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The Crystal Structure of D-Histidinato-L-histidinatocobalt(III) Bromide

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The crystal structure of the title compound has been determined by X-ray crystallographic methods. The crystals are monoclinic, space group $P2_1/c$, with 4 formula units in the unit cell of dimensions $a = 9.834(4)$ Å, $b = 15.104(11)$ Å, $c = 10.772(7)$ Å, and $\beta = 107.16(2)°$. Intensity data were collected using an automatic equi-inclination diffractometer. The structure has been refined to an R value of 0.057. The cobalt atom is octahedrally coordinated to the amino nitrogen atom, an imidazole nitrogen atom, and a carboxylate oxygen atom of each histidinate group. The coordinating atoms of one histidinate group are in *cis* positions to the corresponding atoms of the other histidinate group, *i.e.*, the configuration is all-*cis*.

This paper reports the three-dimensional crystal structure analysis of D-histidinato-L-histidinatocobalt(III)bromide, $[Co(C_6H_8N_3O_2)_2]Br$. The histidinate ion is shown in Fig. 1 with its three metal binding sites indicated.

The preparation of this compound is described by Bagger, Gibson, and Sørensen.[1] They also present and discuss the visible and proton magnetic resonance spectra which suggest an all-*cis* arrangement of the histidinate groups. The present X-ray investigation was initiated to obtain verification of this configuration. Suitable single crystals were provided by Bagger *et al.*

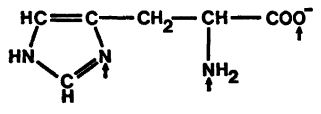

Fig. 1. Histidinate with metal binding sites indicated by arrows.

EXPERIMENTAL

Unit cell and space group. Crystal symmetry and space group were established from precession photographs applying Zr-filtered Mo-radiation. Preliminary unit cell dimensions were also determined from these photographs. Later, the cell dimensions were refined using diffractometer measurements. The observed density of the crystals, as found by the flotation method, is in fair agreement with the calculated value corresponding to four formula units per unit cell. The crystal data are given in Table 1.

Collection of intensity data. A crystal with dimensions approx. $0.1 \times 0.2 \times 0.2$ mm³ was mounted with the b-axis as rotation axis. The intensity measurements were made by means of an automatic equi-inclination diffractometer (Stoe & Cie, Darmstadt, BRD). Mo$K\alpha$-radiation was selected using a graphite monochromator. Harmonics were excluded by means of a pulse height discriminator in combination with the scintillation detector. The relative intensities of reflections $h0l$ through $h16l$ within a hemisphere of $\sin\theta/\lambda < 0.70$ Å^{-1} were measured applying the ω-scan technique. Reflections having averaged net intensities less than three times their standard deviation, calculated from counting statistics, were considered unobserved. This criterion left a total of 2051 unique observations. The intensities were converted to structure factors by conventional Lp correction formulas ignoring the polarization in the

Table 1. Crystal data. Estimated standard deviations are given in parentheses.

Crystal system: Monoclinic (b unique)
Space group: $P2_1/c$ (No. 14)
$a = 9.834(4)$ Å, $b = 15.104(11)$ Å,
$c = 10.772(7)$ Å,
$\beta = 107.16(2)°$, $M = 447.14$ g mol^{-1}, $Z = 4$,
$D_m = 1.93$ g cm^{-3}, $D_x = 1.94$ g cm^{-3},
μ(Mo$K\alpha$) = 37.4 cm^{-1}.

monochromator of the incident beam. No correction for absorption was applied.

Computer programs. The programs V72 and REDIDAT, both written at this laboratory, calculated setting angles for the diffractometer and checked the consistency of diffractometer output data, respectively. The regular structure analysis was performed using the program system X-RAY.[2] Crystal structure illustrations were produced by the program ORTEP.[3] All calculations were carried out on the IBM 370/165 computer and the RC 4000 computer, both situated at the Technical University of Denmark.

STRUCTURE DETERMINATION

A three-dimensional Patterson map was first calculated, but the interpretation of this was not straightforward, and, therefore, direct methods were used to determine the positions of the heavy atoms, cobalt and bromine. The remaining non-hydrogen atoms were found in subsequent electron density maps in the usual heavy atom procedure. Atomic scattering factors for the neutral atoms were generated from the analytical functions given by Cromer and Mann.[4]

The structure thus obtained was then refined by a full matrix minimization of $\sum w(|F_o|-|F_c|)^2$, using first isotropic temperature factors for all atoms and later introducing anisotropic temperature factors for cobalt and bromine. The weighting scheme used was of the type: $1/w = 1 + ((F_o-b)/a)^2$, where a and b were given values minimizing the variation of $\langle w(|F_o|-|F_c|)^2\rangle$ with F_o and sin θ. The actual values

Table 2a. Fractional coordinates and isotropic thermal parameters (Å^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*
Br	0.2194(1)	0.0130(1)	0.5441(1)	
Co	0.2122(1)	0.7289(1)	0.5332(1)	
C1	0.4295(8)	0.8385(6)	0.6535(7)	0.024(2)
C2	0.4407(8)	0.8277(6)	0.5156(7)	0.025(2)
C3	0.5473(9)	0.7530(6)	0.5157(8)	0.028(2)
C4	0.5105(8)	0.6701(6)	0.5719(8)	0.026(2)
C5	0.3752(9)	0.5707(7)	0.6230(8)	0.034(2)
C6	0.5991(10)	0.6038(7)	0.6354(9)	0.041(2)
C11	0.0110(8)	0.6906(6)	0.6513(7)	0.026(2)
C12	−0.0603(8)	0.7544(6)	0.5430(7)	0.024(2)
C13	−0.1454(9)	0.7024(6)	0.4230(8)	0.027(2)
C14	−0.0516(8)	0.6457(5)	0.3675(7)	0.024(2)
C15	0.1383(9)	0.5974(6)	0.3242(8)	0.026(2)
C16	−0.0937(9)	0.5823(6)	0.2756(8)	0.031(2)
N1	0.2979(6)	0.8029(5)	0.4298(6)	0.020(1)
N2	0.3721(7)	0.6490(4)	0.5669(6)	0.023(1)
N3	0.5084(9)	0.5409(6)	0.6651(8)	0.043(2)
N11	0.0533(7)	0.8078(4)	0.5104(6)	0.022(1)
N12	0.0956(7)	0.6567(4)	0.3969(6)	0.021(1)
N13	0.0288(8)	0.5532(6)	0.2502(7)	0.034(2)
O1	0.3230(5)	0.7991(4)	0.6747(5)	0.024(1)
O2	0.5221(6)	0.8777(5)	0.7359(5)	0.034(1)
O11	0.1399(6)	0.6684(4)	0.6556(5)	0.026(1)
O12	−0.0527(7)	0.6602(4)	0.7242(6)	0.033(1)

Table 2b. Anisotropic thermal parameters (Å^2) with estimated standard deviations. The temperature factor is given by exp $[-2\pi^2(h^2a^{*2}U11 + \cdots + 2klb^*c^*U23)]$.

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Br	0.0365(5)	0.0379(6)	0.0277(4)	0.0026(4)	0.0030(3)	0.0062(4)
Co	0.0139(4)	0.0190(6)	0.0117(4)	0.0007(5)	0.0029(3)	−0.0003(4)

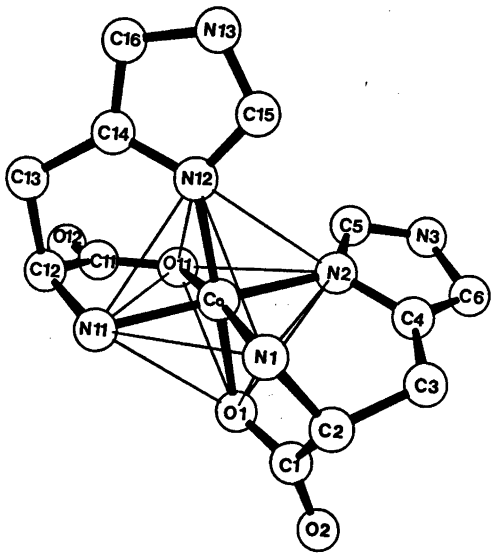

Fig. 2. The structure of the complex ion $[Co(C_6H_8N_3O_2)_2]^+$. The lower right histidinate has D configuration, the other one has L configuration. Thin lines show the coordination polyhedron.

of *a* and *b* were 20 and 45, respectively. The refinement terminated with residuals $R = 0.057$ and $R_w = 0.067$.

Hydrogen atoms have not been included in this structure determination. The final positional and thermal parameters are given in Tables 2a and 2b. A list of observed and calculated structure factors may be obtained from the author upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 2 shows the structure of the complex ion $[Co(C_6H_8N_3O_2)_2]^+$. The cobalt atom is octahedrally coordinated to the amino nitrogen atom, an imidazole nitrogen atom, and a carboxylate oxygen atom of each histidinate group. One of these groups is D-histidinate and the other group is L-histidinate. The configuration is termed all-*cis*, because the coordinating atoms of one histidinate group are all in *cis* positions to the corresponding atoms of the other histidinate group.

Bond distances and angles are given in Tables 3 and 4. A comparison between the two histidinate groups shows that none of the corresponding bond lengths differ significantly (the difference is in each case less than twice its standard deviation). The corresponding bond angles within the histidinate groups are also equal. However, bond angles involving cobalt differ slightly (up to 4°). A small difference in metal–ligand bonding of the two histidinate ions is also seen when considering the imidazole rings. The distances from the cobalt atom to the least squares planes of the imidazole rings are 0.47 and 0.18 Å for D- and L-histidinate, respectively. Correspondingly, the Co–N2 and Co–N12 bonds make angles of 14.0 and 5.8° with their respective imidazole rings. Similar displacements of the metal atom with respect to the imidazole rings have been observed in other histidinate complexes.[5]

The major torsion angles of the two histi-

Table 3. Bond distances (Å) with estimated standard deviations.

Atoms	Distance	Atoms	Distance
Co–N1	1.937(7)	Co–N11	1.923(7)
Co–N2	1.930(7)	Co–N12	1.915(6)
Co–O1	1.912(5)	Co–O11	1.907(6)
C1–O1	1.282(11)	C11–O11	1.298(10)
C1–O2	1.221(9)	C11–O12	1.229(11)
C1–C2	1.531(12)	C11–C12	1.516(11)
C2–N1	1.484(9)	C12–N11	1.502(11)
C2–C3	1.539(12)	C12–C13	1.533(11)
C3–C4	1.482(13)	C13–C14	1.506(13)
C4–C6	1.370(13)	C14–C16	1.351(12)
C4–N2	1.383(11)	C14–N12	1.397(10)
N2–C5	1.324(12)	N12–C15	1.336(11)
C5–N3	1.332(12)	C15–N13	1.317(10)
N3–C6	1.402(15)	N13–C16	1.384(13)

Table 4. Bond angles (°) with estimated standard deviations.

Atoms	Angle	Atoms	Angle
N1–Co–N2	90.0(3)	N11–Co–N12	88.6(3)
N1–Co–O1	84.1(3)	N11–Co–O11	86.0(3)
N2–Co–O1	87.5(3)	N12–Co–O11	89.7(3)
N1–Co–N11	92.5(3)	N2–Co–O11	91.1(3)
N1–Co–N12	98.7(3)	N11–Co–O1	90.5(3)
N2–Co–N12	93.3(3)	O1–Co–O11	87.5(2)
N1–Co–O11	171.4(3)	N2–Co–N11	176.6(3)
N12–Co–O1	177.1(4)		
Co–N1–C2	106.3(5)	Co–N11–C12	105.7(5)
Co–N2–C4	126.9(6)	Co–N12–C14	126.0(6)
Co–N2–C5	123.5(6)	Co–N12–C15	127.6(5)
Co–O1–C1	114.7(5)	Co–O11–C11	114.3(5)
O1–C1–O2	124.6(8)	O11–C11–O12	123.9(7)
C2–C1–O1	114.8(6)	C12–C11–O11	114.6(7)
C2–C1–O2	120.4(8)	C12–C11–O12	121.4(7)
C1–C2–N1	107.8(7)	C11–C12–N11	108.3(6)
C1–C2–C3	108.8(6)	C11–C12–C13	109.7(7)
N1–C2–C3	109.6(7)	N11–C12–C13	109.6(7)
C2–C3–C4	111.8(8)	C12–C13–C14	112.4(6)
C3–C4–N2	122.3(7)	C13–C14–N12	123.9(7)
C3–C4–C6	128.8(8)	C13–C14–C16	127.0(7)
C4–N2–C5	107.4(7)	C14–N12–C15	105.7(6)
N2–C5–N3	110.1(9)	N12–C15–N13	110.7(8)
C5–N3–C6	108.7(8)	C15–N13–C16	108.8(8)
N3–C6–C4	104.8(8)	N13–C16–C14	105.9(7)
C6–C4–N2	108.9(8)	C16–C14–N12	108.9(8)

Table 5. Torsion angles (°) with estimated standard deviations in the histidinate groups. Designations and signs are in accordance with IUPAC-IUB conventions.[6]

Designation	Atoms	Angle (this study)	Angle (Ref. 5)	Angle (Ref. 7)
ψ^2	N1–C2–C1–O2	−163.3(8)	−167	
ψ^2	N11–C12–C11–O12	156.2(7)	167	154.6(5)
χ^1	N1–C2–C3–C4	−64.0(8)	−71	
χ^1	N11–C12–C13–C14	54.9(9)	64	−58.3(6)
$\chi^{2,1}$	C2–C3–C4–N2	28.2(10)	36	
$\chi^{2,1}$	C12–C13–C14–N12	−16.8(11)	−19	56.6(7)

dinate ions are given in Table 5. Numerical differences between corresponding angles are rather small (7–12°). For comparison, the angles in D-histidinato-L-histidinatocobalt(II) dihydrate [5] and in orthorhombic L-histidine [7] are also included in Table 5. The conformations in the two cobalt complexes are very similar, whereas the conformation in histidine is quite different with respect to the angles χ^1 and $\chi^{2,1}$.

The packing of a unit cell is shown in Fig. 3. Apart from weak van der Waals interactions the structure seems to be held together by hydrogen bonds and electrostatic forces. Using Bondi's [8] van der Waals radii for C, N, and O and Pauling's [9] radius for Br^-, the following contact distances are obtained: N···O, 3.07 Å; C···O, 3.22 Å; N···Br^-, 3.50 Å; C···Br^-, 3.65 Å. As apparent from Table 6, some intermolecular distances are fairly short and suggest

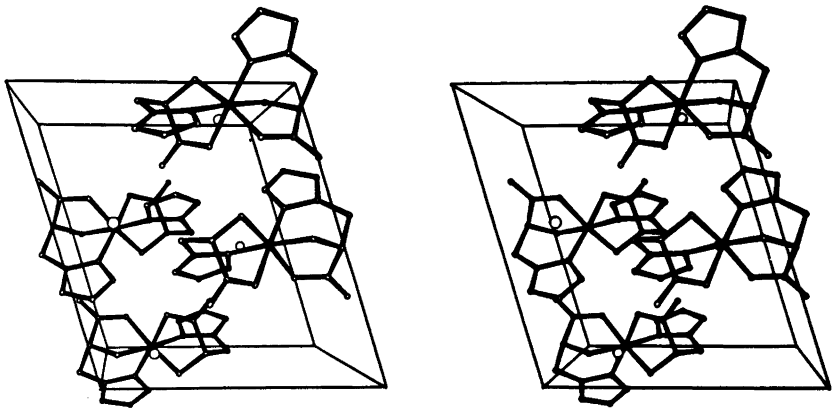

Fig. 3. Stereo view along *b* axis of the structure. Large spheres represent bromide ions.

hydrogen bonds N–H···O and possibly N–H···Br^-. However, a detailed discussion of hydrogen bonds is hardly justifiable, since hydrogen atoms were not located. The close approach between Cl, which has no hydrogen attached, and Br^- can be accounted for by assuming an excess positive charge on Cl leading to considerable Coulomb interaction.

Table 6. Short intermolecular distances (Å) with estimated standard deviations. The symmetry operations involved are: a, $(1-x,y-1/2,3/2-z)$; b, $(x,3/2-y,z-1/2)$; c, $(x,y+1,z)$; d, $(-x,y+1/2,1/2-z)$; e, $(1-x,y+1/2,3/2-z)$; and f, $(x,1/2-y,z-1/2)$.

Atoms	Distance
N3···O2(a)	2.738(12)
N1···O11(b)	2.936(8)
N11···O12(b)	2.987(9)
C15···O1(b)	3.172(11)
Cl···Br(c)	3.342(8)
C16···Br(d)	3.461(9)
N13···Br(d)	3.437(7)
N13···Br(f)	3.449(9)
N11···Br(c)	3.472(7)
N3···Br(e)	3.494(7)

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