of the six peaks in the  $\Delta F$  map phased on the other nonhydrogen atoms were ghost images, the poor phasing power of the methyl C atoms being insufficient to suppress the pseudo-inversion center.

Anisotropic refinement of the nonhydrogen atoms was continued by full-matrix least squares. The three water O atoms behaved normally and the next  $\Delta F$  map showed no residual peaks at the positions first occupied by the ghost atoms. The rest of the refinement (anisotropic for nonhydrogen atoms, isotropic for H) was carried out by block-diagonal least squares. New H atoms were located on *OB*(1) and *OW*(1). Atoms *HC*(12) and *HC*(33) failed to converge to reasonable positions and were fixed at their calculated coordinates. *HOB*(2) was not found. Individual weights  $w = 1/\sigma^2(F_o)$  based on counting statistics were applied to each reflection in the final cycles of refinement. Convergence was attained for  $R = 0.031$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.039$  (nonzero reflections only). The goodness-of-fit ratio was 1.30. The ten highest peaks in the final  $\Delta F$  map ( $< 0.40 \text{ e } \text{Å}^{-3}$ ) were all close to Cr. The deepest valley was  $-0.15 \text{ e } \text{Å}^{-3}$ .

The refined coordinates are listed in Table 1.\* The form factors were those of Cromer & Waber (1965),

\* Lists of structure factors, and anisotropic thermal parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35888 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Refined fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and equivalent  $U$  values ( $\times 10^3$ )

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{12} \cos \gamma + 2U_{13} \cos \beta + 2U_{23} \cos \alpha)/3.$$

	$x$	$y$	$z$	$U_{eq}$ ( $\text{\AA}^2$ )
Cr(1)	0	0	0	20
Cr(2)	217 (1)	-3135 (1)	938 (1)	20
OB(1)	-1896 (6)	-1463 (3)	37 (3)	25
OB(2)	2301 (6)	-1668 (3)	809 (3)	25
O(1)	2134 (6)	-22 (4)	-1696 (3)	29
O(2)	2043 (6)	1320 (3)	207 (3)	25
O(3)	-1771 (7)	-2948 (4)	2652 (3)	29
O(4)	-1872 (6)	-4470 (3)	864 (3)	25
O(5)	2134 (10)	580 (5)	-3778 (4)	59
O(6)	2482 (7)	2514 (4)	1474 (4)	36
O(7)	-2097 (8)	-3734 (5)	4721 (4)	44
O(8)	-2814 (7)	-5530 (4)	-434 (4)	32
N(1)	-2338 (7)	1583 (4)	-1067 (4)	24
N(2)	-2194 (8)	360 (4)	1724 (4)	26
N(3)	2425 (7)	-4747 (4)	2043 (3)	22
N(4)	2233 (7)	-3532 (4)	-780 (4)	26
C(1)	-2723 (14)	2487 (8)	-3382 (6)	52
C(2)	-2034 (13)	1601 (9)	3297 (7)	39
C(3)	3021 (13)	-5334 (7)	4288 (6)	48
C(4)	1861 (13)	-4882 (9)	-2266 (6)	51
C(5)	-1786 (10)	1266 (5)	-2354 (5)	31
C(6)	-1557 (9)	1619 (5)	1932 (5)	26
C(7)	1142 (10)	-5042 (5)	3412 (5)	28
C(8)	477 (9)	-4020 (5)	-1334 (5)	28
C(9)	1101 (11)	565 (6)	-2659 (5)	34
C(10)	1229 (9)	1852 (5)	1157 (5)	25
C(11)	-998 (9)	-3827 (6)	3654 (5)	28
C(12)	-1527 (9)	-4750 (4)	-245 (5)	28
OW(1)	3262 (8)	-1435 (5)	2949 (4)	41
OW(2)	6102 (10)	-2023 (6)	6591 (5)	65
OW(3)	1185 (11)	-1553 (7)	5409 (6)	75
HN(11)	-158 (11)	243 (6)	-112 (6)	48
HN(12)	-382 (8)	152 (4)	-86 (4)	13
HN(21)	-398 (13)	53 (7)	164 (6)	69
HN(22)	-208 (13)	-52 (7)	218 (6)	84
HN(31)	419 (19)	-446 (9)	189 (9)	121
HN(32)	270 (9)	-542 (5)	189 (5)	25
HN(41)	327 (10)	-419 (5)	-68 (5)	44
HN(42)	305 (17)	-278 (8)	-163 (8)	87
HC(5)	-271 (10)	63 (5)	-231 (4)	28
HC(6)	-280 (10)	242 (5)	135 (5)	35
HC(7)	8 (10)	-577 (6)	361 (5)	45
HC(8)	-34 (10)	-320 (5)	-191 (5)	34
HC(11)	-192 (12)	211 (6)	-410 (6)	40
HC(12)	-238	343	-359	101
HC(13)	-466 (13)	246 (7)	-304 (6)	58
HC(21)	-166 (15)	249 (8)	340 (7)	87
HC(22)	-102 (12)	104 (7)	370 (6)	69
HC(23)	-368 (10)	156 (5)	364 (5)	40
HC(31)	417 (14)	-444 (7)	402 (6)	80
HC(32)	429 (11)	-621 (6)	426 (5)	42
HC(33)	197	-544	513	105
HC(41)	300 (11)	-446 (6)	-286 (6)	54
HC(42)	48 (17)	-505 (9)	-271 (8)	105
HC(43)	299 (12)	-571 (6)	-192 (6)	52
HOB(1)	-356 (16)	-137 (9)	27 (8)	120
HW(11)	253 (13)	-158 (7)	366 (6)	56
HW(12)	491 (16)	-201 (9)	288 (8)	114

except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion terms  $f'$  and  $f''$  were used for Cr (Cromer, 1965). The computer programs used are listed elsewhere (Hubert & Beauchamp, 1980).

## Description of the structure

The structure consists of discrete  $\text{Cr}_2(\text{OH})_2(\text{Ala})_4$  molecules, as shown in Fig. 1. The Cr atoms with an approximate octahedral coordination are joined by a pair of symmetrically bridging hydroxo groups. The O and N donors are arranged in a *cis-cis-cis* configuration around Cr and the molecular framework is nearly centrosymmetric if the substituents on the asymmetric C atoms are neglected. Consequently, this compound and the glycine analog are corresponding stereoisomers (Veal, Hatfield, Jeter, Hempel & Hodgson, 1973).

The interatomic distances in the molecule are shown in Fig. 2 and the bond angles are listed in Table 2. The  $\text{Cr}_2(\text{OH})_2$  bridging unit shows the same features as found in the glycine compound: the Cr-OB distances [1.943 (3)-1.983 (3), av. 1.967  $\text{\AA}$ ] and the Cr-OB-Cr [97.6 (1), 99.4 (1) $^\circ$ ] and OB-Cr-OB angles [81.8 (1), 81.1 (1) $^\circ$ ] resemble the corresponding values [1.967 (4)  $\text{\AA}$ , 98.2 (2), 81.8 (2) $^\circ$ ] observed by Veal *et al.* (1973). The amino acid is bonded to Cr by normal bonds: Cr-N [2.051 (4)-2.073 (4), av. 2.065  $\text{\AA}$ ] and Cr-O [1.951 (4)-1.988 (3), av. 1.968  $\text{\AA}$ ] (Veal *et al.*, 1973; Bryan *et al.*, 1971). Comparisons of individual values in a set of presumably equivalent bond lengths (Fig. 2) reveals significant differences (for instance, in the Cr-O set or in ligand distances). The differences remain significant even if the  $\sigma$  values are doubled to balance the effect of using block-diagonal refinement. Such discrepancies are not obviously related to specific bonding or packing effects and they presumably reflect the low symmetry in molecular packing imposed by the chiral ligand.

The ligand geometry is in good agreement with previous studies on (*S*)-alanine (except for the C-O distances) (Simpson & Marsh, 1966) and its Co complex (Herak, Prelesnik & Krstanović, 1978). The ranges and average values of bond lengths are: C-CH<sub>3</sub>, 1.479 (9)-1.513 (9), 1.498  $\text{\AA}$ ; C-N,

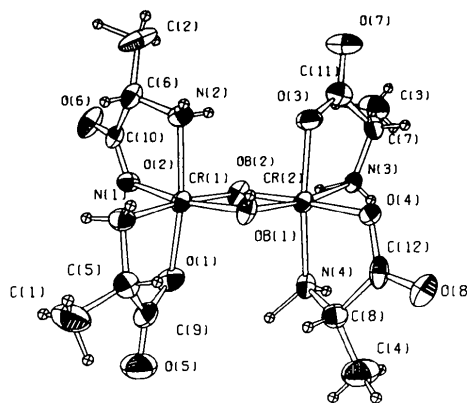


Fig. 1. ORTEP drawing (Johnson, 1965) of  $\text{Cr}_2(\text{OH})_2(\text{S-Ala})_4$ . The ellipsoids correspond to 50% probability. H atoms are shown as small spheres of arbitrary size.

1.470 (7)–1.509 (6), 1.485 Å; C–C, 1.512 (7)–1.548 (8), 1.532 Å; C–O, 1.264 (6)–1.312 (6), 1.288 Å; C=O, 1.208 (6)–1.242 (6), 1.224 Å. As expected, the C–O bonds, which are roughly equal in the free amino acid, have become nonequivalent as a

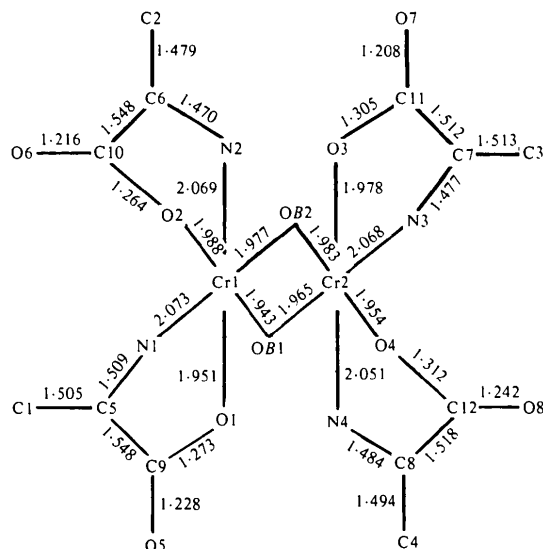


Fig. 2. Interatomic distances in  $\text{Cr}_2(\text{OH})_2(\text{S-Ala})_4$ . The standard deviations are 0.006–0.007 Å, except for Cr–N(O), 0.003–0.004 Å, and C–methyl, 0.009 Å.

Table 2. Bond angles ( $^\circ$ )

Around chromium ( $\sigma = 0.1^\circ$ )

N(1)–Cr(1)–OB(1)	92.7	N(3)–Cr(2)–OB(1)	172.8
N(1)–Cr(1)–OB(2)	171.0	N(3)–Cr(2)–OB(2)	94.2
N(1)–Cr(1)–O(2)	94.6	N(3)–Cr(2)–O(4)	91.1
N(2)–Cr(1)–N(1)	93.4	N(4)–Cr(2)–N(3)	95.7
N(2)–Cr(1)–O(1)	170.8	N(4)–Cr(2)–O(4)	81.8
N(2)–Cr(1)–O(2)	81.0	N(4)–Cr(2)–OB(1)	90.0
N(2)–Cr(1)–OB(1)	94.5	N(4)–Cr(2)–OB(2)	93.8
N(2)–Cr(1)–OB(2)	94.0	O(3)–Cr(2)–N(3)	81.0
O(1)–Cr(1)–OB(1)	93.6	O(3)–Cr(2)–N(4)	174.4
O(1)–Cr(1)–N(1)	81.8	O(3)–Cr(2)–OB(1)	93.6
O(1)–Cr(1)–O(2)	91.5	O(3)–Cr(2)–OB(2)	90.9
O(1)–Cr(1)–OB(2)	91.4	O(4)–Cr(2)–OB(1)	94.0
O(2)–Cr(1)–OB(1)	171.6	O(4)–Cr(2)–OB(2)	173.4
O(2)–Cr(1)–OB(2)	91.4	O(4)–Cr(2)–O(3)	93.8
OB(1)–Cr(1)–OB(2)	81.8	OB(1)–Cr(2)–OB(2)	81.1
Cr(1)–OB(1)–Cr(2)	99.4	Cr(1)–OB(2)–Cr(2)	97.6

In the ligand ( $\sigma = 0.4$ – $0.6^\circ$ )

N(1)–C(5)–C(1)	114.1	C(5)–C(9)–O(5)	118.2
N(2)–C(6)–C(2)	113.5	C(6)–C(10)–O(6)	120.1
N(3)–C(7)–C(3)	113.4	C(7)–C(11)–O(7)	122.1
N(4)–C(8)–C(4)	114.4	C(8)–C(12)–O(8)	120.3
N(1)–C(5)–C(9)	108.5	C(5)–C(9)–O(1)	115.5
N(2)–C(6)–C(10)	108.9	C(6)–C(10)–O(2)	115.7
N(3)–C(7)–C(11)	109.9	C(7)–C(11)–O(3)	116.5
N(4)–C(8)–C(12)	108.4	C(8)–C(12)–O(4)	116.7
C(1)–C(5)–C(9)	116.9	O(1)–C(9)–O(5)	126.3
C(2)–C(6)–C(10)	114.9	O(2)–C(10)–O(6)	124.2
C(3)–C(7)–C(11)	110.4	O(3)–C(11)–O(7)	121.1
C(4)–C(8)–C(12)	113.8	O(4)–C(12)–O(8)	122.9

result of unidentate coordination to Cr. Details on the C–H and N–H bonds have been deposited. The negative O–C–C torsion angles (Table 3) are consistent with the *S* configuration at the asymmetric C atom. The chelate rings have a  $\delta$  conformation as evidenced by their N–C–O(Cr) torsion angles. The absolute configurations at the Cr asymmetric centers have opposite chiralities: Cr(1) has a *A* configuration, Cr(2) has a *A* configuration (Purcell & Kotz, 1977).

The dimer lies in the unit cell with its  $\text{Cr}_2\text{O}_2$  bridging unit roughly parallel to the *ab* plane and the Cr–Cr direction nearly along the *b* axis. Consecutive molecules along the *a* axis are connected by three moderately strong N–H...O interactions [ $\text{N}\cdots\text{O} = 2.992(6)$ – $3.038(5)$  Å] (Table 4). There is a fourth much weaker O–H...O bond between hydroxo groups [ $3.043(5)$  Å]. These rows of molecules are held together by normal van der Waals contacts and by a network of H-bonding interactions involving a hydroxo group, an amino group, carboxyl O atoms and the three water molecules (Fig. 3). Although H atoms were identified only for *OW*(1), those of *OW*(2) and *OW*(3) could be positioned by inspection of their surroundings. The distances and angles in the H bonds are given in Fig. 4 and Table 4.

It is interesting to note that Cr forms the same stereoisomer with glycine and with (*S*)-alanine. This certainly identifies that particular arrangement of donor atoms around Cr as a stable one, but it does not imply that other stereoisomers cannot exist. The present

Table 3. Torsion angles ( $^\circ$ )

N(1)–C(5)–C(9)–O(1)	22.1 (6)	O(5)–C(9)–C(5)–C(1)	–29.6 (8)
N(2)–C(6)–C(10)–O(2)	23.5 (6)	O(6)–C(10)–C(6)–C(2)	–28.0 (7)
N(3)–C(7)–C(11)–O(3)	16.0 (6)	O(7)–C(11)–C(7)–C(3)	–44.3 (7)
N(4)–C(8)–C(12)–O(4)	19.2 (6)	O(8)–C(12)–C(8)–C(4)	–34.8 (7)

Table 4. Hydrogen bonds between complex molecules

<i>A</i> –H... <i>B</i>	<i>A</i> ... <i>B</i> (Å)	H... <i>B</i> (Å)	$\angle$ <i>A</i> –H... <i>B</i> ( $^\circ$ )
N(1)–HN(12)...O(2)	3.012 (5)	2.25 (5)	166 (4)
N(4)–HN(41)...O(8)	2.992 (6)	2.27 (6)	159 (5)
N(3)–HN(31)...O(4)	3.038 (5)	2.12 (10)	150 (8)
OB(1)–HO(1)...OB(2)	3.043 (5)	2.21 (9)	166 (8)
N(3)–HN(32)...O(6)	2.982 (6)	2.28 (5)	166 (5)

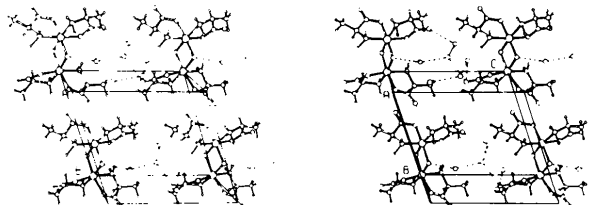


Fig. 3. Packing diagram viewed down the  $a^*$  axis. H atoms are omitted.

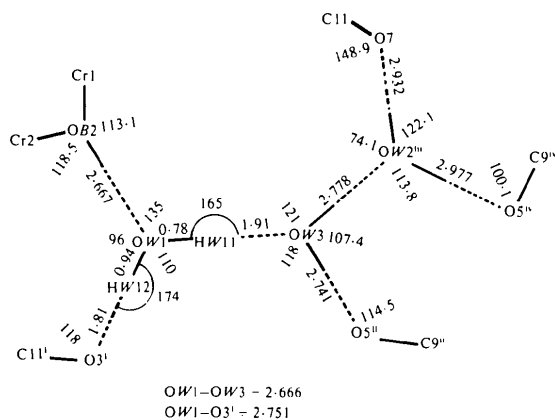


Fig. 4. Schematic representation of the H bonds involving the water molecules. The coordinate transformations are as follows: (i)  $1 + x, y, z$ ; (ii)  $x, y, l + z$ ; (iii)  $-1 + x, y, z$ ; (iv)  $-1 + x, y, l + z$ . The standard deviations on distances are: 0.05–0.09 Å for N(O)—H and 0.006–0.009 Å for N(O)—O; on angles, 5–7° where H is apical, 3–5° when it is terminal, and 0.2–0.4° for angles involving no H atoms.

compound might well have been isolated first because it is the most insoluble. Indeed, for the tris-chelates of cobalt, it has been found that the *fac* isomers are systematically less soluble than the *mer* isomers, a peculiarity that can be ascribed to better packing efficiency through van der Waals contacts and H bonding in the *fac* compound. By analogy, among the 24 possible diastereoisomers of the present dihydroxo-alanine complex, other configurations are likely to exist as more soluble species. In this respect, it would be interesting to study corresponding compounds with amino acids bearing bulkier alkyl or aryl substituents

on the asymmetric C atom. In this manner, the influence of the van der Waals forces would become relatively more important and the stereoisomer first isolated might differ from those obtained with the simplest amino acids.

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## Structure of $\eta^5$ -Cyclopentadienyl( $\eta^6$ -2,4,6-triphenylphosphorin)manganese(I)

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#### Abstract

$C_{28}H_{22}MnP$ ,  $M_r = 444.4$ , triclinic,  $P\bar{1}$ ,  $a = 15.843$  (5),  $b = 13.665$  (3),  $c = 10.155$  (2) Å,  $\alpha = 93.89$  (3),  $\beta = 102.75$  (3),  $\gamma = 89.00$  (3)°,  $V = 2139$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c =$

$1.38$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.735$  mm<sup>-1</sup>. The crystal structure was determined and refined from 4631 diffractometer data to an  $R$  value of 0.063. Mn atoms are sandwiched between ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and [ $\eta^6$ -PC<sub>5</sub>H<sub>2</sub>-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] rings. The difference in C—C bond dis-

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