

Diastereoisomeric β -ethyl aspartate–cobalt(III) complexes: $\Lambda(+)$ ₅₇₈⁻ and $\Delta(-)$ ₅₇₈-bis(ethane-1,2-diamine)-[β -ethyl (*S*)-aspartato]cobalt(III) bis(perchlorate) monohydrate

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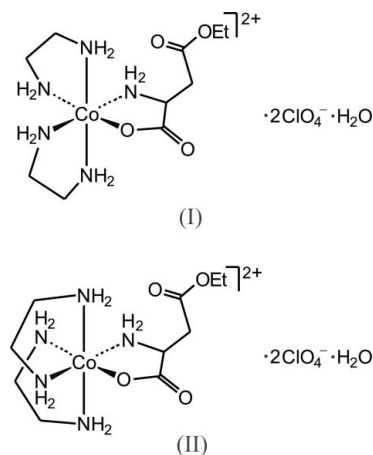
The structures of the diastereoisomers $\Lambda(+)$ ₅₇₈⁻, (I), and $\Delta(-)$ ₅₇₈-bis(ethane-1,2-diamine)[β -ethyl (*S*)-aspartato- κ^2N,O^1]-cobalt(III) bis(perchlorate) monohydrate, (II), both $[\text{Co}(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4)(\text{C}_2\text{H}_8\text{N}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, are compared. In both structures, the ester group of the amino acid side chain is engaged only in intramolecular hydrogen bonding to coordinated amine groups. This interaction is stronger in (I) and correlates with previously observed diastereoisomeric equilibrium ratios for related metal complex systems in aqueous media. The two perchlorate anions of (II) are located on twofold axes. Both perchlorates in (I) and one of the perchlorates in (II) are affected by disorder. Both structures exhibit extensive three-dimensional hydrogen-bonding networks.

Comment

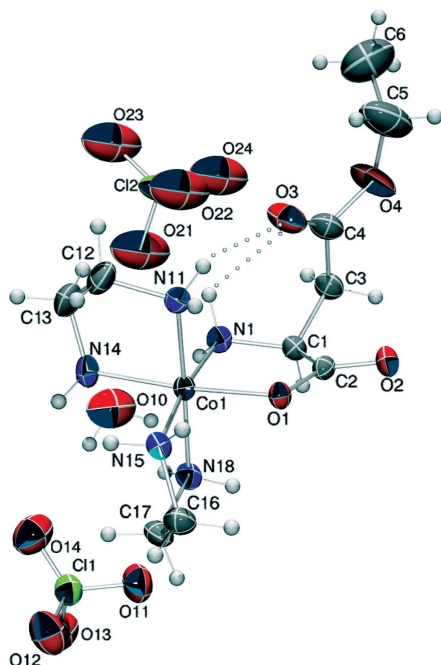
Octahedral Δ/Λ -bis(ethane-1,2-diamine)[(*R/S*)- α -amino acidato- κ^2N,O]cobalt(III) complexes typically comprise two stereogenic centres, the metal and the α -C atom of the amino acid. The diastereoisomeric equilibrium ratio, $K_c = [(\Delta-S, \Lambda-R)]/[(\Delta-R, \Lambda-S)]$, has been determined in 0.010 M NaOH at 298 K for a number of such systems, and values vary with the coordinated amino acid: 0.67 (3) for aspartic acid (Asp), 0.77 (2) for 2,3-diaminopropanoic acid ($A_2\text{pr}$), 0.85 (3) for glutamic acid (Glu), 1.00 (2) for alanine (Ala), 1.2 (1) for phenylalanine (Phe) and 1.9 (1) for valine (Val) (Buckingham *et al.*, 1990; Barfod *et al.*, 1999). Even though these values evince modest levels of selectivity, it is notable that K_c is less than 1 only for those systems which carry side chains with potential hydrogen-bond acceptor sites. Thus, in these instances, the (Δ -*R*, Λ -*S*) diastereoisomer is preferred over the (Δ -*S*, Λ -*R*) diastereoisomer, whereas the opposite preference

applies for systems with bulky apolar side chains. Clearly, such preferences (in solution) are governed to a large extent by a number of intramolecular interactions, but at present it is unclear which interactions are decisive in determining these preferences. Crystal structures of relevant complexes, for example, $\Lambda(+)$ ₄₉₅⁻[Co(en)₂{*S*-Glu(O⁻)O}]ClO₄ (en is ethane-1,2-diamine; Gillard *et al.*, 1970), $\Lambda(+)$ ₅₇₈⁻[Co(en)₂{*S*-Asp(OH)O}](ClO₄)₂ (Barfod *et al.*, 1999) and *rac*-(Δ -*R*, Λ -*S*)-[Co(en)₂{O₂CCH[CH(CO₂Et)₂]NH₂}]ClO₄)₂ (Bendahl *et al.*, 2002), reveal firm intramolecular hydrogen-bonding interactions from coordinated ligand amine groups to side-chain acceptor sites. However, in the structure of the asparagine complex, Λ -[Co(en)₂(*S*-AsnO)]I_{1.6}(NO₃)_{0.4}, the amino acid side chain is not engaged in intramolecular hydrogen bonding with coordinated ethane-1,2-diamine (Keyes *et al.*, 1976). These structures each represent only one of two possible diastereoisomers and, incidentally, this is the thermodynamically favoured diastereoisomer (Δ -*R*, Λ -*S*) in all four instances. Investigations aimed at elucidating the origins of the stability preferences observed in solution for such systems through structural comparison of both diastereoisomers have not yet been published.

The title β -ethyl-(*S*)-aspartate complexes, *viz.* Λ -form (I) and Δ -form (II), constitute such a diastereoisomeric pair. The crystals of (I) and (II) are constitutionally identical, thus providing an optimal basis for comparison. The two structures are illustrated in Figs. 1 and 2, respectively, and selected interatomic distances are given in Tables 1 and 3.



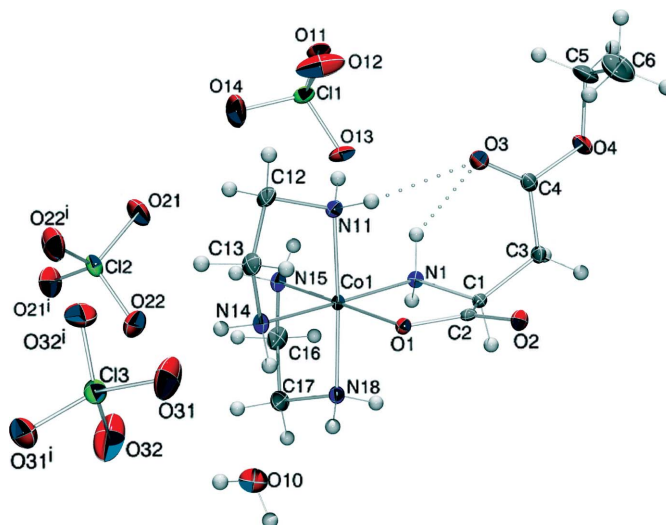
Both structures are characterized by extensive three-dimensional hydrogen-bonding networks (Tables 2 and 4), the only hydrogen-bond donors being the coordinated primary amine groups and the water molecules. The amino acid side chain carries only one hydrogen-bond acceptor, namely the ester carbonyl O atom, but this is not engaged in intermolecular hydrogen bonding. Thus, it is noteworthy that in both structures the ester carbonyl O atoms are only intramolecularly hydrogen bonded to the amine group of the amino acid ligand and to the nearest amine group of one ethane-1,2-diamine ligand (Fig. 3). The interaction of the ester carbonyl group with the amine group of the amino acid ligand results in similar N1...O3 distances in both structures, but the two structures differ with respect to the intramolecular


Figure 1

A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor disorder components of the anions have been omitted for clarity. Dotted lines illustrate the intramolecular hydrogen bonds.

hydrogen-bonding to the nearest ethane-1,2-diamine ligand. Whereas the $N11 \cdots O3(\text{carbonyl})$ distances are identical in the two structures, the associated $H11 \cdots O3$ distances are notably different [in (I), $H11B \cdots O3 = 2.15 \text{ \AA}$; in (II), $H11A \cdots O3 = 2.48 \text{ \AA}$]. From Fig. 3(a), it is evident that the ethane-1,2-diamine chelate is optimally positioned relative to the amino acid ligand, pointing the $N11-H11B$ bond almost directly towards ester carbonyl atom $O3$, allowing the shorter, almost linear, hydrogen bond, consistent with a stronger interaction (Jeffrey, 1997). This is a consequence of the (Δ - S) relative absolute configuration of the complex of this structure. By contrast, in (II), the (Δ - S) relative configuration (Fig. 3b), neither of the relevant ethane-1,2-diamine $N11-H11$ bonds points directly towards the ester carbonyl O atom in a manner similar to the situation for (I). This supports the notion that (I) displays the stronger interaction.

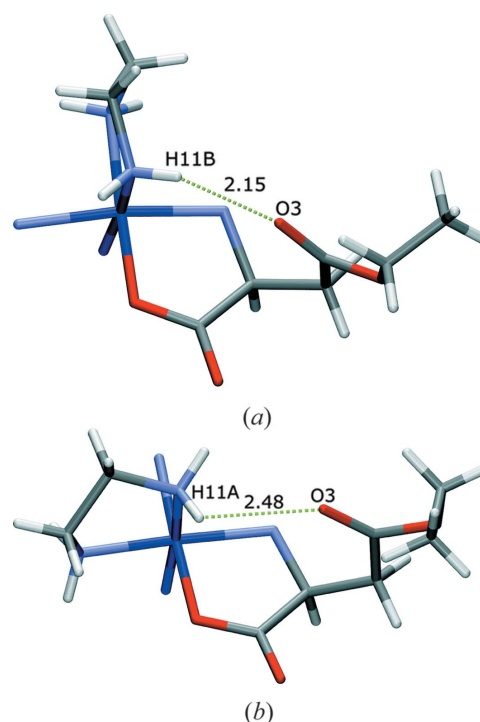
Even though the diastereomeric equilibrium ratio has not been determined in water for the two molecular diastereoisomers of this study (the ester would hydrolyse under the basic conditions required for attaining equilibrium), the observed structural features implying (I) to be the more stable diastereoisomer correlate with the stereochemical preferences observed in aqueous equilibrium studies of complexes bearing polar side chains, as outlined in the introduction (Buckingham *et al.*, 1990; Barfod *et al.*, 1999). The decisive hydrogen-bonding interactions of the amino acid side chains of (I) and (II) are all intramolecular and evidently not much governed by the 'intermolecular' situation within the crystal structure. Thus, the present structures may serve to identify the likely decisive interaction governing the generally observed preferences in solution in the case of similar amino


Figure 2

A view of the molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The minor disorder components of the anions have been omitted for clarity. Dotted lines illustrate the intramolecular hydrogen bonds. [Symmetry code: (i) $y, x, -z$.]

acid complexes with hydrogen-bond accepting side chains. The fact that amino acid complexes with nonpolar side chains display the opposite diastereoisomer stability preference remains unexplained, but since they lack hydrogen-bond acceptors in the side chains, weaker interactions must apply in these instances.

The insight provided by the present study is important for future application of the *cis*-bis(ethane-1,2-diamine)cobalt(III)


Figure 3

Highlighted views of the hydrogen bond between the ester carbonyl group and the amine group of the amino acid ligand in (a) (I) and (b) (II).

moiety as a 'chiral handle' in stereoselective syntheses of amino acids (Hammershøi *et al.*, 1984; Curtis *et al.*, 1987; Drok *et al.*, 1993; Bendahl *et al.*, 1996, 2002; Laval *et al.*, 2002).

Experimental

Complexes (I) and (II) were synthesized and crystallized from water as described by Barfod *et al.* (1999). **Caution!** Although we experienced no difficulty with the perchlorate salts described here, these should be treated as potentially explosive and handled accordingly.

Compound (I)

Crystal data

[Co(C₆H₁₀N₂O₄)(C₂H₈N₂)₂]
(ClO₄)₂·H₂O $\beta = 113.572 (4)^\circ$
 $V = 1096.04 (9) \text{ \AA}^3$
 $M_r = 556.20$ $Z = 2$
Monoclinic, $P2_1$ Mo $K\alpha$ radiation
 $a = 11.6507 (4) \text{ \AA}$ $\mu = 1.10 \text{ mm}^{-1}$
 $b = 8.7600 (5) \text{ \AA}$ $T = 298 \text{ K}$
 $c = 11.7169 (6) \text{ \AA}$ $0.35 \times 0.14 \times 0.13 \text{ mm}$

Data collection

Nonius KappaCCD area-detector 31975 measured reflections
diffractometer 4996 independent reflections
Absorption correction: integration 4684 reflections with $I > 2\sigma(I)$
(Gaussian integration; Coppens, 1970) $R_{\text{int}} = 0.033$
 $T_{\text{min}} = 0.675$, $T_{\text{max}} = 0.898$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$ H-atom parameters constrained
 $wR(F^2) = 0.139$ $\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
 $S = 1.05$ $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
4996 reflections Absolute structure: Flack (1983),
285 parameters with 2329 Friedel pairs
161 restraints Flack parameter: 0.01 (2)

Compound (II)

Crystal data

[Co(C₆H₁₀N₂O₄)(C₂H₈N₂)₂]
(ClO₄)₂·H₂O $V = 4226.1 (2) \text{ \AA}^3$
 $M_r = 556.20$ $Z = 8$
Tetragonal, $P4_32_12$ Mo $K\alpha$ radiation
 $a = 9.2898 (3) \text{ \AA}$ $\mu = 1.14 \text{ mm}^{-1}$
 $c = 48.9696 (14) \text{ \AA}$ $T = 122 \text{ K}$
 $0.20 \times 0.19 \times 0.07 \text{ mm}$

Data collection

Nonius KappaCCD area-detector 84126 measured reflections
diffractometer 4818 independent reflections
Absorption correction: integration 4583 reflections with $I > 2\sigma(I)$
(Gaussian integration; Coppens, 1970) $R_{\text{int}} = 0.055$
 $T_{\text{min}} = 0.810$, $T_{\text{max}} = 0.924$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$ H atoms treated by a mixture of
 $wR(F^2) = 0.064$ independent and constrained
 $S = 1.05$ refinement
4818 reflections $\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$
302 parameters $\Delta\rho_{\text{min}} = -0.87 \text{ e \AA}^{-3}$
5 restraints Absolute structure: Flack (1983),
with 1893 Friedel pairs
Flack parameter: $-0.017 (11)$

Table 1

Selected bond lengths (Å) for (I).

Co1—O1	1.883 (3)	O2—C2	1.231 (5)
Co1—N1	1.960 (3)	O3—C4	1.176 (8)
Co1—N11	1.959 (4)	C1—C2	1.511 (6)
Co1—N14	1.957 (4)	C1—C3	1.525 (6)
Co1—N15	1.957 (3)	C3—C4	1.481 (7)
Co1—N18	1.969 (3)	C4—O4	1.330 (7)
N1—C1	1.485 (6)	O4—C5	1.480 (13)
O1—C2	1.294 (5)	C5—C6	1.516 (5)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<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>
N1—H1 <i>B</i> ···O3	0.90	2.36	2.909 (5)	119
N1—H1 <i>A</i> ···O10	0.90	2.38	3.205 (7)	152
N1—H1 <i>B</i> ···O22	0.90	2.29	3.147 (14)	160
N1—H1 <i>B</i> ···O21 <i>A</i>	0.90	2.64	3.10 (2)	113
N11—H11 <i>A</i> ···O2 ⁱ	0.90	2.13	2.985 (5)	158
N11—H11 <i>B</i> ···O3	0.90	2.15	3.013 (6)	160
N14—H14 <i>A</i> ···O10	0.90	2.24	3.099 (8)	159
N15—H15 <i>A</i> ···O2 ⁱ	0.90	2.03	2.880 (5)	157
N15—H15 <i>B</i> ···O11 ⁱⁱ	0.90	2.32	3.127 (6)	149
N18—H18 <i>B</i> ···O12 ⁱⁱⁱ	0.90	2.21	3.113 (7)	176
O10—H10 <i>A</i> ···O14	0.86	2.17	3.017 (15)	173
O10—H10 <i>A</i> ···O14 <i>A</i>	0.86	1.95	2.778 (19)	165
O10—H10 <i>B</i> ···O23 ^{iv}	0.86	2.16	3.01 (2)	173
O10—H10 <i>B</i> ···O22 <i>A</i> ^{iv}	0.86	2.40	2.99 (2)	127

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

Table 3

Selected bond lengths (Å) for (II).

Co1—O1	1.8948 (14)	O2—C2	1.234 (2)
Co1—N1	1.9552 (16)	O3—C4	1.206 (3)
Co1—N11	1.9586 (17)	C1—C2	1.521 (3)
Co1—N14	1.9655 (17)	C1—C3	1.519 (3)
Co1—N15	1.9600 (17)	C3—C4	1.503 (3)
Co1—N18	1.9575 (18)	O4—C4	1.338 (2)
N1—C1	1.488 (2)	O4—C5	1.455 (3)
O1—C2	1.296 (2)	C5—C6	1.496 (4)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

<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>
N1—H1 <i>A</i> ···O2 ⁱ	0.92	2.19	2.979 (2)	144
N1—H1 <i>A</i> ···O12 ⁱⁱ	0.92	2.51	3.034 (3)	117
N1—H1 <i>B</i> ···O13	0.92	2.39	3.124 (2)	137
N1—H1 <i>B</i> ···O3	0.92	2.42	2.969 (2)	119
N11—H11 <i>A</i> ···O11 ⁱⁱⁱ	0.92	2.20	3.040 (2)	151
N11—H11 <i>A</i> ···O3	0.92	2.48	3.007 (2)	117
N11—H11 <i>B</i> ···O13	0.92	2.20	3.054 (2)	154
N11—H11 <i>B</i> ···O12	0.92	2.35	3.133 (3)	143
N14—H14 <i>A</i> ···O22	0.92	2.12	3.034 (2)	171
N14—H14 <i>B</i> ···O10	0.92	2.19	2.979 (3)	143
N15—H15 <i>A</i> ···O21	0.92	2.30	3.151 (3)	153
N15—H15 <i>A</i> ···O22	0.92	2.34	3.129 (3)	143
N15—H15 <i>B</i> ···O13	0.92	2.13	2.982 (2)	153
N18—H18 <i>A</i> ···O2 ⁱ	0.92	2.12	2.931 (2)	146
N18—H18 <i>A</i> ···O11 ^{iv}	0.92	2.55	3.164 (2)	124
N18—H18 <i>B</i> ···O10	0.92	2.36	3.151 (3)	145
O10—H10 <i>A</i> ···O32	0.80 (2)	2.25 (2)	2.944 (6)	146 (3)
O10—H10 <i>B</i> ···O14 ^{iv}	0.81 (2)	2.56 (3)	3.004 (3)	116 (3)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{4}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{4}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{4}$; (iv) $x, y + 1, z$.

The data set for (I) obtained at 298 K was chosen for refinement, since crystals of (I) disintegrated upon cooling to ~253 K and a tentative data set collected at 273 K showed signs of deterioration, evidenced by data of poor quality.

A distance restraint of 1.540 (5) Å was applied for C5–C6 in (I) to obtain a realistic bond length. For both structures, H atoms were located in difference Fourier maps and included in the refinement as constrained idealized atoms riding on the parent atom, with C–H = 0.96 (CH₃), 0.97 (CH₂) or 0.98 Å (CH) and N–H = 0.90 Å in (I), and C–H = 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (CH) and N–H = 0.92 Å in (II), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. In the final refinement, the coordinates of the H atoms of the solvent water molecule in (I) had to be fixed, with O–H = 0.85 and 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The H atoms of the solvent water molecule in (II) were refined as semi-free with a distance restraint, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Both perchlorate anions of (I) are disordered; this disorder was resolved by refining two of the O atoms on Cl1 in two positions, with site-occupancy factors of 0.546 (9) and 0.454 (9). In the case of the second perchlorate ion, the entire anion was refined in two positions, with site-occupancy factors of 0.596 (9) and 0.404 (9) and with equal anisotropic displacement parameters for all O atoms. Furthermore, the perchlorates were restrained in an approximate tetrahedral geometry.

In (II), the Cl1 perchlorate anion is in a general position, but the other two, centred at Cl2 and Cl3, are located on the crystallographic twofold axis. Furthermore, one of these perchlorates is disordered. This disorder was resolved by refining the O atoms on Cl3 in two positions, with site-occupancy factors of 0.565 (13) and 0.435 (13).

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3040). Services for accessing these data are described at the back of the journal.

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