

Mixed cobalt(III) complexes with aromatic amino acids and diamines. III.¹ Absolute structure of Δ -*trans*(O)-(1,2-diaminoethane- κ^2 N,N)bis(*S*-tyrosinato)cobalt(III) chloride tetrahydrate

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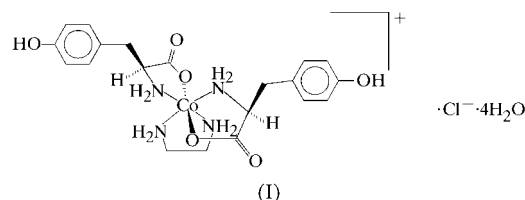
The title compound, [Co(C₉H₁₀NO₃)₂(C₂H₈N₂)]Cl·4H₂O, is one of six possible diastereomers of the (1,2-diaminoethane)-bis(*S*-tyrosinato)cobalt(III) complex. The cobalt(III) ion has an octahedral coordination, with three five-membered chelate rings which have deformed coordination angles and coordinated O atoms in *trans* positions. In comparison with the previously reported crystal structure of the Δ -C₁-*cis*(O) diastereomer [Miodragović *et al.* (2001). *Enantiomer*, **6**, 299–308], the compound presented in this paper has more planar five-membered aminocarboxylate rings. Complex cations, chloride anions and water molecules of crystallization are linked together by a network of hydrogen bonds. The chloride anions lie approximately between two Co atoms and form hydrogen bonds with all coordinated NH₂ groups. In the crystal structure, there is a weak intermolecular $\pi \cdots \pi$ interaction between the phenyl rings.

Comment

The crystal structure of the title compound, (I), represents further work in our investigation of the structures and stereochemistries of cobalt(III) complexes with aromatic amino acids (Miodragović *et al.*, 2001). Complexes of cobalt(III) with aromatic amino acids are interesting as simple model systems for the investigation of non-covalent interactions in which aromatic amino acids are involved (Jitsukawa *et al.*, 1997; Kumita *et al.*, 1998, 2001), because it is known that their side chains, through non-covalent interactions, play an important role in molecular recognition *in vivo* (Fontecave & Pierre, 1996; Ma & Dougherty, 1997; Pomponi *et al.*, 1998;

¹ For part II, see Miodragović *et al.* (2001).

Hofstädter *et al.*, 1999). Mixed bis(*S*-aminocarboxylato)(1,2-diaminoethane)cobalt(III) complexes can occur in the form of three geometrical isomers, and each of them has an optical counterpart.



In a previous paper (Miodragović *et al.*, 2001), we described the synthesis and characterization of five out of six theoretically possible diastereomers of the (1,2-diaminoethane)bis-(*S*-tyrosinato)cobalt(III) complex and presented the X-ray crystal structure of the Δ -C₁-*cis*(O) diastereomer, (II). By a subsequent recrystallization of the diastereomers, high quality single crystals of the Δ -*trans*(O) diastereomer, (I), were obtained, the crystal structure of which is presented in this paper (Fig. 1).

The greatest differences between complexes (I) and (II) are in the different coordinations of the O and N atoms of the *S*-tyrosinate ligands, *viz.* complex (II) has a *cis*(O),*cis*(N) configuration, while complex (I) has a *trans*(O),*trans*(N) configuration, leading to different Co–O bond lengths. Hence, in complex (I), Co–O1 = 1.886 (2) Å and Co–O4 = 1.892 (2) Å, which are shorter than the distances in (II) [Co–O1 = 1.912 (6) Å and Co–O4 = 1.909 (5) Å]. There are also differences in the Co–N(*S*-tyrosinate) bond lengths, *i.e.* in (II), they are different [Co–N1 = 1.939 (7) Å and Co–N1 = 1.965 (6) Å], while in the title complex, (I), they are almost the same [Co–N1 = 1.959 (2) Å and Co–N2 = 1.960 (2) Å].

In addition to the differences in coordination, the complexes also exhibit differences in the conformation of the amino acid chelate rings; namely, although these chelate rings exhibit the same conformation (envelope), in (I), the rings are less puckered. The puckering parameters for the Co–O1–

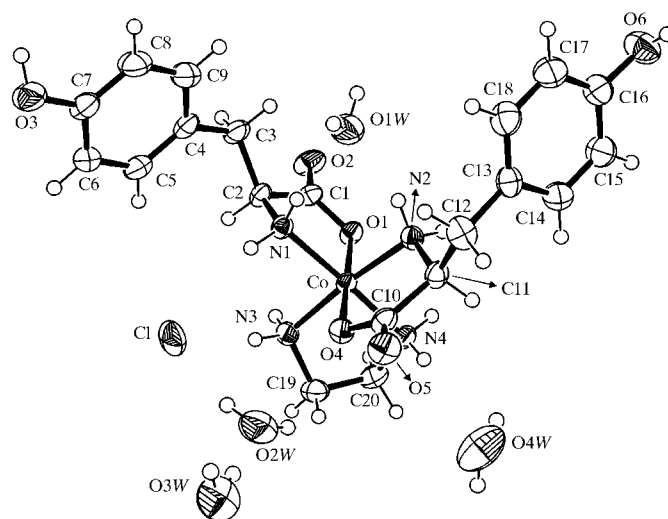


Figure 1
A view of the molecular structure of (I) with the atom labelling. Displacement ellipsoids are shown at the 50% probability level.

C1—C2—N1 (q_2) and Co—O4—C10—C11—N2 (q_2') chelate rings for complex (I) are $q_2 = 0.267(2) \text{ \AA}$ and $q_2' = 0.230(3) \text{ \AA}$, while for complex (II), the puckering parameters are $q_2 = 0.365(8) \text{ \AA}$ and $q_2' = 0.323(7) \text{ \AA}$ (Cremer & Pople, 1975). Such a difference in the planarity of the amino acid chelate rings leads to somewhat smaller H—N1—C2—H and H—N2—C11—H torsion angles in complex (I), *i.e.* the H atoms bonded to chelate-ring N and C atoms are closer to being eclipsed in complex (I).

The puckering parameters of the diamine five-membered chelate ring (Co—N3—C19—C20—N4) are $q_2 = 0.446(3) \text{ \AA}$ and $\varphi = -99.0(3)^\circ$. There are no remarkable differences between the conformations of these chelate rings in the two complexes. In both cases, the chelate ring adopts a conformation which is intermediate between half-chair (with a local pseudo-twofold axis along Co and the midpoint of the C19—C20 bond) and envelope (with a local pseudo-mirror along C19 and the midpoint of the Co—N4 bond).

Due to the formation of three five-membered chelate rings, the coordinate angles deviate markedly from the ideal values of 90 and 180° (Table 1). The crystal structure is stabilized by a large number of hydrogen bonds (Table 2). In the crystal lattice of (I), the chloride anions are located approximately between two neighbouring Co atoms [Co...Cl = 4.120(2) Å and Cl...Coⁱ = 4.132(2) Å; symmetry code: (i) $x - 1, y, z$], forming hydrogen bonds with the NH₂ groups coordinated to the Co atoms. However, in the crystal lattice of complex (II), the complex cations also form intermolecular hydrogen bonds, but these are directly through the —C(O)O and —NH₂ groups from the coordination sphere of the Co atom.

In the crystal lattice of complex (I), there is a weak intermolecular $\pi \cdots \pi$ interaction between the phenyl rings of the amino acid ligands. The phenyl rings are oriented in such a way that the perpendicular distance from the C4—C9 ring to the C13ⁱ—C18ⁱ ring is 3.88 Å, with the closest distance being C8...C17ⁱ of 3.672(6) Å. The distance between the ring centroids is 4.142(3) Å. An unhomogeneous arrangement of π -electron density through the phenyl ring is probably responsible for the mutual orientation of the phenyl rings

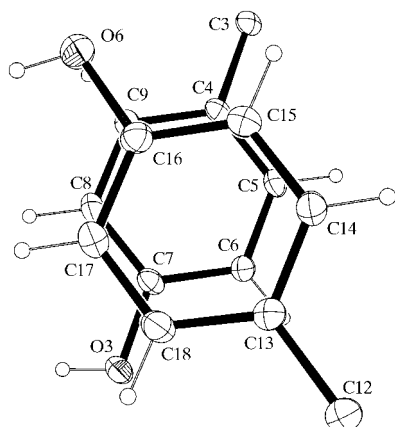


Figure 2
Two projections of the tyrosinate phenyl-ring fragments, showing the $\pi \cdots \pi$ interactions between the rings. Displacement ellipsoids are shown at the 30% probability level.

(Fig. 2) and the parallel-displaced (PD) type of $\pi \cdots \pi$ interactions (Kamishima *et al.*, 2001).

It was subsequently established (*i.e.* it had not been published earlier) that in (II), the phenyl rings of tyrosine are involved in intermolecular C—H... π interactions with the following geometrical parameters: (i) the distance between an H atom bonded to atom C14 and the centre of the C4—C9 aromatic ring is 2.67 Å; (ii) the distance between an H atom bonded to atom C14 and the plane of the C4—C9 aromatic ring is 2.66 Å; (iii) the angle between the line connecting an H atom and the centre of the ring, M , and the normal to the C4—C9 plane is 4.6°; (iv) the angle C14—H... M is 172°.

From the results presented in this paper, it can be concluded that the phenyl rings of amino acids which are present in the same complex, but which have different geometrical configurations, can form two kinds of interactions, namely C—H... π and $\pi \cdots \pi$ interactions. It can also be concluded that in complexes (I) and (II), the complex cations form intermolecular hydrogen bonds of different types. In complex (II), the hydrogen bonds are formed through coordinated —C(O)O and —NH₂ groups, while in complex (I), a chloride anion is located approximately between two complex cations and forms multiple hydrogen bonds with the coordinated NH₂ groups.

Experimental

The title diastereomer was obtained by the action of the *S*-tyrosinate ligand on *trans*-dichlorobis(1,2-diaminoethane)cobalt(III) chloride according to Miodragović *et al.* (2001). Red crystals of (I) were recrystallized from water in a 62% yield.

Crystal data

[Co(C ₉ H ₁₀ NO ₃) ₂ (C ₂ H ₈ N ₂)]Cl·4H ₂ O	$D_x = 1.468 \text{ Mg m}^{-3}$
$M_r = 586.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 8.232(3) \text{ \AA}$	$\theta = 11.3\text{--}15.6^\circ$
$b = 15.348(5) \text{ \AA}$	$\mu = 0.81 \text{ mm}^{-1}$
$c = 10.539(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 94.50(2)^\circ$	Prismatic, red
$V = 1327.4(8) \text{ \AA}^3$	$0.29 \times 0.14 \times 0.11 \text{ mm}$
$Z = 2$	

Table 1
Selected geometric parameters (Å, °).

Co—O1	1.886(2)	O2—C1	1.228(4)
Co—O4	1.892(2)	N1—C2	1.487(4)
Co—N1	1.959(2)	C1—C2	1.526(4)
Co—N2	1.960(2)	O4—C10	1.281(4)
Co—N3	1.950(2)	O5—C10	1.235(4)
Co—N4	1.957(2)	N2—C11	1.499(4)
O1—C1	1.290(4)	C10—C11	1.527(4)
O1—Co—O4	175.55(10)	O4—Co—N4	92.41(10)
O1—Co—N1	84.79(9)	N1—Co—N2	93.81(11)
O1—Co—N2	91.77(10)	N1—Co—N3	90.49(11)
O1—Co—N3	92.66(11)	N1—Co—N4	173.59(11)
O1—Co—N4	90.77(11)	N2—Co—N3	174.08(14)
O4—Co—N1	92.29(10)	N2—Co—N4	90.94(11)
O4—Co—N2	85.07(10)	N3—Co—N4	85.09(11)
O4—Co—N3	90.71(10)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H1N3...Cl	0.90	2.29	3.183 (2)	170
N3—H2N3...O3W ⁱ	0.90	2.24	3.138 (5)	176
N1—H1N1...Cl	0.90	2.58	3.421 (3)	155
N1—H2N1...O1W	0.90	2.05	2.929 (4)	165
N2—H2N2...O1W	0.90	2.08	2.951 (4)	163
N4—H1N4...Cl ⁱⁱ	0.90	2.38	3.202 (3)	152
N2—H1N2...Cl ⁱⁱ	0.90	2.46	3.311 (2)	158
N4—H2N4...O2 ⁱⁱⁱ	0.90	2.06	2.929 (3)	162
O3—H1O3...O5 ^{iv}	0.85	2.10	2.818 (3)	142
O6—H1O6...O3W ^v	0.85	2.33	2.599 (4)	98
O1W—H11W...O3 ⁱⁱ	0.85	1.96	2.784 (4)	165
O1W—H21W...O6 ^{vi}	0.85	1.93	2.758 (4)	163
O2W—H12W...Cl	0.85	2.46	3.263 (4)	157
O2W—H22W...O4	0.85	2.48	3.030 (4)	123
O3W—H13W...O2W	0.85	1.85	2.699 (5)	176
O3W—H23W...O6 ^{vii}	0.85	2.24	2.599 (4)	105
O4W—H14W...O1 ⁱⁱⁱ	0.85	2.17	2.830 (4)	134
O4W—H24W...O3W ⁱⁱ	0.85	2.18	2.815 (5)	132

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

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction: Gaussian
(Spek, 1990, 1998)
 $T_{\min} = 0.882, T_{\max} = 0.926$
11 424 measured reflections
5323 independent reflections
4768 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.088$
 $S = 1.10$
5323 reflections
325 parameters
H-atom parameters constrained

$R_{\text{int}} = 0.011$
 $\theta_{\text{max}} = 27.0^\circ$
 $h = 0 \rightarrow 10$
 $k = -18 \rightarrow 18$
 $l = -13 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 0.7052P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
Absolute structure: (Flack, 1983)
Flack parameter = $-0.008(12)$

All H atoms of the complex cation were placed at calculated positions (C—H = 0.93–0.98 Å and N—H = 0.90 Å) using a riding model and isotropic displacement parameters were set equal to 1.2 times the equivalent isotropic displacement parameter of the parent atoms. Water and hydroxyl H-atom positions were determined by the *HYDROGEN* program (Nardelli, 1999) and were refined using a riding model with a fixed O—H bond length of 0.85 Å; isotropic displacement parameters were set equal to 1.5 times the equivalent

isotropic displacement parameter of the parent atoms. It should be noted that all calculated data for water and hydroxyl H atoms are based on an approximate model. A Gaussian-type absorption correction based on the crystal morphology was applied (Spek, 1990, 1998).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1562). Services for accessing these data are described at the back of the journal.

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