

# The Crystal Structure of *trans*-Amine- bis(L-histidinato)cobalt(III) Perchlorate Dihydrate

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The crystal structure of the title compound has been determined from single crystal X-ray intensity data collected with a four-circle diffractometer. The crystals are orthorhombic, space group  $P2_12_12_1$ , with four formula units in the unit cell of dimensions  $a = 10.712(4)$  Å,  $b = 11.569(4)$  Å and  $c = 16.049(6)$  Å. The structure has been refined to  $R = 0.069$ . The cobalt atom is octahedrally coordinated to the amino nitrogen atom, an imidazole nitrogen atom, and a carboxylate oxygen atom of each histidinate. The configuration of the complex is *trans*-amine, *i.e.*, the two amine ligands are in *trans* positions, whereas the two imidazole groups as well as the two carboxylate groups are ligated *cis* to each other.

The histinate ion (abbreviated  $\text{his}^-$ ) has three metal binding sites, *viz.* the amino nitrogen atom, an imidazole nitrogen atom and a carboxylate oxygen atom. Several bis-tridentate complexes can be formed with cobalt(III).<sup>1,2</sup> The crystal structure of the *racemic* all-*cis*-[Co(D-his)(L-his)]Br has been determined previously.<sup>3</sup> A violet, a red and an orange isomer of [Co(L-his)<sub>2</sub>]<sup>+</sup> have been separated,<sup>1,2,4</sup> and the spectra of these suggest the structures *trans*-carboxylate (*trans*-c), *trans*-imidazole (*trans*-i), and *trans*-amine (*trans*-a), respectively.<sup>2,4,5</sup>

The present X-ray study was initiated to verify the configuration of the orange isomer in the solid [Co(L-his)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O, suitable crystals of which were produced by Dr. S. Bagger.<sup>2</sup> Recently, crystal linear and circular dichroism spectra of this compound as well as that of Ref. 3 have been investigated.<sup>6</sup>

## EXPERIMENTAL

Crystal symmetry, space group, and preliminary unit cell dimensions were deduced from precession photographs. Later, cell dimensions were refined using diffractometer data.

A single crystal with dimensions approx.  $0.3 \times 0.3 \times 0.3$  mm was used for intensity data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromatized MoK $\alpha$  radiation. Harmonics were excluded by means of a pulse height discriminator in combination with the scintillation detector. All reflections  $hkl$  and  $h\bar{k}l$  in the range  $2.5^\circ < \theta < 27.5^\circ$  were measured applying the  $\omega - 2\theta$  scan technique with  $\Delta\omega = 1.00^\circ + 0.35^\circ \tan \theta$ . The stability of the crystal and the measuring system was verified by frequently remeasuring three reflections. The intensities were corrected for Lorentz and polarization as well as absorption effects. Symmetry equivalent reflections were merged to produce a unique set of 2575 reflections (internal consistency index  $R_{\text{ic}} = \sum |F^2 - \langle F^2 \rangle| / \sum F^2 = 0.028$ ). 2313 of these having  $F^2 > 3\sigma(F^2)$  were used in the structure refinement.

The regular structure analysis was performed using the program system XRAY 72,<sup>7</sup> and the illustrations were produced by means of the program ORTEP.<sup>8</sup> For other calculations, locally written programs were used. Atomic scattering factors for the neutral atoms were taken from International Tables for X-Ray Crystallography.<sup>9</sup>

## CRYSTAL DATA

[Co(C<sub>6</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O, Orthorhombic  
Space group:  $P2_12_12_1$  (No. 19).  
 $a = 10.712(4)$  Å,  $b = 11.569(4)$  Å,  $c = 16.049(6)$  Å  
 $Z = 4$ ,  $M = 502.7$  g mol<sup>-1</sup>  
 $D_m$  (Flotation) =  $1.70$  g cm<sup>-3</sup>,  $D_x = 1.68$  g cm<sup>-3</sup>  
 $\mu$ (MoK $\alpha$ ) =  $10.57$  cm<sup>-1</sup>.

Table 1a. Fractional coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) with estimated standard deviations. The temperature factor is given by  $\exp[-8\pi^2 U(\sin \theta/\lambda)^2]$ .

Atom	x	y	z	U
Co	0.45813(8)	0.28192(7)	0.86178(5)	
O1	0.2988(5)	0.3148(4)	0.9070(3)	0.040(1)
O2	0.0968(6)	0.2945(6)	0.8828(4)	0.054(1)
N1	0.3677(5)	0.2597(5)	0.7581(3)	0.033(1)
N2	0.4390(6)	0.1197(5)	0.8864(4)	0.040(1)
N3	0.4682(8)	-0.0505(7)	0.9395(5)	0.059(2)
Cl	0.2039(6)	0.2811(6)	0.8624(5)	0.039(1)
C2	0.2403(6)	0.2167(7)	0.7828(4)	0.039(1)
C3	0.2413(8)	0.0882(7)	0.7991(5)	0.047(2)
C4	0.3412(7)	0.0505(6)	0.8583(5)	0.044(1)
C5	0.5121(8)	0.0555(8)	0.9333(5)	0.048(2)
C6	0.3586(9)	-0.0565(9)	0.8919(6)	0.059(2)
O11	0.4748(5)	0.4435(4)	0.8360(3)	0.037(1)
O12	0.5752(5)	0.6014(5)	0.8760(4)	0.048(1)
N11	0.5242(6)	0.3279(5)	0.9691(4)	0.037(1)
N12	0.6229(6)	0.2563(5)	0.8191(4)	0.039(1)
N13	0.7762(8)	0.2003(8)	0.7368(5)	0.059(2)
C11	0.5474(7)	0.4982(6)	0.8844(4)	0.039(1)
C12	0.6109(7)	0.4267(6)	0.9522(4)	0.040(1)
C13	0.7366(8)	0.3839(7)	0.9237(5)	0.047(2)
C14	0.7317(7)	0.3105(6)	0.8464(5)	0.042(2)
C15	0.6525(8)	0.1909(7)	0.7542(5)	0.048(2)
C16	0.8277(9)	0.2763(9)	0.7956(6)	0.057(2)
Cl	0.1413(5)	0.4415(3)	0.6208(2)	
O3	0.1591(20)	0.5345(22)	0.5642(14)	0.182(8)
O4	0.1733(20)	0.3340(19)	0.5863(13)	0.166(7)
O5	0.0235(20)	0.4247(20)	0.6403(14)	0.174(7)
O6	0.2200(16)	0.4576(15)	0.6905(11)	0.140(5)
O7	0.4171(9)	0.2547(9)	0.4912(6)	0.084(2)
O8	0.2936(16)	0.4360(15)	0.4074(11)	0.072(4)
O9	0.5058(32)	0.9421(31)	0.1614(22)	0.144(11)

Table 1b. Anisotropic thermal parameters ( $\text{\AA}^2$ ) with estimated standard deviations. The temperature factor is given by  $\exp[-2\pi^2(h a^* U_{11} + \dots + 2 k l b^* c^* U_{23})]$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	0.0297(3)	0.0303(3)	0.0256(3)	-0.0028(3)	-0.0028(3)	0.0010(3)
Cl	0.0653(14)	0.0678(14)	0.0807(17)	0.0049(12)	-0.0115(12)	0.0190(13)

## STRUCTURE DETERMINATION

The structure was solved by conventional heavy atom procedure and refined by full matrix minimization of  $\sum w(|F_o| - |F_c|)^2$ . Anisotropic temperature factors were used for Co and Cl whereas the remaining atoms were given isotropic temperature factors. In the last cycles of refinement the following

weighting function was applied:  $1/w = 1 - 0.0372|F_o| + 0.00134|F_o|^2 - 0.987 \sin \theta/\lambda$ .<sup>10</sup> The final residuals were  $R = \sum \|F_o| - |F_c|\| / \sum |F_o| = 0.069$  and  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.087$ . One of the oxygen atoms has been distributed with equal occupancy on two different positions (O8 and O9), and hydrogen atoms have not been included in this structure determination. Positional and thermal

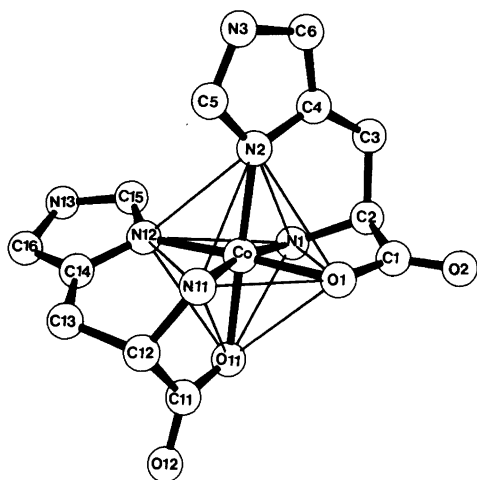


Fig. 1. The structure of the complex ion [Co(L-his)<sub>2</sub>]<sup>+</sup>. Thin lines show the coordination polyhedron.

parameters of the atoms are given in Tables 1a and 1b. A list of observed and calculated structure factors may be obtained from the author upon request.

DISCUSSION

The structure of the complex ion [Co(L-his)<sub>2</sub>]<sup>+</sup> is shown in Fig. 1. Cobalt has octahedral coordination with bonds to the amino nitrogen atom, an imidazole nitrogen atom and a carboxylate oxygen

Table 2. Bond distances (Å) with estimated standard deviations.

Atoms	Distance	Atoms	Distance
Co-N1	1.942(6)	Co-N11	1.936(6)
Co-N2	1.929(6)	Co-N12	1.916(6)
Co-O1	1.894(5)	Co-O11	1.922(5)
C1-O1	1.304(9)	C11-O11	1.268(9)
C1-O2	1.204(9)	C11-O12	1.237(9)
C1-C2	1.529(10)	C11-C12	1.528(10)
C2-N1	1.505(9)	C12-N11	1.497(10)
C2-C3	1.510(12)	C12-C13	1.506(12)
C3-C4	1.497(12)	C13-C14	1.504(11)
C4-C6	1.363(13)	C14-C16	1.371(12)
C4-N2	1.393(10)	C14-N12	1.394(10)
N2-C5	1.315(11)	N12-C15	1.325(10)
C5-N3	1.316(12)	C15-N13	1.359(12)
N3-C6	1.402(14)	N13-C16	1.404(13)
Cl-O3	1.42(2)	Cl-O4	1.40(2)
Cl-O5	1.31(2)	Cl-O6	1.41(2)

atom of each histidinate. The two coordinating imidazole nitrogen atoms are in *cis* positions which is also the case for the carboxylate groups. The amino groups, however, are in *trans* positions. Therefore, the configuration is termed *trans*-amine or *trans-a* (amine rather than amino as viewed from the central metal atom).

Bond distances and bond angles are given in Tables 2 and 3. The corresponding bond distances of the two histidinate moieties generally agree. The most pronounced difference is that between Co-O1 and Co-O11 which amounts to four times its

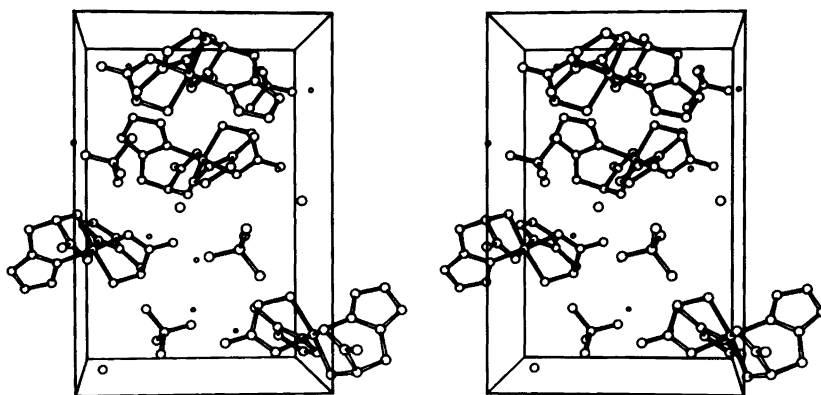


Fig. 2. Stereo view along the *b* axis of the structure. Smaller spheres represent oxygen positions with occupancy 0.5.

Table 3. Bond angles ( $^{\circ}$ ) with estimated standard deviations.

Atoms	Angle	Atoms	Angle
N1-Co-N2	89.6(2)	N11-Co-N12	91.4(3)
N1-Co-O1	84.6(2)	N11-Co-O11	83.7(2)
N2-Co-O1	91.2(2)	N12-Co-O11	89.3(2)
N1-Co-N12	97.6(2)	N11-Co-O1	86.2(2)
N2-Co-N12	91.2(3)	O1-Co-O11	88.3(2)
N1-Co-O11	89.5(2)	N2-Co-N11	97.1(3)
Co-N1-C2	105.7(4)	Co-N11-C12	106.0(4)
Co-N2-C4	124.9(5)	Co-N12-C14	126.0(5)
Co-N2-C5	127.1(6)	Co-N12-C15	126.1(5)
Co-O1-C1	115.6(5)	Co-O11-C11	114.3(4)
O1-C1-O2	123.7(7)	O11-C11-O12	124.3(7)
C2-C1-O1	114.0(6)	C12-C11-O11	116.0(6)
C2-C1-O2	122.3(7)	C12-C11-O12	119.5(7)
C1-C2-N1	106.9(6)	C11-C12-N11	105.4(6)
C1-C2-C3	109.7(6)	C11-C12-C13	111.1(6)
N1-C2-C3	111.4(6)	N11-C12-C13	111.1(6)
C2-C3-C4	113.7(7)	C12-C13-C14	113.9(7)
C3-C4-N2	125.2(7)	C13-C14-N12	122.9(7)
C3-C4-C6	127.8(8)	C13-C14-C16	128.8(8)
C4-N2-C5	108.0(6)	C14-N12-C15	107.7(6)
N2-C5-N3	110.9(8)	N12-C15-N13	110.4(7)
C5-N3-C6	107.7(8)	C15-N13-C16	107.2(8)
N3-C6-C4	106.5(8)	N13-C16-C14	106.6(8)
C6-C4-N2	106.9(7)	C16-C14-N12	108.1(7)
O3-C1-O4	113(1)	O4-C1-O5	101(1)
O3-C1-O5	113(1)	O4-C1-O6	106(1)
O3-C1-O6	109(1)	O5-C1-O6	114(1)

standard deviation. The differences between corresponding bond angles are all less than three times their standard deviation. The cobalt atom lies approximately in the planes of the imidazole rings, the deviations being 0.07 and 0.15 Å. Correspondingly, the Co-N2 and Co-N12 bonds make

angles of 2.0 and 4.3 $^{\circ}$  with their respective imidazole rings.

The major torsion angles of the two histidinate ions are given in Table 4. The largest difference between corresponding angles is 9.1 $^{\circ}$ . The conformations compare well with those found in

Table 4. Torsion angles ( $^{\circ}$ ) with estimated standard deviations in the histidinate groups. The notation is in accordance with IUPAC-IUB rules.<sup>12</sup>

Designations	Atoms	Angle
$\psi^1$	N1-C2-C1-O1	-27.1(8)
$\psi^1$	N11-C12-C11-O11	-27.6(8)
$\psi^2$	N1-C2-C1-O2	155.8(7)
$\psi^2$	N11-C12-C11-O12	157.2(7)
$\chi^{1,1}$	N1-C2-C3-C4	51.4(8)
$\chi^{1,1}$	N11-C12-C13-C14	58.3(8)
$\chi^{1,2}$	C1-C2-C3-C4	-66.7(8)
$\chi^{1,2}$	C11-C12-C13-C4	-58.7(9)
$\chi^{2,1}$	C2-C3-C4-N2	-10.5(11)
$\chi^{2,1}$	C12-C13-C14-N12	-19.6(11)

Table 5. Intermolecular distances shorter than 3.0 Å.

The symmetry operations involved are:

a( $1-x, -\frac{1}{2}+y, 3/2-z$ ); b( $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ );

c( $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$ ); d( $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ ).

Atoms	Distance
N1...O6	2.987(19)
N1...O12(a)	2.892(8)
N3...O7(a)	2.799(14)
N11...O2(c)	2.875(9)
N11...O3(d)	2.952(24)
N13...O8(b)	2.806(19)
O7...O12(a)	2.773(12)
O7...O8	2.822(20)

other histidinate complexes, *i.e.*, a closed form ( $\chi^{1,2}$  about  $-50^\circ$ ) as opposed to the open form ( $\chi^{1,2}$  about  $180^\circ$ ) found in L-histidine.<sup>3,11</sup>

The perchlorate ion is irregular and probably somewhat disordered as indicated by the large values of the thermal parameters of the oxygen atoms (O3, O4, O5 and O6), a feature which is not unusual for perchlorate salts. One of the water molecules is disordered and its oxygen atom has been placed on two different sites (O8 and O9) each with an occupancy of 0.5. Although the present description of the perchlorate ion and the water of hydration may not be quite satisfactory it is not considered essential for this study which has focussed on the complex cation.

The packing of the structure is depicted in Fig. 2. As seen from Table 5 a number of short intermolecular distances suggest hydrogen bonding N—H···O and O—H···O. However, since hydrogen atoms were not located the hydrogen bonding scheme has not been analyzed in any detail.

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