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## L-(+)<sub>546</sub>-L-Phenylalaninatobis(acetylacetonato)cobalt(III)–Chloroform

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The crystal structure of L-(+)<sub>546</sub>-L-phenylalaninatobis(acetylacetonato)cobalt(III)–chloroform,  $\text{Co}(\text{C}_{19}\text{H}_{24}\text{O}_6\text{N})\cdot\text{CHCl}_3$ , has been determined and refined by three-dimensional least-squares techniques. The space group is  $P3_1$  with unit-cell dimensions  $a = b = 12.319$  (1),  $c = 14.504$  (2) Å. The final weighted  $R$  value for all 1793 data is 0.060. The structure is the  $\Delta$ -*cis* isomer, in agreement with the identification made by Laurie [*J. Chem. Soc. Dalton* (1972), pp. 573–576] from spectroscopic data. The Co ion is in a distorted octahedral environment with the amino acid and acetylacetonate ions acting as bidentate ligands.

### Introduction and experimental

The synthesis of the title compound has been reported by Laurie (1968). Recrystallization from chloroform–*n*-hexane yielded violet, hexagonal needles. The data crystal had the dimensions  $0.086 \times 0.121 \times 0.129 \times 0.535$  mm. All X-ray measurements were made at room temperature (22 °C) with an Enraf–Nonius CAD-4 diffractometer and Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) with a Zr filter. The space group was determined as  $P3_1$  from the systematic absences,  $000l$  ( $l \neq 3n$ ), and the known absolute configuration of the amino acid used in the formation of the compound. Least-square cell dimensions were determined from averages of  $+2\theta$  and  $-2\theta$  values of 30 reflections. The reported uncertainties are three times the calculated standard deviations. Intensities of 1793 independent reflections ( $\theta \leq 23^\circ$ ) were measured with  $\theta$ – $2\theta$  scans. The data were corrected for background radiation. Lorentz,

polarization and absorption corrections ( $\mu = 10.51 \text{ cm}^{-1}$ ) were applied with the program of Coppens, Leiserowitz & Rabinovich (1965) for 216 sampling points. Intensities of 336 data could not be distinguished from the background, being less than  $1.4 T^{1/2}$  ( $T = \text{total count}$ ). They were assigned intensities of  $0.63T^{1/2}$  for the purpose of least-squares refinement. Each structure amplitude was assigned a weight of  $w_F = \sigma_F^{-2}$ , where  $\sigma_F$  is the standard deviation of the amplitude and is given by  $\sigma_F = \frac{1}{2} \{[\sigma^2 + (0.05P)^2]/(\text{Lp})P\}^{1/2}$ , in which:  $\sigma = VT^{1/2}$ ,  $V = \text{scan speed}$ ,  $\text{Lp} = \text{Lorentz-polarization factor}$ ,  $P = V(\text{background-corrected peak count})$ .

### Structure determination and refinement

The  $x$  and  $y$  coordinates of Co were determined from a Patterson map and  $z$  was set at 0.10. The remaining non-hydrogen atoms were located from difference Fourier maps. The structure was refined by full-matrix

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least-squares methods with a modified version of the program of Busing, Martin & Levy (1962), minimizing  $\Sigma w_F \Delta^2$ , where  $\Delta = (|F_o| - |F_c|)$ . When the weighted  $R$  [ $= (\Sigma w_F \Delta^2 / \Sigma w_F |F_o|^2)^{1/2}$ ] had dropped to 0.073, after two cycles of anisotropic refinement on all non-hydrogen atoms, a difference Fourier synthesis was calculated.

The most prominent peak near each methyl C atom

and the N atom were picked as H positions. They showed bond lengths close to 1.0 Å and near-tetrahedral angles. All other H positions were calculated from geometric considerations with 1.0 Å bond lengths and were in good agreement with positions observed in the difference Fourier map. The isotropic temperature factor assigned to each H was 1.0 Å<sup>2</sup> larger than that of the atom to which it was bonded,

Table 1. Atomic fractional coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^3$ )

The temperature factor is expressed as:  $\exp[-2\pi^2\{U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k lb^*c^*\}]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Co(1)	1231 (1)	2937 (1)	1000 (1)	55 (1)	68 (1)	64 (1)	30 (1)	-1 (1)	-13 (1)
Cl(1)	4705 (5)	2649 (5)	-542 (3)	187 (5)	148 (4)	97 (3)	-8 (3)	-11 (3)	22 (3)
Cl(2)	3908 (4)	3116 (3)	-2242 (4)	169 (4)	88 (2)	188 (4)	67 (3)	-42 (3)	-3 (3)
Cl(3)	5843 (5)	2529 (5)	-2207 (5)	116 (3)	176 (5)	229 (6)	59 (3)	22 (3)	-40 (4)
O(1)	2502 (7)	3160 (7)	1834 (5)	72 (5)	89 (5)	84 (5)	44 (4)	-13 (4)	-27 (5)
O(2)	869 (7)	4115 (7)	1561 (6)	75 (5)	81 (5)	84 (6)	38 (4)	4 (5)	-15 (4)
O(3)	2497 (7)	4211 (7)	270 (6)	68 (5)	68 (5)	104 (6)	34 (4)	11 (5)	-5 (5)
O(4)	-105 (6)	2546 (6)	178 (5)	57 (4)	73 (4)	61 (4)	33 (4)	5 (3)	6 (4)
O(5)	46 (6)	1656 (7)	1775 (4)	64 (4)	83 (5)	48 (4)	39 (4)	-2 (3)	-3 (4)
O(6)	-1113 (6)	-428 (6)	1903 (5)	64 (4)	76 (5)	57 (4)	15 (4)	8 (3)	8 (4)
N(1)	1461 (8)	1651 (8)	445 (5)	65 (5)	71 (6)	55 (5)	36 (5)	9 (4)	3 (4)
C(1)	3783 (11)	3792 (12)	3126 (8)	81 (8)	95 (9)	84 (8)	23 (7)	-29 (7)	-5 (7)
C(2)	2799 (10)	3852 (10)	2555 (8)	70 (8)	61 (7)	70 (8)	20 (6)	5 (6)	-7 (6)
C(3)	2245 (11)	4536 (10)	2797 (8)	81 (8)	59 (7)	75 (8)	13 (6)	-4 (7)	-32 (6)
C(4)	1351 (11)	4634 (11)	2320 (10)	61 (7)	80 (8)	92 (9)	29 (6)	4 (7)	-9 (7)
C(5)	863 (12)	5495 (12)	2683 (11)	106 (10)	84 (9)	146 (12)	40 (8)	13 (9)	-51 (9)
C(6)	3437 (13)	5582 (12)	-986 (12)	96 (9)	68 (8)	182 (15)	30 (7)	73 (10)	35 (8)
C(7)	2271 (14)	4569 (11)	-507 (11)	106 (11)	51 (7)	123 (12)	45 (8)	42 (10)	2 (7)
C(8)	1122 (14)	4055 (11)	-921 (8)	92 (9)	70 (8)	82 (8)	32 (7)	16 (8)	6 (6)
C(9)	26 (11)	3117 (11)	-593 (8)	92 (9)	79 (8)	72 (8)	49 (8)	11 (7)	-1 (7)
C(10)	-1165 (12)	2639 (13)	-1140 (8)	94 (9)	122 (10)	69 (8)	48 (8)	-14 (7)	-4 (7)
C(11)	-281 (9)	514 (11)	1525 (7)	53 (6)	74 (7)	60 (7)	28 (6)	-7 (5)	-9 (6)
C(12)	386 (8)	397 (9)	671 (6)	57 (6)	78 (7)	43 (5)	25 (5)	2 (5)	0 (5)
C(13)	714 (11)	-659 (9)	747 (7)	105 (8)	59 (6)	61 (7)	45 (6)	7 (6)	-17 (5)
C(14)	1639 (12)	-429 (10)	1500 (7)	102 (9)	83 (7)	59 (7)	66 (7)	11 (6)	-6 (6)
C(15)	1234 (13)	-950 (11)	2374 (8)	114 (10)	92 (9)	55 (7)	60 (8)	11 (8)	7 (7)
C(16)	2100 (16)	-667 (14)	3075 (10)	117 (11)	129 (11)	80 (9)	90 (10)	6 (9)	4 (8)
C(17)	3363 (17)	102 (18)	2935 (13)	128 (15)	190 (17)	117 (12)	113 (13)	-3 (11)	-3 (12)
C(18)	3792 (13)	550 (17)	2073 (14)	87 (10)	197 (16)	158 (16)	107 (11)	-12 (11)	-3 (13)
C(19)	2932 (15)	293 (13)	1350 (9)	118 (11)	119 (10)	110 (11)	91 (9)	46 (9)	24 (8)
C(20)	4481 (11)	2254 (10)	-1699 (8)	89 (8)	65 (7)	90 (8)	16 (6)	-4 (7)	1 (6)

Table 2. Hydrogen-atom parameters: positional coordinates ( $\times 10^3$ ) and isotropic temperature factor parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(C1)1	347	315	364	8.6	H(C10)3	-117	226	-174	8.8
H(C1)2	448	378	279	8.6	H(N1)1	225	175	80	6.0
H(C1)3	425	460	350	8.6	H(N1)2	174	178	-21	6.0
H(C3)	252	503	338	7.5	H(C12)	-16	24	13	6.0
H(C5)1	7	509	305	10.2	H(C13)1	107	-74	15	6.8
H(C5)2	60	585	210	10.2	H(C13)2	-7	-147	89	6.8
H(C5)3	149	629	300	10.2	H(C15)	32	-153	250	7.6
H(C6)1	380	525	-144	10.5	H(C16)	178	-105	370	8.6
H(C6)2	411	615	-54	10.5	H(C17)	399	35	346	11.3
H(C6)3	325	625	-140	10.5	H(C18)	471	106	198	11.4
H(C8)	107	442	-152	7.7	H(C19)	324	61	71	9.0
H(C10)1	-150	325	-140	8.8	H(C20)	386	134	-176	8.2
H(C10)2	-195	207	-79	8.8					

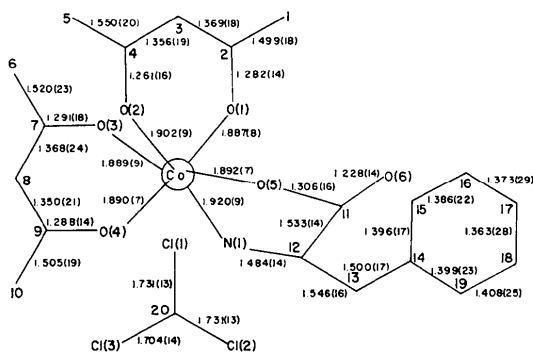


Fig. 1. Bond distances (Å) and atom numbering. Standard deviations are in parentheses.

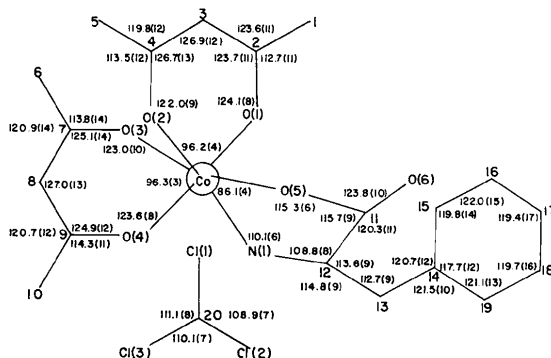


Fig. 2. Bond angles (°).

and neither the temperature factors nor the positions of the H atoms were allowed to vary in subsequent refinement. Anomalous dispersion corrections were made for Co and Cl. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Least-squares refinement was stopped when the largest parameter shift was less than 5% of its standard deviation. The weighted  $R$  for all data at this point was 0.060. The magnitude,  $[(\sum w_F \Delta^2)/(m - n)]^{1/2}$ , where  $m$  is the number of reflections and  $n$  is the number of parameters refined, was 1.28. In a structure factor analysis the average values of  $w_F \Delta^2$  did not show a significant variation with either  $|F_o|$  or  $\sin \theta/\lambda$ .<sup>\*</sup> The final parameters are shown in Tables 1 and 2 and bond distances and angles in Figs. 1 and 2.

## Discussion

Synthesis of  $[\text{Co}(\text{acac})_2(\text{L-phenylalanine})]$  yields

<sup>\*</sup> A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32275 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

diastereoisomers which can be separated by repeated fractional crystallization (Laurie, 1968, 1972). This structure analysis was initiated to confirm that the isomer identification based on optical rotatory dispersion (ORD) and circular dichroism (CD) spectra is valid. From a study of  $\text{Co}^{\text{III}}$  complexes of amino acids, Gillard (1967) has formulated a general empirical rule that the isomer with the D configuration at the metal center shows a dominantly positive Cotton effect for the longest-wavelength, spin-allowed  $d-d$  transition. D configurations were also assigned to the isomers of  $\text{Co}^{\text{III}}$  complexes with hydroxymethylenecamphor (hmc) which show a dominantly positive Cotton effect on the basis of proton resonance spectra and by relating stereoselectivity with molecular models (Dunlap, Gillard & Ugo, 1966). Configuration assignments for the isomers of  $[\text{Co}(\text{acac})_2(\text{L-phenylalanine})]$  were made from the similarities of their ORD and CD spectra with those of  $[\text{Co}(\text{hmc})_3]$ . We have confirmed the configuration assignments of Laurie (1972) by showing that the L configuration obtained for this crystal structure, the  $\Delta$ -*cis* isomer, is for the one with a dominantly negative Cotton effect.

The complex exists as a monomeric species (Fig. 3) with the coordinating atoms forming a distorted octahedral symmetry about the Co ion. The two largest ligand-metal-ligand angles,  $96.3(3)$  and  $96.2(4)^\circ$ , are formed by the chelation of the acac ions and are in good agreement with the values of  $96.2(2)$ – $96.7(2)^\circ$  reported by Kruger & Reynhardt (1974) for  $[\text{Co}(\text{acac})_3]$ . The amino acid chelation forms the smallest angle about Co,  $86.1(4)^\circ$ . This compares quite well with the angles of  $85.8(2)$  and  $84.7(2)^\circ$  formed by the chelation of L-arginine to  $\text{Co}^{\text{III}}$  (Watson, Johnson, Celap & Kamberi, 1972) and the O–Co–N angles of  $84.7(2)$  and  $85.0(2)^\circ$  in  $[\text{Co}(\text{glygly})]$  (Hsu, 1971). Co–O bond lengths range from 1.887(8) to 1.902(9) Å, in good agreement with the 1.883(4)–1.892(4) Å range for like distances reported for  $[\text{Co}(\text{acac})_3]$ . The Co–N distance of 1.920(9) Å is slightly shorter than some reported  $\text{Co}^{\text{III}}$ -amino N distances [1.935(6) and 1.977(6) Å (Watson *et al.*, 1972); 1.949(5) and 1.955(5) Å (Hsu, 1971); and 1.94 Å (Svetich, Voge, Brushmiller & Berends, 1972)], but is in close agreement with the values of 1.937(7) and 1.923(7) Å for the  $\text{Co}^{\text{III}}$  complex of histidine (Thorup, 1975).

Least-squares planes through Co and the acac ions show no deviations from planarity in each plane greater than 0.05 Å. A plane fitted to the chelate ring formed with the amino acid shows N(1), C(11) and O(5) on one side of the plane at 0.14, 0.02 and 0.07 Å, while Co and C(12) are on the other side at 0.10 and 0.12 Å respectively. The phenylalanine residue is in the least-common conformation (Cody, Duax & Hauptman, 1973; van der Helm & Tatch, 1972) with a  $\chi^1[\text{N}(1)\text{C}(12)\text{C}(13)\text{C}(14)]$  of  $62^\circ$ .

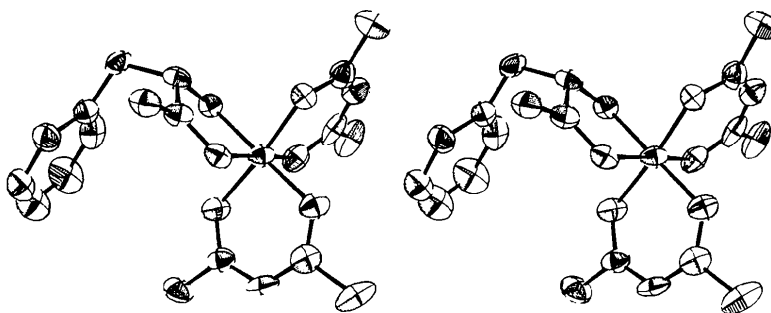


Fig. 3. Stereoscopic view of a single molecule (Johnson, 1965).

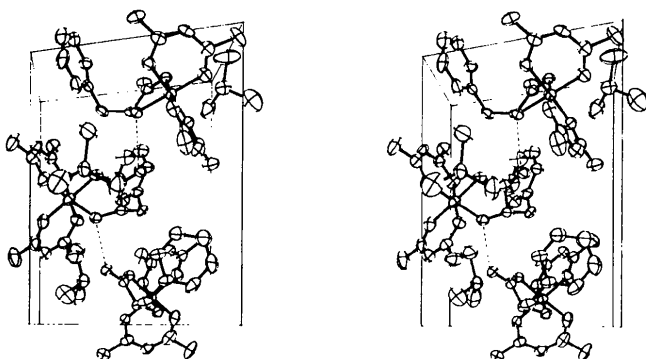


Fig. 4. Molecular packing. The hydrogen bonding is indicated.

The carboxyl O atom not used in chelation is hydrogen bonded to the N atom of the complex related by a  $3_1$  operation. The O...N distance is 2.848 Å with a N-H...O angle of 126°. The chloroform molecule is drawn into one octant of the complex approaching three O atoms, approximately at hydrogen-bond distances (Hamilton & Ibers, 1968). The chloroform H atom is 2.43, 2.52 and 2.44 Å from O(2), O(4) and O(5) respectively, while the distances from the chloroform C atom to the same O atoms are 3.358, 3.253 and 3.249 Å respectively.

The molecular packing is shown in Fig. 4.

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