

Structures of three *cis*- $\beta_1$  and three *cis*- $\beta_2$  isomers of [Co(trien)(aminoacidato)]<sup>2+</sup> complexesJiwen Cai,<sup>a\*</sup> Xiaopeng Hu,<sup>b</sup>  
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The crystal structures and absolute configurations of three *cis*- $\beta_1$  and three *cis*- $\beta_2$  isomers of [Co(trien)(L-aminoacidato)]<sup>2+</sup>, namely  $\beta_1$ - $\Lambda$ (*SSS*)( $\lambda\lambda\delta$ )/( $\lambda\delta\delta$ )-[Co(trien)(L-isoleucinato)]-(ClO<sub>4</sub>)<sub>2</sub>, L-isoleucinato(triethylenetetramine)cobalt(III) diperchlorate (1),  $\beta_1$ - $\Lambda$ (*SRS*)( $\lambda\delta\lambda$ )-[Co(trien)(L-valinato)](ClO<sub>4</sub>)<sub>2</sub>, L-valinato(triethylenetetramine)cobalt(III) diperchlorate (2),  $\beta_1$ - $\Delta$ (*RSS*)( $\delta\lambda\delta$ )-[Co(trien)(L-pyroglutamato)]ClO<sub>4</sub>, L-pyroglutamato(triethylenetetramine)cobalt(III) perchlorate (3),  $\beta_2$ - $\Delta$ (*RRS*)( $\delta\delta\lambda$ )-[Co(trien)(L-isoleucinato)]L<sub>2</sub>·H<sub>2</sub>O, L-isoleucinato(triethylenetetramine)cobalt(III) diiodide monohydrate (4),  $\beta_2$ - $\Delta$ (*RRS*)( $\delta\delta\lambda$ )-[Co(trien)(L-isoleucinato)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, L-isoleucinato(triethylenetetramine)cobalt(III) diperchlorate dihydrate (5), and  $\beta_2$ - $\Lambda$ (*SSS*)( $\delta\lambda\lambda$ )[Co(trien)(L-leucinato)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, L-leucinato(triethylenetetramine)cobalt(III) diperchlorate dihydrate (6), have been determined. Both  $\beta_1$  and  $\beta_2$  isomers form inter-cation hydrogen-bonding interactions through double or triple hydrogen bonds which link the cations into helices. However, the motifs of the interactions are different in  $\beta_1$  and  $\beta_2$  isomers, resulting in different packing structures. A localized hydrophobic area is observed in the packing structure of (1), a unique feature amongst these six structures. This work describes the first synthesis of the  $\beta_1$  isomer by direct reaction between amino acids and *cis*- $\alpha$ -[Co(trien)Cl<sub>2</sub>]Cl in mildly basic solution.

## 1. Introduction

Since the discovery that the cation [Co(trien)(OH)(H<sub>2</sub>O)]<sup>2+</sup> can catalyze the hydrolysis of amino acid esters and peptides (Collman & Buckingham, 1963; Buckingham *et al.*, 1967, 1974; Kimure *et al.*, 1970; Gillard & Phipps, 1970), studies have been undertaken to further investigate the mechanism of these processes (Girgis & Legg, 1972; Bentley & Creaser, 1974; Sutton & Buckingham, 1987). A few crystal structures of complexes with the general formula [Co(trien)(aminoacidato)]<sup>2+</sup> have been reported on cleavage products and other structural systems sharing common features (Anderson *et al.*, 1977; Buckingham *et al.*, 1974, 1975; Freeman & Maxwell, 1970; Freeman *et al.*, 1970; Eduok *et al.*, 1994). Energy minimization calculations based upon the crystal structures were performed (Buckingham *et al.*, 1970, 1974, 1975; Yamaguchi, Yano *et al.*, 1980) to explain, and predict, the configurations and conformations adopted by the final coordination products. The stereochemistry of the coordination compounds has a wealth of variation arising from the absolute configuration of the cobalt center, the absolute configuration of the two secondary amino N atoms of trien upon coordination, the strain energy of the three N—C—N chelate rings of the trien, as well as packing and counteranion effects. It was

**Table 1**

Experimental details.

	(1)	(2)	(3)
<b>Crystal data</b>			
Chemical formula	C <sub>12</sub> H <sub>30</sub> CoN <sub>5</sub> O <sub>2</sub> <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup>	C <sub>11</sub> H <sub>28</sub> CoN <sub>5</sub> O <sub>2</sub> <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup>	C <sub>11</sub> H <sub>23</sub> CoN <sub>5</sub> O <sub>3</sub> <sup>+</sup> ·ClO <sub>4</sub> <sup>-</sup>
Chemical formula weight	534.24	520.21	431.72
Cell setting, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub>	Orthorhombic, <i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.7972 (13), 8.8272 (11), 11.9248 (14)	8.9877 (7), 8.8829 (7), 12.8157 (10)	9.4009 (5), 13.3659 (8), 13.6588 (8)
$\beta$ (°)	110.794 (2)	101.577 (1)	90
<i>V</i> (Å <sup>3</sup> )	1062.5 (2)	1002.35 (14)	1716.25 (17)
<i>Z</i>	2	2	4
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.670	1.724	1.671
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	1.119	1.184	1.201
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form, color	Block, red	Block, red	Block, red
Crystal size (mm)	0.40 × 0.30 × 0.30	0.30 × 0.25 × 0.23	0.30 × 0.25 × 0.23
<b>Data collection</b>			
Diffractionmeter	Bruker SMART CCD area detector	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Data collection method	$\varphi$ and $\omega$ scans	$\varphi$ and $\omega$ scans	$\varphi$ and $\omega$ scans
No. of measured, independent and observed reflections	6477, 4129, 3818	6012, 3835, 3672	10 571, 3939, 3573
Criterion for observed reflections	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.0291	0.0220	0.0438
$\theta_{\max}$ (°)	27.01	27.03	27.54
Range of <i>h</i> , <i>k</i> , <i>l</i>	-13 → <i>h</i> → 13 -10 → <i>k</i> → 11 -15 → <i>l</i> → 12	-11 → <i>h</i> → 11 -10 → <i>k</i> → 11 -13 → <i>l</i> → 16	-12 → <i>h</i> → 10 -15 → <i>k</i> → 17 -17 → <i>l</i> → 17
<b>Refinement</b>			
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.0496, 0.1266, 1.054	0.0446, 0.1230, 1.069	0.0366, 0.0943, 1.053
No. of reflections and parameters used in refinement	4129, 280	3835, 262	3939, 227
H-atom treatment	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 1.0375P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.5521P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.008	0.002	0.000
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.48, -0.54	0.68, -0.39	0.65, -0.35
Extinction method	None	None	<i>SHELXL</i>
Extinction coefficient	-	-	0.0015 (8)
Flack parameter (Flack, 1983)	0.08 (2)	0.08 (2)	0.001 (15)
	(4)	(5)	(6)
<b>Crystal data</b>			
Chemical formula	C <sub>12</sub> H <sub>30</sub> CoN <sub>5</sub> O <sub>2</sub> <sup>2+</sup> ·2I <sup>-</sup> ·H <sub>2</sub> O	C <sub>12</sub> H <sub>30</sub> CoN <sub>5</sub> O <sub>2</sub> <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup> ·2H <sub>2</sub> O	C <sub>12</sub> H <sub>30</sub> CoN <sub>5</sub> O <sub>2</sub> <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup> ·2H <sub>2</sub> O
Chemical formula weight	606.15	570.27	570.27
Cell setting, space group	Orthorhombic, <i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>	Orthorhombic, <i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>	Orthorhombic, <i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.053 (2), 11.540 (2), 18.664 (4)	11.5333 (11), 13.3726 (14), 15.0622 (15)	8.7716 (8), 12.6294 (15), 21.413 (4)
<i>V</i> (Å <sup>3</sup> )	2165.2 (7)	2323.0 (4)	2372.1 (5)
<i>Z</i>	4	4	4
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.859	1.631	1.597
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	3.662	1.035	1.014
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form, color	Block, yellow	Block, yellow	Plate, yellow
Crystal size (mm)	0.30 × 0.15 × 0.10	0.35 × 0.30 × 0.28	0.34 × 0.25 × 0.13
<b>Data collection</b>			
Diffractionmeter	Bruker SMART1000 CCD area detector	Bruker SMART1000 CCD area detector	Bruker SMART1000 CCD area detector
Data collection method	$\varphi$ and $\omega$ scans	$\varphi$ and $\omega$ scans	$\varphi$ and $\omega$ scans
No. of measured, independent and observed reflections	7861, 4811, 4240	8345, 4922, 3537	17 247, 6815, 5824
Criterion for observed reflections	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.0222	0.0323	0.0224
$\theta_{\max}$ (°)	27.49	27.00	30.07

Table 1 (continued)

	(4)	(5)	(6)
Range of $h, k, l$	$-13 \rightarrow h \rightarrow 5$ $-13 \rightarrow k \rightarrow 15$ $-24 \rightarrow l \rightarrow 7$	$-13 \rightarrow h \rightarrow 13$ $-17 \rightarrow k \rightarrow 7$ $-19 \rightarrow l \rightarrow 6$	$-12 \rightarrow h \rightarrow 12$ $-17 \rightarrow k \rightarrow 11$ $-30 \rightarrow l \rightarrow 21$
Refinement			
Refinement on	$F^2$	$F^2$	$F^2$
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.0318, 0.0776, 1.022	0.0412, 0.0854, 0.896	0.0359, 0.1000, 0.999
No. of reflections and parameters used in refinement	4811, 317	4922, 293	6815, 289
H-atom treatment	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.021	0.000	0.001
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ )	1.16, $-0.77$	0.59, $-0.32$	0.55, $-0.26$
Extinction method	<i>SHELXL</i>	None	None
Extinction coefficient	0.0022 (2)	—	—
Flack parameter (Flack, 1983)	0.02 (2)	$-0.007$ (17)	$-0.003$ (11)

Computer programs used: *SMART* (Bruker, 1998a); *SAINT* and *SHELXTL* (Bruker, 1998b, 1999); *SHELXS97* (Sheldrick, 1997); *SHELXL97* (Sheldrick, 1997).

pointed out that the isomeric trend was complicated and it seemed to be difficult to explain the energy difference among the diastereomers on the basis of only the nonbonded interaction between the amino acidate and tetraamine. Finally, it was suggested that solvation cages may have a non-trivial effect on the overall structure adopted (Yamaguchi, Yano *et al.*, 1980).

We are especially interested in comparing the crystal structures and crystallization behaviors of complexes which are closely related and have only minor differences in their geometries, either conformational and configurational (Cai *et al.*, 1995; Bernal, Myrczek & Cai, 1993; Bernal, Cetrullo *et al.*, 1993; Bernal *et al.*, 1994, 1995, 1997). Thus, the diastereoisomers of  $[\text{Co}(\text{trien})(\text{aminoacidato})]^{2+}$  cations will provide a unique opportunity to explore a system exhibiting those steric features. Here we report the crystal structures and absolute configurations of complexes, namely  $\beta_1$ - $\Delta$ (*SSS*)( $\lambda\lambda\delta$ )/( $\lambda\delta\delta$ )- $[\text{Co}(\text{trien})(\text{L-isoleucinato})](\text{ClO}_4)_2$  (1),  $\beta_1$ - $\Delta$ (*SRS*)( $\lambda\delta\lambda$ )- $[\text{Co}(\text{trien})(\text{L-valinato})](\text{ClO}_4)_2$  (2),  $\beta_1$ - $\Delta$ (*RSS*)( $\delta\lambda\delta$ )- $[\text{Co}(\text{trien})(\text{L-$

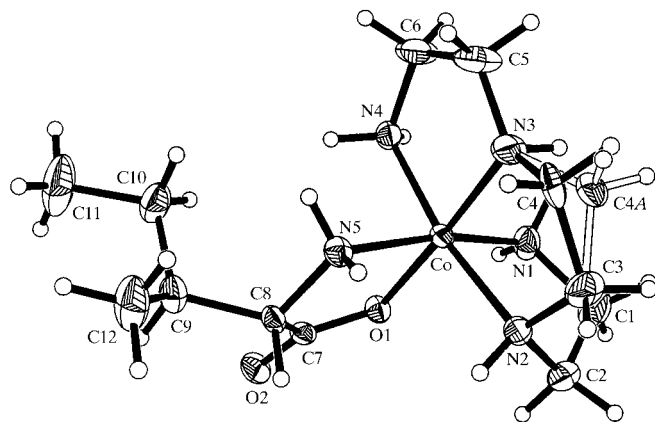
pyroglutamicacidato)] $\text{ClO}_4$  (3),  $\beta_2$ - $\Delta$ (*RRS*)( $\delta\delta\lambda$ )- $[\text{Co}(\text{trien})(\text{L-isoleucinato})]\text{I}_2 \cdot (\text{H}_2\text{O})$  (4),  $\beta_2$ - $\Delta$ (*RRS*)( $\delta\delta\lambda$ )- $[\text{Co}(\text{trien})(\text{L-isoleucinato})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (5) and  $\beta_2$ - $\Delta$ (*SSS*)( $\delta\lambda\lambda$ )- $[\text{Co}(\text{trien})(\text{L-leucinato})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (6).<sup>1</sup>

The  $\beta_1$  isomers of  $[\text{Co}(\text{trien})(\text{aminoacidato})]^{2+}$  were obtained for the first time as products of the direct reaction between amino acids and *cis*- $\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]\text{-Cl}$  at pH 7.5–8.0.

## 2. Crystallography

All diffraction data were collected at room temperature on a Bruker SMART1000 CCD area detector diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ; Bruker, 1998a, 1999). Absorption corrections were applied (Blessing, 1995; Bruker, 1999). Space groups were determined from systematic absences and confirmed by the results of refinement. In all cases, structures were solved by direct methods and refined using full-matrix least-squares/difference-Fourier techniques (Sheldrick, 1997; Bruker, 1998b). All non-H atoms were refined with anisotropic displacement parameters. All H atoms of the ligands were placed in idealized positions and refined as riding atoms with the relative isotropic parameters. H atoms of the water molecule were found from the difference-Fourier map in (5) and (6), while for (4) and one of the two water molecules in (6), H atoms of water molecules were not located. In (1) C4 is disordered and was refined over two positions. The absolute configurations of the structures were determined by refinement of their Flack parameters (Flack, 1983).

<sup>1</sup> The terms  $\beta_1$  and  $\beta_2$  refer to the two configurational isomers obtained using different or unsymmetrical donor ligands in the two remaining octahedral sites. For the aminoacidato,  $\beta_1$  refers to the isomer with the carboxylic oxygen of the amino acid *trans* to the secondary amino nitrogen atom of trien, and  $\beta_2$  refers to this oxygen *trans* to  $\text{NH}_2$  of trien; while  $\Delta$  and  $\Lambda$  refer to the absolute configuration of the central cobalt atom upon coordination. *R* and *S* refer to the absolute configurations of the two secondary N atoms of trien and the alpha carbon of amino acid.  $\delta$  and  $\lambda$  define the conformations of the five-membered chelate rings of trien.



**Figure 1**  
Cation of (1), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity. The disorder components (see text) are distinguished by filled and hollow bonds.

**Table 2**  
Selected bond distances (Å) and angles (°) for (1)–(6).

	(1)	(2)	(3)	(4)	(5)	(6)
Co–N1	1.947 (4)	1.956 (4)	1.992 (2)	1.954 (4)	1.951 (3)	1.9642 (17)
Co–N2	1.967 (4)	1.955 (3)	1.960 (2)	1.951 (4)	1.964 (3)	1.961 (2)
Co–N3	1.919 (5)	1.921 (4)	1.921 (2)	1.944 (3)	1.940 (3)	1.9389 (19)
Co–N4	1.957 (4)	1.957 (4)	1.955 (2)	1.976 (4)	1.963 (3)	1.968 (2)
Co–N5	1.981 (4)	1.966 (4)	1.907 (2)	1.966 (4)	1.961 (3)	1.9740 (19)
Co–O1	1.900 (3)	1.901 (3)	1.9273 (19)	1.898 (3)	1.895 (2)	1.8933 (15)
N1–Co–N2	84.31 (18)	84.44 (16)	84.60 (11)	85.44 (17)	86.41 (13)	86.28 (8)
N2–Co–N3	85.72 (19)	86.23 (17)	86.85 (11)	85.29 (16)	84.81 (13)	85.29 (9)
N3–Co–N4	85.7 (2)	86.15 (17)	85.75 (11)	85.39 (16)	85.88 (13)	86.45 (10)
N3–Co–N1	95.9 (3)	96.22 (19)	96.78 (11)	95.17 (16)	94.09 (13)	93.49 (8)
N1–Co–N4	91.90 (18)	91.91 (16)	92.77 (10)	95.81 (19)	93.78 (13)	93.21 (9)
N2–Co–N5	92.88 (17)	92.21 (15)	93.41 (11)	95.50 (17)	96.16 (13)	95.64 (9)
N3–Co–N5	94.8 (2)	93.23 (17)	93.68 (10)	174.93 (16)	174.35 (12)	172.51 (8)
N4–Co–N5	92.50 (17)	92.71 (16)	90.58 (11)	93.75 (18)	93.16 (13)	92.69 (9)
O1–Co–N1	84.56 (18)	85.36 (15)	85.36 (9)	173.26 (16)	175.75 (13)	177.62 (8)
O1–Co–N2	97.46 (16)	96.83 (14)	91.84 (10)	90.76 (15)	92.02 (12)	92.30 (8)
O1–Co–N4	91.09 (16)	90.90 (15)	95.70 (10)	88.84 (17)	88.41 (12)	88.47 (19)
O1–Co–N5	85.01 (15)	85.41 (13)	84.11 (9)	84.94 (13)	84.72 (11)	84.25 (2)
O1–Co–N3	176.82 (18)	176.69 (17)	177.36 (10)	90.05 (14)	89.69 (12)	88.29 (7)
N1–Co–N5	168.74 (19)	169.74 (16)	169.22 (10)	89.88 (16)	91.52 (12)	93.98 (7)
N4–Co–N2	170.26 (18)	171.15 (17)	171.80 (10)	170.67 (16)	170.68 (13)	171.67 (9)

Crystal data are listed in Table 1. Selected bond distances and angles are shown in Table 2. The coordinates, anisotropic displacement parameters, bond distances, valence angles and torsion angles for these complexes are submitted as supplementary materials in CIF format.<sup>2</sup>

### 3. Syntheses

All reagents were commercially available and were used as received. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. <sup>1</sup>H NMR spectra were recorded on a Varian UNITY/NOVA 500 NMR spectrometer using D<sub>2</sub>O or DMSO-*d*<sub>6</sub> as the solvent and TMS as the internal standard.

**Safety Note:** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great care.

Complexes (1)–(6) were prepared according to the synthetic procedure of Buckingham *et al.* (1967), using *cis-α*-[Co(trien)Cl<sub>2</sub>]Cl in place of *cis-β*-[Co(trien)Cl<sub>2</sub>]Cl. To an aqueous solution of *cis-α*-[Co(trien)Cl<sub>2</sub>]Cl (1.0 g, 0.003 mol), 10% NaOH solution was added with stirring until the pH was adjusted to 7.5–8.0. An equimolar amount of amino acid was added and the pH was again adjusted to 7.5–8.0. After heating at 333 K for 1–2 h in a water bath, the solution was cooled to room temperature and filtered. The desired iodide or perchlorate was obtained by adding excess KI or NaClO<sub>4</sub> to the resultant chloride solution. Crystals suitable for X-ray diffraction were obtained from the solution after a few days. In the case of L-isoleucine, the first crop of crystals to appear

were yellow and were shown by X-ray diffraction to be the β<sub>2</sub> isomer. Another crop, of red crystals, was subsequently obtained from the mother liquor and shown to be the β<sub>1</sub> isomer. The remarkable difference in solubility between these isomers allowed their separation by fractional crystallization.

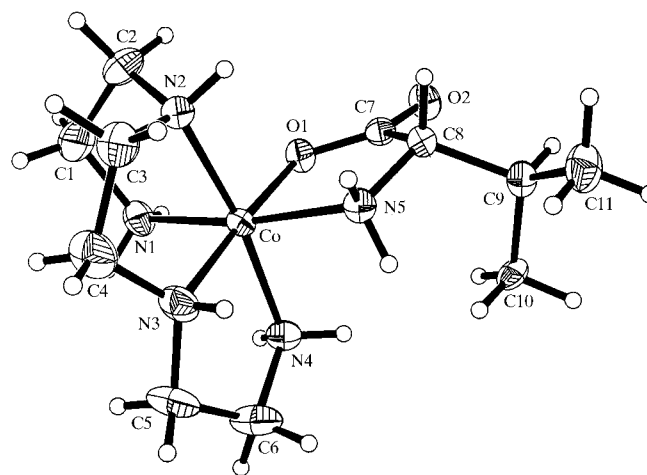
### 3.1. Elemental analyses and <sup>1</sup>H NMR data

**3.1.1. [Co(trien)(L-isoleucinato)](ClO<sub>4</sub>)<sub>2</sub> (1).** Found: C 26.79, N 12.83, H 5.60; C<sub>12</sub>H<sub>30</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>10</sub> requires C 26.98, N 13.11, H 5.66. <sup>1</sup>H NMR data (p.p.m., solvent D<sub>2</sub>O): 3.75 (1H, m, CH), 3.28–2.75 (12H, br, 6 CH<sub>2</sub>), 1.99 (1H, m, CH), 1.34 (2H, m, CH<sub>2</sub>), 1.11 (m, 3H, CH<sub>3</sub>), 0.95 (3H, m, CH<sub>3</sub>).

**3.1.2. [Co(trien)(L-valinato)](ClO<sub>4</sub>)<sub>2</sub> (2).** Found: C 26.12, N 13.67, H 5.04; C<sub>11</sub>H<sub>28</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>10</sub> requires C 25.40, N 13.47, H 5.43.

**3.1.3. [Co(trien)(L-pyroglutamato)]ClO<sub>4</sub> (3).** Found: C 29.94, N 15.83, H 5.26; C<sub>11</sub>H<sub>23</sub>ClCoN<sub>5</sub>O<sub>7</sub> requires C 30.60, N 16.23, H 5.37. <sup>1</sup>H NMR data (p.p.m., solvent DMSO-*d*<sub>6</sub>): 9.60 (1H, s, OH), 6.06 (1H, s, NH), 4.78 (1H, m, NH), 4.68 (1H, m, NH), 4.66 (1H, m, NH), 4.34 (1H, m, NH), 4.08 (1H, m, NH), 3.49 (1H, m, CH), 2.51–2.89 (12H, br, 6 CH<sub>2</sub>), 2.34 (1H, m, CH), 2.18 (1H, m, CH), 2.0 (1H, m, CH), 1.93 (1H, m, CH).

**3.1.4. [Co(trien)(L-isoleucinato)]I<sub>2</sub>·H<sub>2</sub>O (4).** Found: C 23.63, N 11.47, H 5.28; C<sub>12</sub>H<sub>32</sub>CoI<sub>2</sub>N<sub>5</sub>O<sub>3</sub> requires C 23.74, N 11.54, H 5.31. <sup>1</sup>H NMR data (p.p.m., solvent DMSO-*d*<sub>6</sub>): 6.89 (1H, s, NH), 6.67 (1H, s, NH), 5.12 (1H, t, NH), 4.66 (1H, m, NH), 4.47 (2H, m, NH<sub>2</sub>), 4.06 (1H, m, NH), 3.82 (1H, m, NH), 3.49 (1H, m, CH), 2.61–3.31 (12H, br, 6 CH<sub>2</sub>), 1.84 (1H, m, CH), 1.46 (1H, m, CH), 1.20 (1H, m, CH), 1.07 (3H, d, CH<sub>3</sub>), 0.90 (3H, t, CH<sub>3</sub>).



**Figure 2**  
Cation of (2), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity.

<sup>2</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0032). Services for accessing these data are described at the back of the journal.

**3.1.5. [Co(trien)(L-isoleucinato)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (5).** Found: C 26.29, N 12.83, H 5.69; C<sub>12</sub>H<sub>34</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>12</sub> requires C 25.27, N 12.27, H 6.01. <sup>1</sup>H NMR data (p.p.m., solvent D<sub>2</sub>O): 3.76 (1H, d, CH), 2.79–3.26 (12H, br, 6 CH<sub>2</sub>), 2.00 (1H, m, CH), 1.31 (1H, m, CH), 1.22 (1H, m, CH), 1.13 (3H, d, CH<sub>3</sub>), 0.95 (3H, t, CH<sub>3</sub>).

**3.1.6. [Co(trien)(L-leucinato)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (6).** Found C 25.98, N 12.47, H 5.98; C<sub>12</sub>H<sub>34</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>12</sub> requires C 25.27, N 12.28, H 6.01.

## 4. Results and discussion

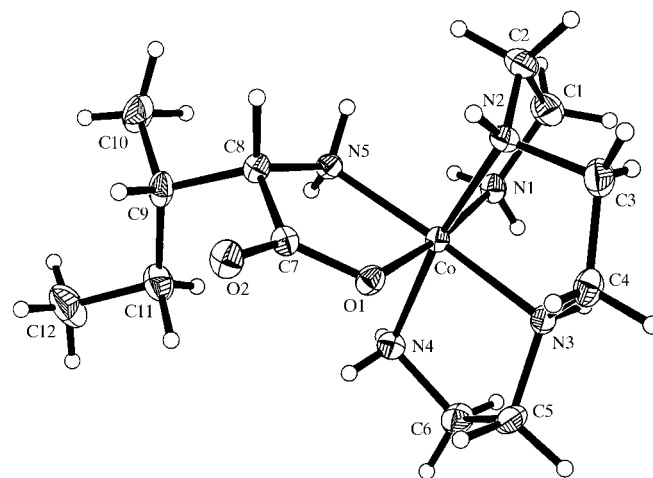
### 4.1. Crystal structures and absolute configurations

**4.1.1. β<sub>1</sub> isomers of (1)–(3).** The absolute configurations of these three complexes can be described as β<sub>1</sub>-Δ(SSS)(λλδ)/(λδδ), β<sub>1</sub>-Δ(SRS)(λδλ) and β<sub>1</sub>-Δ(RSS)(δλδ), as shown in Figs. 1–3 for (1) (there are two different conformations of the N2–C3–C4–N3 chelate ring due to disordered C4), (2) and (3), respectively. The geometrical parameters of (1) and (2) are very similar to each other, and also match the reported β<sub>1</sub> isomers of glycinate complexes (Buckingham *et al.*, 1974). The distance Co–N3 = 1.919 (5) Å, with N3 in the *trans* position to the coordinated oxygen of amino acid, is the shortest one among the four Co–N bonds of trien. The other three are in the range 1.94–1.96 Å. The abnormally short single bond distances, N3–C4a = 1.318 (14), C5–C6 = 1.413 (10) and C5–N3 = 1.415 (8) Å, observed in (1) could be the result of *gauche* disorder since all the atoms involved have large displacement parameters. The same phenomenon was reported in our previous studies (Hu *et al.*, 2000) as well as in the structure determination of β<sub>2</sub>-Δ-[Co(ala)(S-pyht)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (Yamaguchi, Yamamatsu *et al.*, 1980). The large displacement parameters of these atoms also cause the flattened torsion angles of the chelate rings of trien, which are –30.1 (12), 23.9 (15) and 7.2 (12)° for N2–C3–C4–N3, N2–C3–C4a–N3 and N3–C5–C6–N4, respectively. These are to be contrasted with the normal torsion angles of –42.4 (6),

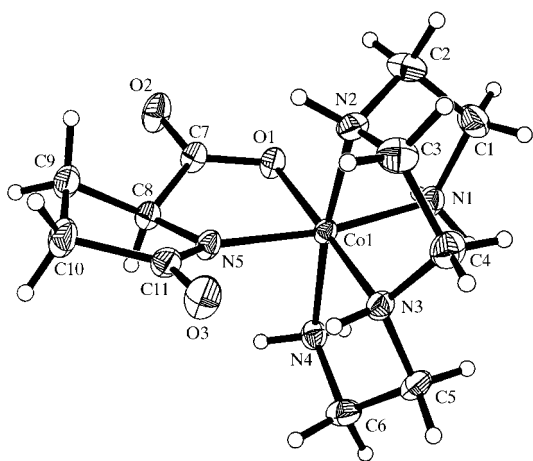
39.4 (7) and –37.7 (8)° observed in (2); and 42.0 (4), –45.4 (4) and 49.6 (3)° observed in (3), for N1–C1–C2–N2, N2–C3–C4–N3 and N3–C5–C6–N4, respectively.

For (3), the N and O atoms of the amino acid have significantly closer contact with the central Co cation, with Co–N5 = 1.907 (2) and Co–O1 = 1.927 (2) Å; which thus compel the trien ligand to adopt a longer Co–N1 bond length of 1.992 (2) Å. The bond distance N5–C11 = 1.317 (4) Å is abnormal for a single bond. The angle C11–N5–Co = 135.4 (2)° is also significantly expanded from the normal tetrahedral value.

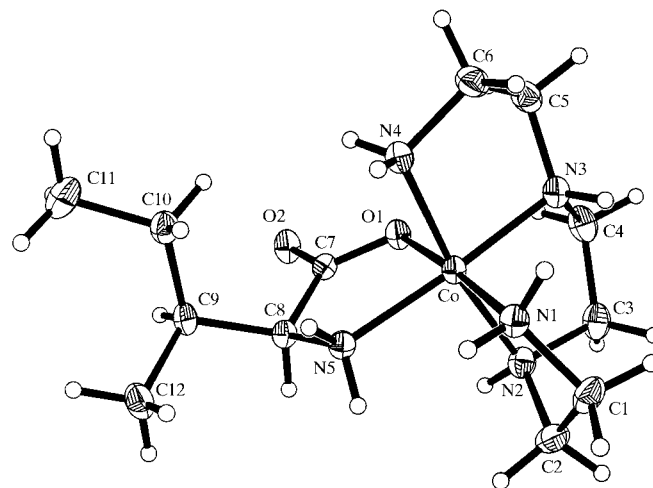
It is interesting to note that the absolute configurations of the coordinated secondary trien N atoms exhibit a variety of combinations. For complex (1), the protons of the secondary N atoms N2 and N3 lie on opposite sides of the N–N vector. In (2) and (3), they are on the same side, which is a more strained situation.



**Figure 4**  
Cation of (4), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity.



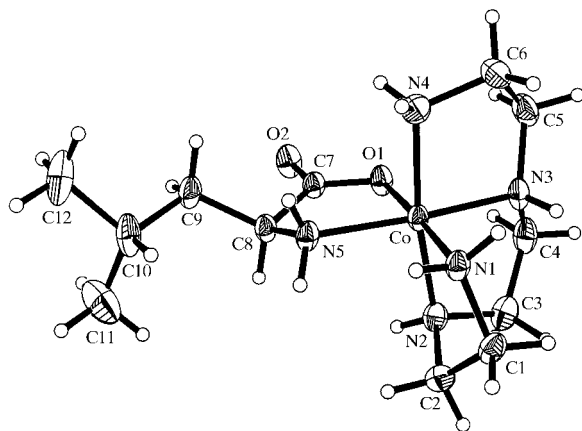
**Figure 3**  
Cation of (3), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity.



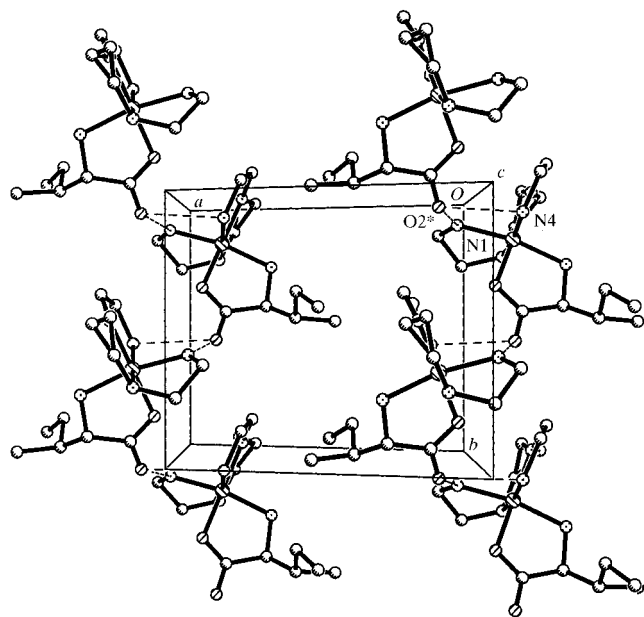
**Figure 5**  
Cation of (5), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity.

**4.1.2.  $\beta_2$  isomers of complexes (4)–(6).** The absolute configurations of these three complexes can be described as  $\beta_2$ - $\Delta(RRS)(\delta\delta\lambda)$ ,  $\beta_2$ - $\Delta(RRS)(\delta\delta\lambda)$  and  $\beta_2$ - $\Delta(SSS)(\delta\lambda\lambda)$ , as indicated in Figs. 4–6, for (4), (5) and (6), respectively. Here, once more, changing the amino acids has a profound effect upon the Co–N distance owing to intramolecular steric factors. The averages of the four trien Co–N distances are 1.958 (6), 1.956 (5) and 1.962 (4) Å for (4), (5) and (6), respectively, compared with the literature average of 1.945 (3) Å for the  $\beta_2$ -glycinato complexes (Eduok *et al.*, 1994).

All three complexes crystallize in the favored strain energy state with the absolute configuration of the overall cation



**Figure 6**  
Cation of (6), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary radius for clarity.



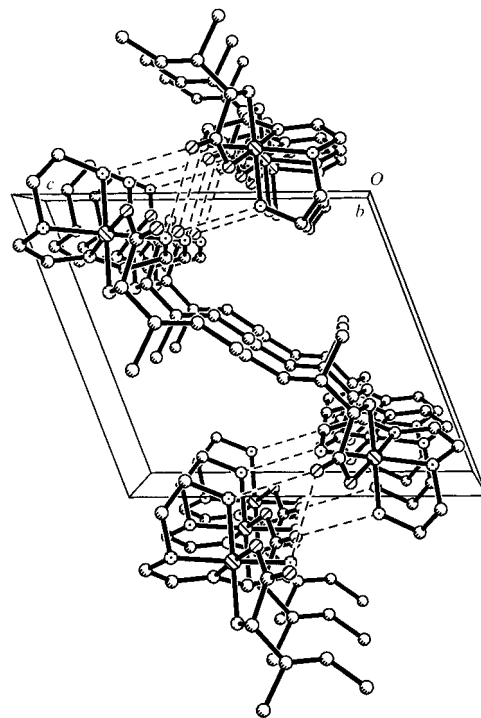
**Figure 7**  
Packing diagram of (1) viewed along the *c* axis. Perchlorates and H atoms are omitted for clarity. The inter-cation hydrogen bonds are: N1...O2\* [ $d(D\cdots A)$  2.905 (6) Å,  $\angle(DHA)$  121.7°] and N4...O2\* [ $d(D\cdots A)$  2.958 (6) Å,  $\angle(DHA)$  168.5°]. O2\* is related to O2 by the symmetry operation  $-x, y - \frac{1}{2}, -z - 1$ .

center and the secondary amino nitrogen of trien described as either  $\Delta(RR)$  or  $\Lambda(SS)$ .

#### 4.2. Packing features of $\beta_1$ and $\beta_2$ isomers

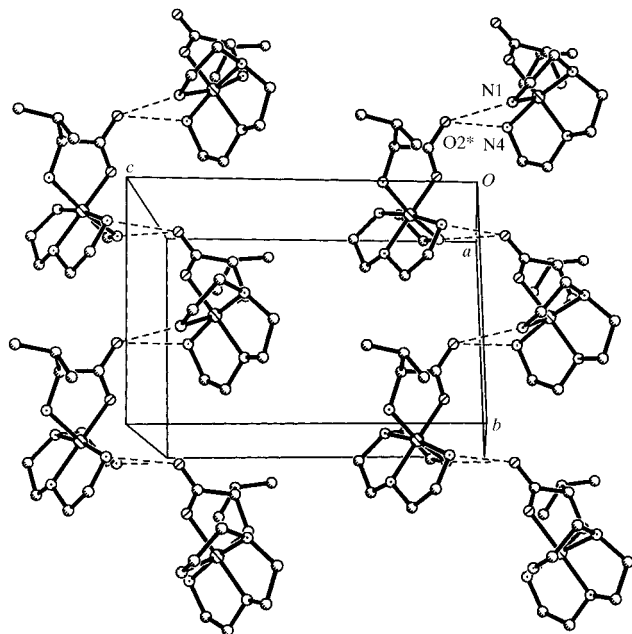
A common inter-cation hydrogen-bonding interaction is observed in complexes (1) and (2). The carboxylic oxygen of the amino acid forms double hydrogen-bonding interactions with both the primary  $-\text{NH}_2$  H atoms of trien and thus holds the cations together in helices along the *b* axis, as indicated in Figs. 7, 8 and 9. The other amino protons of trien and amino acid are involved in extensive hydrogen-bonding interactions with perchlorates. It is interesting to note that in (1) the isoleucine alkyl side chains of two adjacent columns are directed towards each other, forming a localized hydrophobic area, as indicated in Fig. 8. For (2), the hydrogen-bonding motif is similar to that in (1). However, there are no close contacts observed for the alkyl side chain of valine groups, as shown in Fig. 10, they are simply rotated away from each other. In the case of (3), the inter-cationic interactions are different from (1) and (2), with the carbonyl oxygen from the amino acid also involved and a two-dimensional network is observed, as indicated in Fig. 11.

As was observed for (1) and (2), there is a common inter-cationic hydrogen-bonding motif in (4)–(6), although this differs from that in the  $\beta_1$  isomers. The carboxylic oxygen of the amino acid forms triple and double hydrogen-bonding interactions with amino protons from both the amino acid and trien ligand for (5) and (6), as indicated in Figs. 12 and 13, respectively, and stitching the cations together to form a zigzag

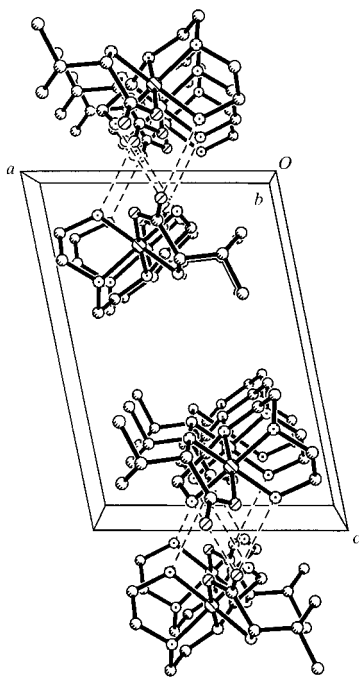


**Figure 8**  
Packing of cations in (1) viewed along the *b* axis. Note the hydrophobic area formed by the alkyl side chains of isoleucine. The shortest contact between the terminal  $-\text{CH}_3$  C atoms is about 4.41 Å.

chain along their crystallographic axes. This inter-cationic helix formation is also observed in the crystal structures of  $[\text{Co}(\text{tren})(\text{aminoacidato})]^{2+}$  (Cai *et al.*, 2000; Yamanari & Fuyuhira, 1996). The distance between the cobalt centers of adjacent cations is approximately 7.25, 7.29 and 7.63 Å for (4),



**Figure 9**  
Packing diagram of (2). Perchlorates and H atoms are omitted for clarity. The inter-cation hydrogen bonds are:  $\text{N1}\cdots\text{O2}^*$  [ $d(D\cdots A)$  2.923 (5) Å,  $\angle(DHA)$  127.3°] and  $\text{N4}\cdots\text{O2}^*$  [ $d(D\cdots A)$  2.901 (5) Å,  $\angle(DHA)$  167.6°].  $\text{O2}^*$  is related to  $\text{O2}$  by the symmetry operation  $-x - 1, y + \frac{1}{2}, -z - 2$ .



**Figure 10**  
Packing diagram of cations in (2) viewed along the  $b$  axis. Note that the orientation of the alkyl side chains of valines are different from that shown for (1) in Fig. 8. Perchlorates are packed between the columns of cations.

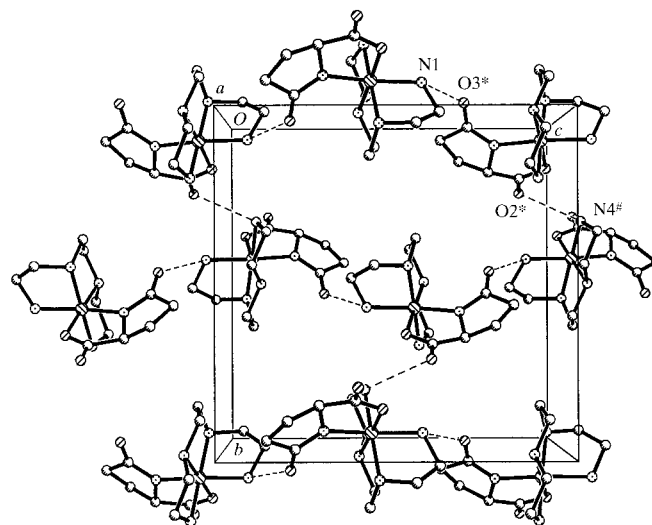
(5) and (6), respectively. In comparison to the separation of 6.85 Å observed in the  $\beta_1$  isomers of (1) and (2), the complex cations are further apart from each other, providing more space for the alkyl side chain. They wrap around the chain formed by inter-cationic hydrogen-bonding interactions and occupy the space between two cations, as indicated in Figs. 12 and 13. The anions and water molecules pack between the columns of cations.

#### 4.3. Separation and strain energy calculations of the $[\text{Co}(\text{tren})(\text{aminoacidato})]^{2+}$ diastereoisomers

There are ten possible diastereoisomers for  $[\text{Co}(\text{tren})(\text{aminoacidato})]^{2+}$  with asymmetric amino acids (Marzilli & Buckingham, 1967; Buckingham *et al.*, 1983). Ion-exchange chromatography, selective crystallization and HPLC have been extensively used by Buckingham *et al.* (1974, 1975, 1983) to effect separation of the isomers. In our study all isomers were obtained by fractional crystallization.

So far, only two  $\beta_1$  isomers of  $[\text{Co}(\text{tren})(\text{glycinnato})]^{2+}$  have been reported (Buckingham *et al.*, 1974; Eduok *et al.*, 1994) and it was pointed out that the only method which gave  $\beta_1$  products was the reaction of a freshly prepared solution of  $\beta\text{-}[\text{Co}(\text{tren})(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$  with glycine ethyl ester at room temperature (Buckingham *et al.*, 1974). Thus, our case is the first report of  $\beta_1$  isomers of  $[\text{Co}(\text{tren})(\text{aminoacidato})]^{2+}$  prepared and isolated by the direct reaction of  $\text{cis-}[\text{Co}(\text{tren})(\text{Cl}_2)_2]\text{Cl}$  with amino acids in slightly basic solution.

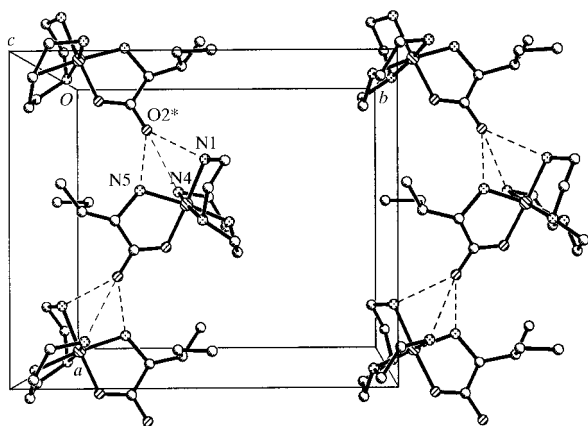
The calculated energy difference between the  $\Delta(RRS)$  and  $\Lambda(SSS)$  isomers of  $\beta_2\text{-}[\text{Co}(\text{tren})(\text{L-prolinato})]^{2+}$  is 6.69 kJ mol $^{-1}$  in favor of the former (Buckingham *et al.*, 1970) and it was predicted that L-proline would react stereospecifically with racemic  $\beta_2\text{-}[\text{Co}(\text{tren})(\text{OH})(\text{H}_2\text{O})]^{2+}$  to give exclusively  $\beta_2\text{-}\Delta(RRS)\text{-}[\text{Co}(\text{tren})(\text{L-prolinato})]^{2+}$ . However, for the  $\beta_2$  isomers, we obtain both  $\Delta(RRS)$  [(4) and (5)] and



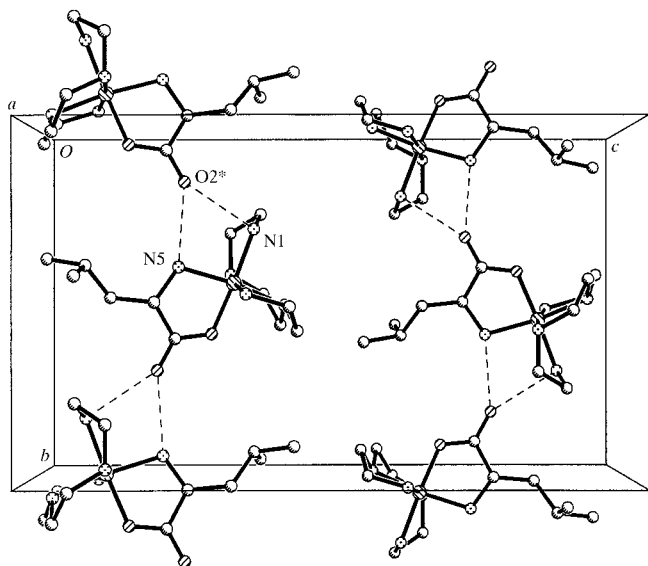
**Figure 11**  
Packing diagram of (3) viewed along the  $a$  axis showing the formation of a two-dimensional net. The inter-cation hydrogen bonds are:  $\text{N1}\cdots\text{O3}^*$  [ $d(D\cdots A)$  2.876 (3) Å,  $\angle(DHA)$  139.3°] and  $\text{N4}^\#\cdots\text{O2}^*$  [ $d(D\cdots A)$  2.873 (3) Å,  $\angle(DHA)$  171.2°]. The \* denotes the symmetry operation  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ , while # denotes  $x - \frac{1}{2}, -y + \frac{1}{2}, -z$ .

$\Lambda(SSS)$  (6) as the thermally stable products. This indicates that the energy difference among these isomers is small and could easily be overcome by other factors, such as solvation effects and lattice forces.

A report of the relative energies of the five diastereoisomeric species possible for  $\Delta$ -[Co(trien)(glycinato)]<sup>2+</sup> cations (Buckingham *et al.*, 1975) indicated that the  $\beta_2$ -RR cation has the lowest energy both by calculation and observation. This is consistent with what we report here, namely that all three  $\beta_2$  isomers obtained adopt the  $\beta_2$ - $\Delta(RR)$  or



**Figure 12**  
Packing diagram of (5). Note the chains running along the *a* axis formed by triple hydrogen bonds, perchlorates and water molecules pack between the cation strings. The inter-cation hydrogen bonds are: N1...O2\* [*d*(D...A) 2.928 (4) Å, ∠(DHA) 131°], N4...O2\* [*d*(D...A) 2.916 (4) Å, ∠(DHA) 145°] and N5...O2\* [*d*(D...A) 2.825 (4) Å, ∠(DHA) 145°]. O2\* is related to O2 by the symmetry operation  $x + \frac{1}{2}, -y + \frac{3}{2}, -z$ .



**Figure 13**  
Packing diagram of (6). Note the chains of molecules formed by double hydrogen bonds running along the *b* axis. The inter-cation hydrogen bonds are: N1...O2\* [*d*(D...A) 2.888 (3) Å, ∠(DHA) 163.1°] and N5...O2\* [*d*(D...A) 2.916 (3) Å, ∠(DHA) 116.6°]. O2\* is related to O2 by the symmetry operation  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ .

$\beta_2$ - $\Lambda(SS)$  configuration. Calculations also indicated that the energy difference between the  $\beta_2$ - $\Delta(RR)(\delta\delta\lambda)$  and  $\beta_1$ - $\Delta(RR)(\delta\delta\lambda)$  isomers resulted largely from interactions between protons on the N atom of the glycinato moiety and protons of the planar N2—C3—C4—N3 and apical N4—C5—C6—N3 trien rings, respectively. Our results indicate that it is more difficult to rationalize the conformations of the five-membered chelate rings of trien, since different combinations are observed in both the  $\beta_1$  and  $\beta_2$  isomers.

With regard to the absolute configuration of the two coordinated secondary N atoms, the total strain energy calculations on  $\beta$ - $\Delta$ -[Co(trien)(glycinato)]<sup>2+</sup> showed that the  $\beta_1$ - $\Delta(RR)$  isomer was 3.347 kJ mol<sup>-1</sup> more stable than the  $\beta_1$ - $\Delta(RS)$  isomer; while the  $\beta_2$ - $\Delta(RR)$  was 14.64 kJ mol<sup>-1</sup> more stable than the  $\beta_2$ - $\Delta(RS)$  isomer (Buckingham *et al.*, 1974). This means that the energy barrier to inversion of one of the N atoms is lower for the  $\beta_1$  isomer than for the  $\beta_2$  isomer. This is consistent with our results since we recorded two out of the three possible inversions in the  $\beta_1$  isomers, while no inversion was observed for the  $\beta_2$  isomers.

It is difficult to predict and rationalize the thermal stabilities of the ten diastereoisomers of [Co(trien)(aminoacidato)]<sup>2+</sup> cations with different amino acid ligands. However, we hope that the reported six isomers will provide starting models for energy minimization calculation studies of similar complexes.

#### 4.4. <sup>1</sup>H NMR spectra

NMR spectra of two  $\beta_1$  isomers [(1) and (3)], and two  $\beta_2$  isomers [(4) and (5)] were recorded. The most striking difference between the  $\beta_1$  and  $\beta_2$  isomers of [Co(trien)(isoleucinato)]<sup>2+</sup> is the splitting of the broad peak from the isoleucine —CH<sub>2</sub> protons [1.34 p.p.m. in (1)] into two signals at 1.46 and 1.20 p.p.m. in (4). The signals of the two —CH<sub>3</sub> groups from isoleucine were broadened in the  $\beta_1$  isomer, while in the  $\beta_2$  isomer the usual splitting into triplet and doublet were recorded. This feature can be used to assess the purity of the  $\beta_1/\beta_2$  isomers of the isolated products.

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