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trans-Imidazole isomer of the bis(L-histidinato)cobalt(III) complex

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The title compound, bis(L-histidinato)cobalt(III)–chloride–nitrate–water (1/0.4/0.6/2.5), $[Co(C_6H_8N_3O_2)_2]Cl_{0.4}(NO_3)_{0.6}\cdot 2.5H_2O$, crystallizes as a mixed chloride/nitrate hydrate salt. This crystallographic experiment validates earlier research which concluded that the red chromatographic fraction contains the *trans*-imidazole isomer of the complex. The asymmetric unit contains two complex cations, 0.80-chloride, 1.20-nitrate, and five solvent water molecules.

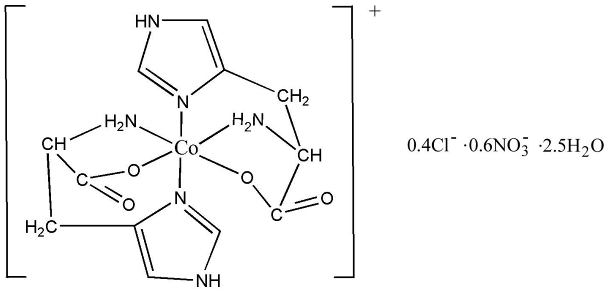
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.007 Å
H-atom completeness 84%
Disorder in solvent or counterion
R factor = 0.038
wR factor = 0.103
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The synthesis and isolation of three geometrical isomers of bis(L-histidinato)cobalt(III) has been reported in the literature (Zompa, 1969; Bagger *et al.*, 1972). The isomers are described by the unique positions occupied by the donor groups of the L-histidine on the octahedral cobalt(III) coordination sites and designated as *trans*-imidazole, *trans*-amine, and *trans*-carboxylate. The angular overlap method, based on electronic spectra (Schmidtke, 1969), and circular dichroism and ^{1}H NMR (Bagger *et al.*, 1972), were used to make tentative structural assignments of the isomers. Only the *trans*-amine isomer has been studied by X-ray crystallography (Thorup, 1979).



(I)

An aqueous mixture of the isomers may be separated by column chromatography into violet, red, and red–orange components by elution with strong acid or salt solutions (hydrochloric acid or potassium bromide) on a Dowex 50W–X4 column and have been assigned *trans*-carboxylate, *trans*-imidazole and *trans*-amine structures, respectively. Crystalline salts of the *trans*-imidazole isomer are obtained by concentrating solutions of the reaction products (see *Experimental*) followed by slow evaporation at room temperature. The electronic spectrum of the dissolved crystalline material shows only a single absorption band at 500 nm and is identical to that of the red chromatographic fraction.

The crystals of the mixed chloride/nitrate salt are monoclinic (space group *C*2) and the asymmetric unit contains two unique complex cations, 0.80-chloride, 1.20-nitrate, and five solvent water molecules. The water molecules are disordered and modeled as discussed in the *Experimental* section. The dichloride and the dinitrate salts have been synthesized in a similar manner to the mixed anion salt, but the crystals are not of sufficient quality for single-crystal X-ray diffraction study.

Both [Co(L-histidine)$_2$]$^+$ cations adopt the *trans*-imidazole configuration and contain the CoN_4O_2 coordination polyhedron in approximately C_{2v} point-group symmetry. The bond distances and angles involving the Co atom are given in Table 1. The Co—N$_I$(imidazole) and Co—N$_a$(amine) bond distances are virtually identical [1.93 (1) and 1.921 (6) Å respective average distances]. The Co—O distance averages 1.90 (2) Å. The Co—N and C—O distances are similar to those reported for the *trans*-isomer (Thorup, 1979), except that, in that case, the Co—N$_a$ distances are 0.02 Å longer than the Co—N$_I$ distances. The structure of [Co(D-histidinato-L-histidinato]cobalt(III) bromide has also been reported (Thorup, 1977) and the Co—N distances vary between 1.937 and 1.915 Å, with no apparent trend in Co—N$_I$ and Co—N$_a$ distances. The Co—O distance averages 1.909 Å in the racemic complex. The bond distances and angles of L-histidine in the *trans*-imidazole isomer are also in agreement with those previously reported for the other isomers. The different geometrical arrangements in the [Co(histidine)$_2$]$^+$ isomers appear to have little impact on bond distances or angles.

The hydrogen bonding in the structure is less clear because the positions of many of the H atoms in the solvent water molecules cannot be located and several of the solvent O atoms occupy partially occupied sites. However, strong hydrogen bonding exists between the complex ions, and between complex ions and solvent, complex ions and nitrate, and nitrate and solvent (see Table 2). The amine and uncoordinated carboxylate O atoms form strong intermolecular bonds (N6—H6N*A*···O8^{ii} and N7—H7*B*···O2^{iii}; symmetry codes as in Table 2). The uncoordinated amine atom of the imidazole ring also forms a strong hydrogen bond with solvent water.

Experimental

The compound reported in this paper was prepared by heating a 40 ml aqueous solution containing [Co(NH$_3$)$_6$]Cl$_3$ (1.00 g, 6.45 mol) and L-histidine (0.862 g, 3.22 mol) on a steam bath for 3 h in the presence of activated charcoal . During heating, the pH was maintained between 5 and 7 by the addition of nitric acid. After filtration, the solution was concentrated and slowly evaporated, yielding large red crystals that analyzed as [Co(L-histidine)$_2$]Cl$_{0.4}$(NO$_3$)$_{0.6}$·2.5H$_2$O. These crystals were suitable for single-crystal X-ray diffraction.

Crystal data

$[Co(C_6H_8N_3O_2)_2]\cdot Cl_{0.4}\cdot(NO_3)_{0.6}\cdot$-
$2.5H_2O$
$M_r = 463.65$
Monoclinic, $C2$
$a = 29.398$ (3) Å
$b = 9.839$ (1) Å
$c = 13.590$ (1) Å
$\beta = 108.189$ (6)°
$V = 3734.4$ (6) Å^3
$Z = 8$
$D_x = 1.65$ Mg m^{-3}

$D_m = 1.65$ Mg m^{-3}
D_m measured by flotation in $CHCl_3$ and CH_2Br_2
Mo $K\alpha$ radiation
Cell parameters from 62 reflections
$\theta = 12.4$–17.1°
$\mu = 1.04$ mm^{-1}
$T = 293$ (2) K
Plate, red
0.5 × 0.4 × 0.2 mm

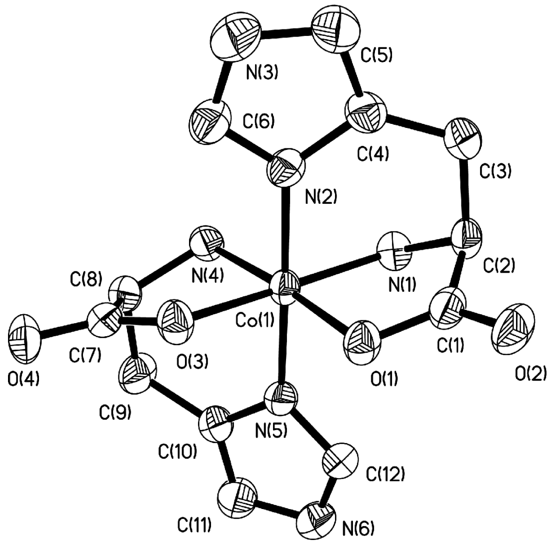


Figure 1
One of the [Co(L-histidine)$_2$]$^+$ cations of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1999)
$T_{min} = 0.769$, $T_{max} = 0.813$
5319 measured reflections
5037 independent reflections
4589 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = -38 \rightarrow 1$
$k = -12 \rightarrow 1$
$l = -16 \rightarrow 17$
3 standard reflections every 75 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 1.08$
5037 reflections
547 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 2.4496P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Absolute structure: Flack (1983), 218 Friedel pairs
Flack parameter = 0.008 (15)

Table 1
Selected geometric parameters (Å, °).

Co1—O3	1.882 (3)	Co2—O5	1.907 (3)
Co1—O1	1.886 (3)	Co2—N7	1.915 (3)
Co1—N4	1.916 (3)	Co2—N8	1.919 (4)
Co1—N1	1.928 (3)	Co2—O7	1.920 (3)
Co1—N2	1.941 (3)	Co2—N10	1.926 (3)
Co1—N5	1.942 (3)	Co2—N11	1.928 (4)
O3—Co1—O1	90.36 (13)	O5—Co2—N7	85.02 (13)
O3—Co1—N4	85.55 (14)	O5—Co2—N8	89.58 (16)
O1—Co1—N1	85.33 (14)	N7—Co2—N8	87.94 (16)
N4—Co1—N1	98.90 (15)	O5—Co2—O7	94.04 (12)
O3—Co1—N2	89.48 (15)	N8—Co2—O7	90.73 (16)
O1—Co1—N2	90.41 (14)	N7—Co2—N10	96.78 (14)
N4—Co1—N2	91.82 (15)	N8—Co2—N10	91.80 (16)
N1—Co1—N2	86.73 (14)	O7—Co2—N10	84.19 (13)
O3—Co1—N5	89.56 (15)	O5—Co2—N11	89.78 (16)
O1—Co1—N5	90.46 (15)	N7—Co2—N11	92.44 (16)
N4—Co1—N5	87.24 (15)	O7—Co2—N11	88.88 (16)
N1—Co1—N5	94.30 (14)	N10—Co2—N11	88.83 (16)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O4$^{\rm i}$	0.90	2.25	3.121 (6)	162
N3—H3NA···O12	0.86	1.97	2.764 (5)	154
N4—H4A···O3$^{\rm i}$	0.90	2.19	2.880 (5)	134
N4—H4A···O1$^{\rm i}$	0.90	2.54	3.219 (5)	133
N4—H4B···O13$^{\rm i}$	0.90	2.12	2.988 (6)	162
N6—H6NA···O8$^{\rm ii}$	0.86	2.18	3.024 (5)	166
N7—H7B···O2$^{\rm iii}$	0.90	2.01	2.845 (5)	154
N7—H7A···O9$^{\rm iv}$	0.90	2.02	2.922 (5)	175
N9—H9NA···O16$^{\rm v}$	0.86	1.96	2.807 (9)	169
N9—H9NA···O17$^{\rm v}$	0.86	1.98	2.811 (17)	162
N10—H10A···O9$^{\rm vi}$	0.90	2.23	3.032 (5)	149
N10—H10B···Cl$^{\rm iii}$	0.90	2.42	3.309 (4)	169
N12—H12N···O14$B^{\rm vii}$	0.86	2.14	2.80 (3)	134
N12—H12N···O14$A^{\rm vii}$	0.86	2.21	2.86 (3)	132
N12—H12N···O6$^{\rm iii}$	0.86	2.36	2.971 (6)	129

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, 1 - z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, -z$; (iv) $x, y, z - 1$; (v) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (vi) $2 - x, y, 1 - z$; (vii) $x, 1 + y, z$.

The structure contains disordered solvent and was modeled using several fractional positions for the O atoms. Because of this disorder no H atoms were included on O atoms with partial occupancy. The region around the Cl^- shows some spurious electron density, probably from partially substituted NO_3^-. A model was employed that added NO_3^- with positional restraints on the atoms and 0.20 occupancy. The Cl^- was assigned 0.80 occupancy, which is in agreement with elemental analysis (Cl: calculated 3.06%, found 2.94%).

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* (Bruker, 1999); software used to prepare material for publication: *XSCANS*.

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