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The Relation between Crystal Structure and Solubility for the Diastereoisomeric Salts formed when Enantiomers of Bis(ethylenediamine)glycinatocobalt(III) are Resolved with Di- μ -[(*R,R*)-tartrato(4-)]-diantimonate(III)

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Abstract

The structures of the two diastereoisomeric salts which are obtained when bis(ethylenediamine)glycinatocobalt(III) is resolved with di- μ -[(*R,R*)-tartrato(4-)]-diantimonate(III) have been determined by X-ray diffraction methods. Both compounds crystallize in space group $P2_1$ with $Z=2$ and four water molecules of hydration per formula unit. The less soluble salt, Δ -bis(ethylenediamine)glycinatocobalt(III) di- μ -[(*R,R*)-tartrato(4-)]-diantimonate(III) tetrahydrate, Δ -[Co(C₂H₈N₂)₂(C₂H₄NO₂)][Sb₂(C₄H₂O₆)₂].4H₂O, $M_r = 860.76$, has, at 105 K, $a = 12.696$ (2), $b = 7.837$ (2), $c = 13.271$ (2) Å, $\beta = 95.18$ (1)°, $V = 1315.1$ (7) Å³, $D_x(105)$ K = 2.174(1), $D_m(296$ K) = 2.152 (1) g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 27.5$ cm⁻¹, $F(000) = 848$, $R(F) = 0.022$ for 5423 reflections with $I \geq 2\sigma(I)$. The more soluble salt, Λ -bis(ethylenediamine)glycinatocobalt(III) di- μ -[(*R,R*)-tartrato(4-)]-diantimonate(III) tetrahydrate, Λ -[Co(C₂H₈N₂)₂(C₂H₄NO₂)][Sb₂(C₄H₂O₆)₂].4H₂O, $M_r = 860.6$, has, at 100 K, $a = 7.968$ (2), $b = 17.232$ (2), $c = 9.983$ (2) Å, $\beta = 105.38$ (1)°, $V = 1321.6$ (6) Å³, $D_x(100)$ K =

2.163 (1), $D_m(296$ K) = 2.137 (1) g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 27.5$ cm⁻¹, $F(000) = 848$, $R(F) = 0.026$ for 5646 reflections with $I \geq 2\sigma(I)$. The number and strength of the hydrogen bonds appear similar in the two structures, but the structure of the optically active cation is significantly different in the two compounds. In the less soluble salt the stereochemistry and absolute configuration of the cation can be described as $\Delta(\lambda\delta\lambda)$, compared with the stereochemistry in the more soluble salt which is $\Lambda(\lambda\lambda\lambda)$. This difference in stereochemistry is accompanied by significant structural differences involving the glycinato ligand. The chiral discrimination as expressed in the different solubilities of the two salts appears partly to be caused by the difference in conformational energy of the cation in the two salts.

Introduction

A widely used method to isolate one of the enantiomers from a racemic mixture is to add a suitable chiral reagent. When resolution is desired for a cationic racemate precipitation with an optically active anion is often attempted. Two different diastereoisomeric salts may result and sometimes their difference in solubility allows both of them to

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be isolated. In other cases the difference either in solubility or in the rate constants for the precipitation kinetics may be so large that an almost quantitative isolation of one of the diastereoisomers is achieved. This paper is part of a study where the differences in the crystalline state between two diastereoisomeric salts are related to their thermodynamic properties.

The diastereoisomers investigated are obtained when racemic bis(ethylenediamine)glycinatocobalt(III), $[\text{Co}(\text{en})_2\text{gly}]^{2+}$, is resolved with the di- μ -(*R,R*)-tartrato(4-)-diantimonate(III) ion; the latter ion is often referred to as antimonyl tartrate. Both compounds crystallize with four water molecules per formula unit.

Similar investigations have previously been undertaken for the diastereoisomeric salts obtained when bis(ethylenediamine)oxalatocobalt(III) (Kuramoto, Kushi & Yoneda, 1978, 1980), tris(biguanide)cobalt(III) (Tada, Kushi & Yoneda, 1981, 1982) and ethylenediaminebis(glycinato)cobalt(III) (Kuramoto, 1979) are resolved as hydrogen tartrates. In these diastereoisomeric salts the number of water molecules cocrystallized is different for the two salts with identical composition of the cation and the hydrogen tartrate ion, and this makes a direct comparison of the interactions in the diastereoisomeric salts difficult. The difference in solubility may very well be caused by the different number of water molecules in the two salts.

The $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion can exist as several possible isomers. The isomers are classified according to IUPAC's (1970) nomenclature. The different configurations of the chelate rings are described as Δ or Λ and each puckered chelate ring may adopt a δ or λ conformation. The cation was resolved by Liu & Douglas (1964), who also postulated its absolute configuration, which turns out to be opposite to the result reported in this paper.

Experimental

Crystallographic study

Crystals of the two diastereoisomeric salts were prepared by the method described by Liu & Douglas (1964) with minor modifications. The crystalline samples were generously supplied by Dr Anders Hammershøi. Table 1 lists the chemical and crystallographic characteristics of the two compounds as well as some experimental details about data collection and refinement; other crystal data are in the *Abstract*. The density of the compounds at 296 K was measured by flotation in a mixture of bromobenzene and 1,2-dibromoethane. Both compounds crystallize as red prismatic crystals. The low-temperature data sets were corrected for background, Lorentz, polarization and absorption effects. The intensities of the standard reflections measured for the more soluble salt

Table 1. *Experimental data*

	$\Delta(\lambda\delta\lambda)$ -Co(en) ₂ gly]- [Sb ₂ (tart) ₂].4H ₂ O	$\Lambda(\lambda\lambda\lambda)$ -[Co(en) ₂ gly]- [Sb ₂ (tart) ₂].4H ₂ O
Specific optical rotations at 298 K, (α) _{λ}	(-82) _{589i} , (-251) _{546i} , (851) ₄₇₀	(248) _{589i} , (506) _{546i} , (-495) ₄₇₀
Solubility at 298 K	Less soluble (0.0024 mol kg ⁻¹)	More soluble (0.0055 mol kg ⁻¹)
Space group	P2 ₁	P2 ₁
Z	2	2
Diffractometer	CAD-4	Picker FACS I
Radiation, λ	Mo K α , 0.71073 Å	Mo K α , 0.71073 Å
Temperature	105 K \pm 0.5 K	100 K \pm 0.5 K
Number and θ range for reflections used in determination of lattice parameters	19 14-22°	15 24-27°
Developed forms	{100}, {010}, {001}, {021}	{100}, {010}, {001}
Crystal size	0.100 \times 0.410 \times 0.200 mm	0.285 \times 0.285 \times 0.315 mm
Range of transmission factors	0.5399-0.7758	0.4121-0.5711
Scan type	ω -2 θ	ω -2 θ
2 θ	3-69°	2.4-69°
Standard reflections	12, 0, 0, 020, 008, 1, 1, $\bar{1}$, $\bar{2}$	$\bar{2}$ 20, 005, 601, 0, 12, 7, 0, 20, 0
Number of reflections measured	6136	8315
Range in indices	0 < h < 20 0 < k < 12 -21 < l < 20	0 < h \leq 12 0 \leq k \leq 27 -15 \leq l \leq 15
R _{int}	0.020	0.023
Number of independent reflections	5919	5725
Number of observed reflections	5423	5646
Number of variables	432	432
R	0.022	0.026
w ⁻¹	$\sigma^2(F) + 0.003 F ^2$	2.5 $\sigma^2(F) + 0.003F$ + 0.0001 F ^2
wR	0.027	0.031
Maximum least-squares shift to e.s.d., (Δ/σ) _{max}	0.33	0.62
S	0.80	1.66

decreased during the X-ray exposure. The data were corrected for this deterioration by a function linear with the exposure time. The intensities of the standard reflections recorded for the less soluble salt did not show any systematic variations during the experiment. Both structures were solved by the heavy-atom method and refined by the method of least squares minimizing $\sum w(|F_o| - |F_c|)^2$. The H atoms were located in $\Delta\rho$ maps. Anisotropic temperature factors were used for all the non-hydrogen atoms. The H atoms were given a common isotropic thermal parameter ($U = 0.05 \text{ \AA}^2$). The positional parameters for the H atoms bonded to the water O atoms were not included in the refinement. The peaks in the final $\Delta\rho$ map were between -0.5 and 0.3 e\AA^{-3} except in the regions around the Sb atoms, where peaks of 1.5 e\AA^{-3} were observed, that could be interpreted as lone-pair densities. In both structures the y coordinate of one of the Sb atoms was fixed in order to define the origin.

Hamiltons R-value test performed as described by Rogers (1981) confirms the known (*R,R*) configuration of the tartrate groups in the two structures.

The atomic scattering factors employed were those listed by Cromer & Mann (1968) except for H, where the values of Stewart, Davidson & Simpson (1965) were used. The anomalous-dispersion corrections added to the scattering factors of Co and Sb were

calculated by Cromer & Liberman (1970). The crystallographic computations were performed by means of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The final parameters* are listed in Tables 2 and 3.

Thermogravimetry

The measurements were performed on the thermobalance described by Pedersen (1968).

Results and discussion

Comparison of the two crystal structures

Both diastereoisomeric salts are built of discrete di- μ -(*R,R*)-tartrato(4-)-diantimonate(III) and bis-(ethylenediamine)glycinatocobalt(III) ions linked by the water of crystallization. In the search for the origins of the difference in solubility between the salts, the two structures were analyzed for differences in their structural building units and for differences in the packing arrangements.

The packing arrangements

The packing in the two diastereoisomeric salts is influenced by hydrogen bonds between the cation, anion and water molecules of crystallization. The possible hydrogen bonds in the two structures are listed in Table 4. It is remarkable that all the atoms that could be expected to participate in hydrogen bonding are involved in the formation of hydrogen bonds in both structures. Not only the number but also the strength of the hydrogen bonds measured by the donor-acceptor separations are very similar in the two salts. A summation over donor-acceptor distances leads to 52.44 Å in the less soluble and 53.12 Å in the most soluble salt. The hydrogen-bonding systems are illustrated on the stereopairs shown in Figs. 1 and 2. From these drawings as well as Table 4 we conclude that though the intermolecular interactions due to the formation of hydrogen bonds are very alike in the two compounds they lead to quite different arrangements in the crystal structures.

The most significant differences between the systems of hydrogen bonds in the two salts are in the interactions between cations and anions. The cations in the less soluble salt are hydrogen bonded to three different cations and three different anions. In the more soluble salt there is only one cation-cation hydrogen bond, but six hydrogen bonds are formed to two different anions that are related by translational

Table 2. Fractional coordinates for the less soluble isomer, $\Delta(\lambda\delta\lambda)$ -[Co(en)₂gly][Sb₂(tart)₂].4H₂O

$$U_{\text{iso}} = \frac{1}{3} \sum_i \sum_j U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j a_i^* a_j^*$$

	x	y	z	U_{iso} (Å ²)
Cation				
Co	0.38485 (3)	0.05024 (6)	0.85092 (3)	0.00917
N(1)	0.3598 (2)	0.0722 (3)	0.9934 (2)	0.0120
N(2)	0.2989 (2)	0.2565 (4)	0.8299 (2)	0.0120
N(3)	0.5161 (2)	0.1838 (4)	0.8751 (2)	0.0135
N(4)	0.4188 (2)	0.0422 (4)	0.7091 (2)	0.0141
N(5)	0.2617 (2)	-0.0932 (4)	0.8184 (2)	0.0118
O(1)	0.4583 (2)	-0.1593 (3)	0.8819 (2)	0.0126
O(2)	0.4394 (2)	-0.4428 (3)	0.8786 (2)	0.0151
C(1)	0.3078 (3)	0.2378 (4)	1.0116 (2)	0.0140
C(2)	0.2348 (2)	0.2779 (4)	0.9179 (2)	0.0143
C(3)	0.5557 (3)	0.2333 (5)	0.7763 (3)	0.0177
C(4)	0.5329 (3)	0.0833 (5)	0.7059 (3)	0.0183
C(5)	0.4051 (2)	-0.2971 (4)	0.8592 (2)	0.0120
C(6)	0.2970 (2)	-0.2708 (4)	0.8035 (2)	0.0126
Anion				
Sb(1)	0.94184 (1)	0.50000	0.83450 (1)	0.01138
Sb(2)	0.87178 (2)	-0.04788 (3)	0.64081 (1)	0.01123
C(11)	0.9969 (2)	-0.0739 (4)	0.8390 (2)	0.0120
C(12)	0.8890 (2)	-0.0051 (5)	0.8598 (2)	0.0116
C(13)	0.9078 (2)	0.1650 (4)	0.9155 (2)	0.0109
C(14)	0.8033 (2)	0.2549 (4)	0.9240 (2)	0.0128
O(11)	1.0658 (2)	-0.0928 (3)	0.9095 (2)	0.0154
O(12)	1.0079 (2)	-0.1112 (3)	0.7454 (2)	0.0145
O(13)	0.8197 (2)	0.0153 (4)	0.7713 (2)	0.0146
O(14)	0.9799 (2)	0.2624 (3)	0.8650 (2)	0.0129
O(15)	0.7345 (2)	0.1895 (4)	0.9704 (2)	0.0173
O(16)	0.7947 (2)	0.4036 (3)	0.8816 (2)	0.0142
C(21)	0.7937 (2)	0.2702 (4)	0.5448 (2)	0.0137
C(22)	0.9143 (2)	0.2918 (4)	0.5624 (2)	0.0125
C(23)	0.9365 (2)	0.4628 (5)	0.6165 (2)	0.0127
C(24)	1.0550 (2)	0.4751 (4)	0.6518 (2)	0.0128
O(21)	0.7397 (2)	0.3799 (4)	0.4971 (2)	0.0194
O(22)	0.7555 (2)	0.1340 (3)	0.5812 (2)	0.0154
O(23)	0.9615 (2)	0.1553 (3)	0.6190 (2)	0.0123
O(24)	0.8719 (2)	0.4807 (3)	0.6962 (2)	0.0137
O(25)	1.1207 (2)	0.4789 (3)	0.5889 (2)	0.0165
O(26)	1.0775 (2)	0.4789 (3)	0.7484 (2)	0.0143
Water molecules				
O(31)	0.1815 (2)	0.0967 (3)	0.6430 (2)	0.0169
O(32)	0.6642 (2)	-0.1177 (4)	0.3863 (2)	0.0226
O(33)	0.5650 (2)	0.2016 (4)	0.3976 (2)	0.0201
O(34)	0.3567 (3)	0.2037 (5)	0.4344 (3)	0.0164

symmetry along the *c* axis. This arrangement results in a chain of alternating anions and cations in the direction of the *c* axis. From these strong cation-anion interactions in the solid state we would predict that the enantiomer of the cation found in the more soluble salt has a larger association constant with the [Sb₂(tart)₂]²⁻ ion in aqueous solution than the isomer of the cation isolated in the less soluble salt. This result turns out to be in agreement with the findings derived from an ion-exchange separation of the enantiomers (see below).

The crystal structures of other diastereoisomeric salts have also been studied in order to obtain information of the chiral discrimination observed as a difference in solubility. The investigators of these systems have explained the chiral discrimination as a result of strong 'face to face' or close contacts between cation and anion (Okazaki, Sakaguchi & Yoneda, 1983; Magill, Korp & Bernal, 1981).

The present pair of diastereoisomeric salts does obviously not conform to these previous observations,

* Lists of structure factors, anisotropic thermal parameters, parameters for the H atoms and thermograms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42533 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional coordinates for the more soluble isomer, $\Lambda(\lambda\lambda\lambda)$ -[Co(en)₂gly][Sb₂(tart)₂].4H₂O

$$U_{\text{iso}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$
Cation				
Co	0.06741 (5)	0.70816 (3)	0.62015 (4)	0.01108
N(1)	0.0347 (4)	0.6155 (2)	0.5019 (3)	0.0150
N(2)	-0.1204 (4)	0.6656 (2)	0.6917 (3)	0.0155
N(3)	-0.0941 (4)	0.7674 (2)	0.4731 (3)	0.0153
N(4)	0.0907 (4)	0.8053 (2)	0.7280 (3)	0.0163
N(5)	0.2537 (4)	0.6580 (2)	0.7642 (3)	0.0169
O(1)	0.2528 (3)	0.7455 (2)	0.5481 (3)	0.0146
O(2)	0.5404 (3)	0.7446 (2)	0.5830 (3)	0.0193
C(1)	-0.0682 (5)	0.5559 (2)	0.5528 (4)	0.0177
C(2)	-0.2057 (5)	0.5988 (2)	0.6045 (4)	0.0178
C(3)	-0.1302 (5)	0.8466 (2)	0.5273 (4)	0.0180
C(4)	0.0371 (5)	0.8708 (2)	0.6284 (4)	0.0172
C(5)	0.4055 (4)	0.7201 (2)	0.6086 (3)	0.0153
C(6)	0.4128 (4)	0.6547 (2)	0.7127 (4)	0.0181
Anion				
Sb(1)	0.26415 (2)	0.70555 (2)	0.21862 (2)	0.01302
Sb(2)	-0.18934 (3)	0.50000	0.01485 (2)	0.01724
C(11)	-0.2865 (4)	0.6172 (2)	0.1920 (3)	0.0163
C(12)	-0.2559 (4)	0.6617 (2)	0.0675 (3)	0.0152
C(13)	-0.1167 (4)	0.7235 (2)	0.1275 (3)	0.0153
C(14)	-0.0547 (5)	0.7590 (2)	0.0078 (3)	0.0161
O(11)	-0.3344 (3)	0.6514 (2)	0.2825 (3)	0.0207
O(12)	-0.2567 (3)	0.5432 (2)	0.1926 (3)	0.0210
O(13)	-0.2032 (4)	0.6128 (2)	-0.0271 (3)	0.0180
O(14)	0.0212 (3)	0.68943 (14)	0.2303 (2)	0.0146
O(15)	-0.1589 (4)	0.7898 (2)	-0.0905 (3)	0.0205
O(16)	0.1100 (4)	0.7525 (2)	0.0186 (3)	0.0187
C(21)	0.1447 (5)	0.4941 (2)	-0.0617 (4)	0.0182
C(22)	0.1894 (5)	0.4834 (2)	0.0959 (4)	0.0171
C(23)	0.3269 (4)	0.5440 (2)	0.1610 (4)	0.0162
C(24)	0.3479 (4)	0.5457 (2)	0.3179 (4)	0.0182
O(21)	0.2588 (4)	0.4934 (2)	-0.1253 (3)	0.0247
O(22)	-0.0186 (4)	0.5034 (2)	-0.1231 (3)	0.0223
O(23)	0.0413 (3)	0.4927 (2)	0.1466 (3)	0.0154
O(24)	0.2815 (3)	0.6169 (2)	0.0968 (3)	0.0164
O(25)	0.3883 (5)	0.4871 (2)	0.3887 (4)	0.0322
O(26)	0.3161 (3)	0.6124 (2)	0.3672 (3)	0.0168
Water molecules				
O(31)	0.4433 (4)	0.8805 (2)	0.4181 (3)	0.0245
O(32)	0.0893 (4)	0.8637 (2)	0.2988 (3)	0.0239
O(33)	0.5630 (5)	0.8600 (2)	0.1746 (4)	0.0304
O(34)	0.4597 (4)	0.8050 (2)	-0.0980 (3)	0.0284

as the most soluble salt contains the strongest cation-anion interactions.

The di- μ -(*R,R*)-tartrato(4-)-diantimonate(III) ion

The molecular geometry of the binuclear anion observed in the two diastereoisomeric salts is illus-

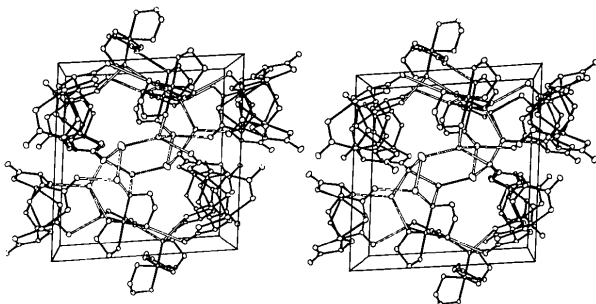


Fig. 1. ORTEP stereoview (Johnson, 1965) showing the packing in the less soluble isomer, $\Delta(\lambda\delta\lambda)$ -[Co(en)₂gly][Sb₂(tart)₂].4H₂O, seen along *b*. The ellipsoids are scaled to 50% probability. The hydrogen bonds are drawn as open bonds.

trated by the drawings in Fig. 3 and by the bond lengths and bond angles listed in Table 5. An examination of these results shows that the stereochemistry of the anion is very similar in the two salts and resembles the structures found in other crystal determinations (Zalkin, Templeton & Ueki, 1973; Gress & Jacobsen, 1974; Bohaty, Frölich & Tebbe, 1983).

The four independent tartrate moieties (two in each structure) have almost identical dimensions. The coordination geometry around Sb exhibits the most significant structural differences. The variations of the Sb-O bond lengths and the O-Sb-O angles are so large that they can hardly be explained by the experimental errors. The Sb-O(alcoxido) bond lengths are in the range 1.957–1.995 Å and Sb-O(carboxy) vary between 2.120 and 2.202 Å. It has not been possible to correlate these variations with the number and strengths of the hydrogen bonds to the O atoms of the tartrate ions. A comparison of the results with those from other structures containing this anion reveals that similar variations are common for this dinuclear ion. Three of these structures are K, Ca and Ba salts (Gress & Jacobsen, 1974; Bohaty, Frölich & Tebbe, 1983). This could indicate that the observed variations of the coordination geometry around Sb are not due to the diastereomeric interactions with the chiral cations.

The coordination of Sb to O atoms of the same tartrate group results in a five-membered ring. The eight independent rings in the two structures are all planar within the experimental accuracy, which is similar to the results from other crystal structure determinations.

The bis(ethylenediamine)glycinatocobalt(III) ion

The two optically active antipodes of [Co(en)₂gly]²⁺ as observed in the diastereoisomeric salts are illustrated in Fig. 4. These drawings as well as the torsion angles listed in Table 6 show that the

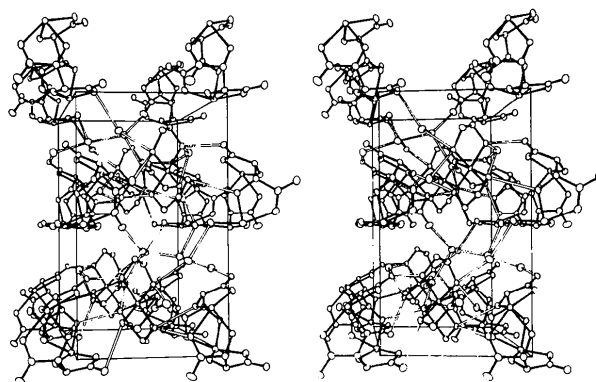


Fig. 2. ORTEP stereoview showing the packing in the more soluble isomer, $\Lambda(\lambda\lambda\lambda)$ -[Co(en)₂gly][Sb₂(tart)₂].4H₂O, drawn as in Fig. 1. The unit cell is viewed along *a**.

Table 4. *Hydrogen bonds D-H...A in the two diastereoisomeric salts*

$\Delta(\lambda\delta\lambda)$ -[Co(en) ₂ gly][Sb ₂ (tart) ₂].4H ₂ O (less soluble salt)			$A(\lambda\lambda\lambda)$ -[Co(en) ₂ gly][Sb ₂ (tart) ₂].4H ₂ O (more soluble salt)		
D-H...A	D...A (Å)	D-H...A (°)	D-H...A	D...A (Å)	D-H...A (°)
N(1)-H(20)-O(2 ⁱⁱ)	2.926 (3)	173 (6)	N(1)-H(20)-O(14)	2.972 (4)	149 (7)
N(1)-H(21)-O(16 ⁱⁱ)	2.989 (4)	154 (6)	N(1)-H(21)-O(26)	2.904 (4)	141 (7)
N(2)-H(22)-O(3 ⁱ)	3.046 (4)	164 (7)	N(2)-H(22)-O(13 ⁱ)	3.183 (4)	131 (5)
N(2)-H(23)-O(2 ⁱⁱⁱ)	2.991 (4)	153 (7)	N(2)-H(23)-O(2 ⁱⁱ)	2.963 (4)	152 (6)
N(3)-H(24)-O(15)	2.941 (4)	156 (8)	N(3)-H(24)-O(32)	3.044 (5)	149 (7)
N(3)-H(25)-O(2 ⁱⁱⁱ)	3.086 (4)	131 (5)	N(3)-H(25)-O(11)	3.059 (4)	146 (8)
N(4)-H(26)-O(33 ^{iv})	3.038 (4)	165 (5)	N(4)-H(26)-O(15 ⁱ)	3.037 (5)	165 (6)
N(4)-H(27)-O(32 ⁱⁱⁱ)	3.095 (4)	175 (6)	N(4)-H(27)-O(34 ⁱ)	2.992 (4)	175 (7)
N(5)-H(28)-O(31)	2.871 (4)	151 (7)	N(5)-H(28)-O(34 ⁱ)	3.131 (5)	130 (7)
N(5)-H(29)-O(11 ^v)	2.861 (4)	158 (5)	N(5)-H(29)-O(21 ⁱ)	3.040 (5)	159 (7)
O(31)-H(40)-O(23 ^v)	2.820 (3)	150	O(31)-H(40)-O(25 ⁱⁱⁱ)	2.742 (4)	167
O(31)-H(41)-O(21 ^{iv})	2.772 (4)	165	O(31)-H(41)-O(2)	2.850 (4)	167
O(32)-H(42)-O(25 ^{vi})	2.824 (4)	154	O(32)-H(42)-O(22 ^{iv})	2.944 (4)	168
O(32)-H(43)-O(33)	2.811 (4)	178	O(32)-H(43)-O(31)	2.769 (4)	179
O(33)-H(44)-O(34)	2.732 (4)	174	O(33)-H(44)-O(31)	2.859 (5)	167
O(33)-H(45)-O(21)	2.844 (4)	179	O(33)-H(45)-O(21)	2.813 (5)	117
O(34)-H(46)-O(32 ^{vii})	2.793 (5)	144	O(34)-H(46)-O(33)	2.791 (5)	178
O(34)-H(47)-O(21 ^{iv})	2.994 (5)	179	O(34)-H(47)-O(15 ^{vi})	3.031 (4)	133

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

Table 5. *Bond lengths (Å), bond angles (°) and dihedral angles (°) in the di-μ-(R,R)-tartrato(4-)diantimonate(III) ions*

$\Delta(\lambda\delta\lambda)$ -[Co(en) ₂ gly][Sb ₂ (tart) ₂].4H ₂ O (less soluble salt)				$A(\lambda\lambda\lambda)$ -[Co(en) ₂ gly][Sb ₂ (tart) ₂].4H ₂ O (more soluble salt)			
Sb(1)-O(14)	1.957 (2)	Sb(2)-O(23)	1.995 (2)	Sb(1)-O(14)	1.989 (3)	Sb(2)-O(23)	1.959 (2)
Sb(1)-O(16)	2.159 (2)	Sb(2)-O(22)	2.151 (2)	Sb(1)-O(16)	2.201 (3)	Sb(2)-O(22)	2.178 (3)
Sb(1)-O(24)	1.972 (2)	Sb(2)-O(13)	1.972 (2)	Sb(1)-O(24)	1.979 (3)	Sb(2)-O(13)	1.983 (3)
Sb(1)-O(26)	2.157 (2)	Sb(2)-O(12)	2.174 (2)	Sb(1)-O(26)	2.149 (3)	Sb(2)-O(12)	2.120 (3)
C(14)-O(16)	1.295 (4)	C(21)-O(22)	1.285 (4)	C(14)-O(16)	1.292 (5)	C(21)-O(22)	1.293 (4)
C(14)-O(15)	1.226 (4)	C(21)-O(21)	1.237 (4)	C(14)-O(15)	1.226 (4)	C(21)-O(21)	1.239 (5)
C(14)-C(13)	1.515 (4)	C(21)-C(22)	1.536 (4)	C(14)-C(13)	1.536 (5)	C(21)-C(22)	1.529 (5)
C(13)-O(14)	1.407 (4)	C(22)-O(23)	1.409 (4)	C(13)-O(14)	1.416 (4)	C(22)-O(23)	1.411 (5)
C(13)-C(12)	1.532 (5)	C(22)-C(23)	1.535 (5)	C(13)-C(12)	1.539 (5)	C(22)-C(23)	1.527 (5)
C(12)-O(13)	1.412 (3)	C(23)-O(24)	1.403 (4)	C(12)-O(13)	1.410 (5)	C(23)-O(24)	1.412 (4)
C(12)-C(11)	1.520 (4)	C(23)-C(24)	1.538 (4)	C(12)-C(11)	1.533 (5)	C(23)-C(24)	1.530 (5)
C(11)-O(11)	1.231 (4)	C(24)-O(25)	1.232 (4)	C(11)-O(11)	1.221 (5)	C(24)-O(25)	1.224 (5)
C(11)-O(12)	1.296 (4)	C(24)-O(26)	1.288 (3)	C(11)-O(12)	1.295 (5)	C(24)-O(26)	1.300 (5)
O(14)-Sb(1)-O(16)	79.1 (1)	O(23)-Sb(2)-O(22)	78.4 (1)	O(14)-Sb(1)-O(16)	77.7 (1)	O(23)-Sb(2)-O(22)	78.2 (1)
O(14)-Sb(1)-O(24)	101.6 (1)	O(23)-Sb(2)-O(13)	99.7 (1)	O(14)-Sb(1)-O(24)	99.0 (1)	O(23)-Sb(2)-O(13)	101.2 (1)
O(14)-Sb(1)-O(26)	81.0 (1)	O(23)-Sb(2)-O(12)	81.0 (1)	O(14)-Sb(1)-O(26)	82.4 (1)	O(23)-Sb(2)-O(12)	82.0 (1)
O(16)-Sb(1)-O(24)	85.1 (1)	O(22)-Sb(2)-O(13)	83.3 (1)	O(16)-Sb(1)-O(24)	80.7 (1)	O(22)-Sb(2)-O(13)	81.3 (1)
O(16)-Sb(1)-O(26)	151.6 (1)	O(22)-Sb(2)-O(12)	150.0 (1)	O(16)-Sb(1)-O(26)	149.2 (1)	O(22)-Sb(2)-O(12)	149.2 (1)
O(24)-Sb(1)-O(26)	79.3 (1)	O(13)-Sb(2)-O(12)	78.9 (1)	O(24)-Sb(1)-O(26)	79.4 (1)	O(13)-Sb(2)-O(12)	79.7 (1)
Sb(1)-O(16)-C(14)	113.5 (2)	Sb(2)-O(22)-C(21)	114.8 (2)	Sb(1)-O(16)-C(14)	114.6 (2)	Sb(2)-O(22)-C(21)	114.5 (2)
O(16)-C(14)-O(15)	123.9 (3)	O(22)-C(21)-O(21)	123.9 (3)	O(16)-C(14)-O(15)	124.1 (4)	O(22)-C(21)-O(21)	122.8 (3)
O(15)-C(14)-C(13)	120.8 (3)	O(21)-C(21)-C(22)	120.1 (3)	O(15)-C(14)-C(13)	120.4 (3)	O(21)-C(21)-C(22)	121.6 (3)
O(16)-C(14)-C(13)	115.3 (3)	O(22)-C(21)-C(22)	116.0 (3)	O(16)-C(14)-C(13)	115.5 (3)	O(22)-C(21)-C(22)	115.7 (3)
C(14)-C(13)-O(14)	113.2 (3)	C(21)-C(22)-O(23)	111.6 (3)	C(14)-C(13)-O(14)	112.4 (3)	C(21)-C(22)-O(23)	111.5 (3)
C(13)-O(14)-Sb(1)	117.1 (2)	C(22)-O(23)-Sb(2)	117.5 (2)	C(13)-O(14)-Sb(1)	118.7 (2)	C(22)-O(23)-Sb(2)	119.4 (2)
O(14)-C(13)-C(12)	108.8 (2)	O(23)-C(22)-C(23)	111.3 (2)	O(14)-C(13)-C(12)	109.6 (3)	O(23)-C(22)-C(23)	110.1 (3)
C(14)-C(13)-C(12)	110.0 (2)	C(21)-C(22)-C(23)	107.8 (2)	C(14)-C(13)-C(12)	108.6 (3)	C(21)-C(22)-C(23)	107.5 (3)
C(13)-C(12)-C(11)	107.0 (2)	C(22)-C(23)-C(24)	109.3 (2)	C(13)-C(12)-C(11)	106.5 (3)	C(22)-C(23)-C(24)	108.6 (3)
C(13)-C(12)-O(13)	111.1 (3)	C(22)-C(23)-O(24)	110.1 (3)	C(13)-C(12)-O(13)	111.2 (3)	C(22)-C(23)-O(24)	110.2 (2)
C(12)-O(13)-Sb(2)	118.0 (2)	C(23)-O(24)-Sb(1)	117.7 (2)	C(12)-O(13)-Sb(2)	117.0 (2)	C(23)-O(24)-Sb(1)	117.2 (2)
C(11)-C(12)-O(13)	113.1 (2)	C(24)-C(23)-O(24)	112.8 (2)	C(11)-C(12)-O(13)	112.6 (3)	C(24)-C(23)-O(24)	113.2 (3)
O(12)-C(11)-C(12)	115.5 (2)	O(26)-C(24)-C(23)	115.3 (2)	O(12)-C(11)-C(12)	115.3 (3)	O(26)-C(24)-C(23)	115.1 (3)
O(11)-C(11)-C(12)	119.6 (2)	O(25)-C(24)-C(23)	119.9 (2)	O(11)-C(11)-C(12)	120.4 (3)	O(25)-C(24)-C(23)	121.1 (4)
O(11)-C(11)-O(12)	124.8 (3)	O(26)-C(24)-O(25)	124.8 (2)	O(11)-C(11)-O(12)	124.3 (4)	O(26)-C(24)-O(25)	123.8 (4)
Sb(2)-O(12)-C(11)	114.4 (2)	Sb(1)-O(26)-C(24)	114.5 (1)	Sb(2)-O(12)-C(11)	115.4 (2)	Sb(1)-O(26)-C(24)	114.8 (2)
C(11)-C(12)-C(13)-C(14)	171.0 (2)			C(11)-C(12)-C(13)-C(14)	168.9 (3)		
C(21)-C(22)-C(23)-C(24)	170.3 (2)			C(21)-C(22)-C(23)-C(24)	168.9 (3)		

cation is stereochemically different in the two compounds. One of the ethylenediamine ligands [N(1)-C(1)-C(2)-N(2)] does not show the expected mirror-image symmetry, but takes almost identical conformations in the two structures. In accordance with the structural results for the [Co(en)(gly)₂]⁺ ion (Kuramoto, 1979) the glycinato ligand exhibits significant variations from planarity in the

[Co(en)₂gly]²⁺ ion. The dihedral angles defined by the atoms N(5)-C(6)-C(5)-O(1) are -19.3 (4) and -24.1 (4)° respectively in the two structures, which shows that the *gauche* conformations of the glycinato ligands in the two enantiomers are not related by mirror-plane symmetry. The less soluble isomer has the ligands in a Δ configuration, the three bidentate ligands (en, en, gly) are in an *lel, ob, lel* arrangement

so the stereochemistry of the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion in the less soluble salt can uniquely be described as $\Delta(\lambda\delta\lambda)$. A similar analysis of the more soluble salt shows that here the cation has the three bidentate ligands in an *ob, ob, ob* arrangement and is stereochemically characterized as a $\Lambda(\lambda\lambda\lambda)$ isomer.

This absolute configuration is at variance with the result Liu & Douglas (1964) derived by comparing the CD spectra of the bis(ethylenediamine)glycinatocobalt(III) ion with those of $[\text{Co}(\text{en})_3]^{3+}$, which had its absolute configuration determined from X-ray diffraction measurements of Bijvoet pairs. With respect to the determination of absolute configuration from CD spectra the present structure determinations represent good examples of the difficulty of deriving the correct absolute configuration solely from CD spectra of *d-d* transitions.

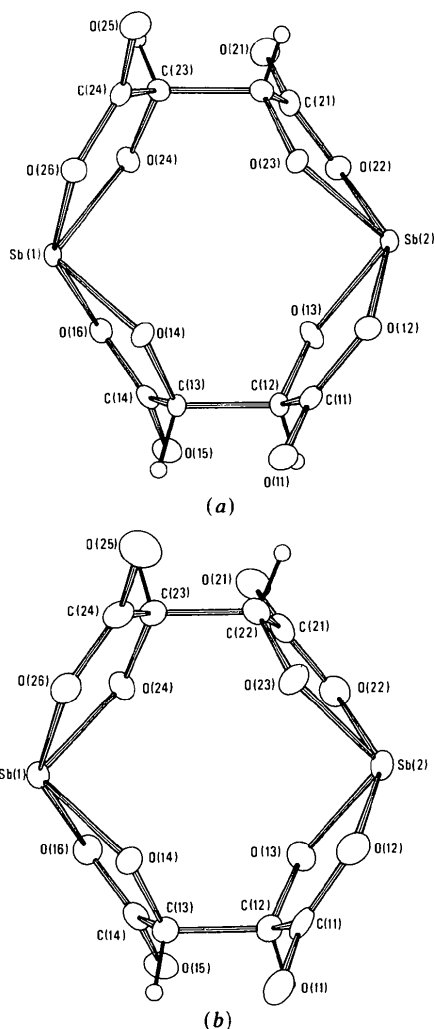


Fig. 3. ORTEP drawings of the di- μ -[(*R,R*)-tartrato(4-)]-diantimonate(III) ion as it is observed in the two diastereoisomeric salts. The thermal ellipsoids are scaled to enclose 50% probability; the H atoms are drawn as spheres with a radius of 0.1 Å. (a) The ion in the less soluble salt. (b) The ion in the more soluble salt.

A similar study for the bis(ethylenediamine)oxalatocobalt(III) ion resolved as hydrogen tartrates (Kuramoto, Kushi & Yoneda, 1978, 1980) showed that the less soluble isomer contains the complex cation in a Λ configuration with the two en groups *lel, ob* ($\delta\lambda$) and that the more soluble Δ isomer has conformational disorder of one of the en groups which was described as an equal distribution between the λ and δ isomer, the other (ordered) en ligand taking a $\delta(\text{ob})$ conformation. This system presents another example where the enantiomers precipitated with a common anion differ stereochemically.

The structures of the diastereoisomeric salts obtained when optically active ethylenediaminebis(glycinato)cobalt(III) is resolved as hydrogen tartrate have been determined by Kuramoto (1979). Some of the stereochemical details for these compounds have been calculated from the reported coordinates. The less soluble isomer isolated as a trihydrate contains the cation in a Λ configuration. The dihedral angles for the three (en, gly, gly) bidentate ligands are 49.8 (8), 11.7 (7) and 17.3 (6) $^\circ$ respectively which correspond to a ($\delta\delta\delta$) or *lel, lel, lel* arrangement. In the more soluble Δ enantiomer, which has been precipitated as a monohydrate, the equivalent dihedral

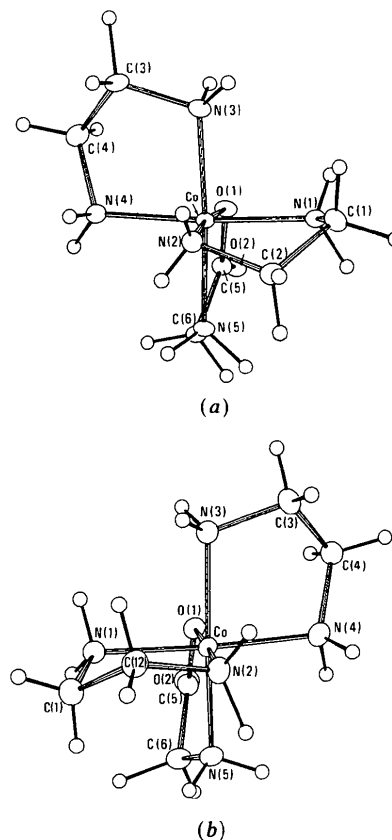


Fig. 4. ORTEP drawings of the 'enantiomers' of the cation. The atoms are drawn as described in Fig. 3. (a) shows the $\Delta(\lambda\delta\lambda)$ - $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion in the less soluble salt and (b) the $\Lambda(\lambda\lambda\lambda)$ - $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion in the more soluble salt.

Table 6. Bond lengths (Å), bond angles (°) and torsion angles for the two enantiomers of the bis(ethylenediamine)glycinatocobalt(III) ion

$\Delta(\lambda\delta\lambda)$ -[Co(en) ₂ gly]- [Sb ₂ (tart) ₂].4H ₂ O (less soluble salt)	$\Lambda(\lambda\lambda\lambda)$ -[Co(en) ₂ gly]- [Sb ₂ (tart) ₂].4H ₂ O (more soluble salt)		
Co-N(1)	1.953 (3)	Co-N(1)	1.961 (3)
Co-N(2)	1.956 (3)	Co-N(2)	1.962 (3)
Co-N(3)	1.970 (3)	Co-N(3)	1.962 (3)
Co-N(4)	1.969 (3)	Co-N(4)	1.970 (3)
Co-N(5)	1.943 (3)	Co-N(5)	1.971 (3)
Co-O(1)	1.915 (2)	Co-O(1)	1.917 (3)
N(1)-C(1)	1.486 (4)	N(1)-C(1)	1.485 (5)
N(2)-C(2)	1.493 (4)	N(2)-C(2)	1.493 (5)
N(3)-C(3)	1.497 (4)	N(3)-C(3)	1.491 (5)
N(4)-C(4)	1.488 (4)	N(4)-C(4)	1.489 (5)
N(5)-C(6)	1.481 (4)	N(5)-C(6)	1.490 (5)
O(1)-C(5)	1.295 (4)	O(1)-C(5)	1.283 (4)
C(1)-C(2)	1.516 (4)	C(1)-C(2)	1.521 (6)
C(3)-C(4)	1.513 (5)	C(3)-C(4)	1.511 (5)
C(5)-C(6)	1.513 (4)	C(5)-C(6)	1.523 (5)
C(5)-O(2)	1.240 (4)	C(5)-O(2)	1.243 (5)
N(1)-Co-N(2)	85.9 (1)	N(1)-Co-N(2)	85.6 (1)
N(1)-Co-N(3)	90.3 (1)	N(1)-Co-N(3)	91.0 (1)
N(1)-Co-N(4)	175.4 (1)	N(1)-Co-N(4)	176.1 (1)
N(1)-Co-N(5)	93.9 (1)	N(1)-Co-N(5)	92.1 (1)
N(1)-Co-O(1)	89.2 (1)	N(1)-Co-O(1)	92.3 (1)
N(2)-Co-N(3)	92.1 (1)	N(2)-Co-N(3)	93.1 (1)
N(2)-Co-N(4)	93.3 (1)	N(2)-Co-N(4)	95.1 (1)
N(2)-Co-N(5)	91.1 (1)	N(2)-Co-N(5)	94.0 (1)
N(2)-Co-O(1)	173.7 (1)	N(2)-Co-O(1)	177.7 (2)
N(3)-Co-N(4)	85.3 (1)	N(3)-Co-N(4)	85.1 (1)
N(3)-Co-N(5)	174.9 (1)	N(3)-Co-N(5)	172.4 (2)
N(3)-Co-O(1)	91.9 (1)	N(3)-Co-O(1)	87.8 (1)
N(4)-Co-N(5)	90.6 (1)	N(4)-Co-N(5)	91.7 (1)
N(4)-Co-O(1)	91.9 (1)	N(4)-Co-O(1)	87.1 (1)
N(5)-Co-O(1)	85.3 (1)	N(5)-Co-O(1)	85.1 (1)
Co-N(1)-C(1)	110.4 (2)	Co-N(1)-C(1)	110.7 (2)
N(1)-C(1)-C(2)	107.2 (2)	N(1)-C(1)-C(2)	107.1 (3)
C(1)-C(2)-N(2)	106.4 (2)	C(1)-C(2)-N(2)	108.3 (3)
C(2)-N(2)-Co	108.5 (2)	C(2)-N(2)-Co	110.4 (2)
Co-N(3)-C(3)	109.9 (2)	Co-N(3)-C(3)	110.1 (2)
N(3)-C(3)-C(4)	106.2 (3)	N(3)-C(3)-C(4)	106.7 (3)
C(3)-C(4)-N(4)	106.4 (3)	C(3)-C(4)-N(4)	105.4 (3)
C(4)-N(4)-Co	108.6 (2)	C(4)-N(4)-Co	108.1 (2)
Co-O(1)-C(5)	115.6 (2)	Co-O(1)-C(5)	115.9 (2)
O(1)-C(5)-C(6)	115.6 (2)	O(1)-C(5)-C(6)	115.7 (3)
C(5)-C(6)-N(5)	109.6 (2)	C(5)-C(6)-N(5)	108.9 (3)
C(6)-N(5)-Co	109.0 (2)	C(6)-N(5)-Co	108.1 (2)
O(2)-C(5)-O(1)	123.6 (3)	O(2)-C(5)-O(1)	123.5 (3)
O(2)-C(5)-C(6)	120.8 (3)	O(2)-C(5)-C(6)	120.8 (3)
Co-N(1)-C(1)-C(2)	34.4 (3)	Co-N(1)-C(1)-C(2)	37.3 (3)
Co-N(2)-C(2)-C(1)	42.5 (3)	Co-N(2)-C(2)-C(1)	33.8 (3)
Co-N(3)-C(3)-C(4)	-37.1 (3)	Co-N(3)-C(3)-C(4)	35.7 (4)
Co-N(4)-C(4)-C(3)	-43.6 (3)	Co-N(4)-C(4)-C(3)	45.8 (3)
Co-N(5)-C(6)-C(5)	23.7 (3)	Co-N(5)-C(6)-C(5)	26.1 (3)
Co-O(1)-C(5)-C(6)	5.1 (3)	Co-O(1)-C(5)-C(6)	9.4 (4)
N(1)-C(1)-C(2)-N(2)	-49.8 (3)	N(1)-C(1)-C(2)-N(2)	-45.7 (3)
N(3)-C(3)-C(4)-N(4)	52.3 (3)	N(3)-C(3)-C(4)-N(4)	-52.8 (4)
N(5)-C(6)-C(5)-O(1)	-19.5 (4)	N(5)-C(6)-C(5)-O(1)	-24.1 (4)

angles are -56.9 (9), -20.7 (11) and -19.4 (9)°. The glycinato ligands are closer to planarity in the less soluble isomer, but the intramolecular dimensions for the [Co(en)(gly)₂]⁺ ion in the two structures are so alike that here it seems justified to state that the enantiomers of [Co(en)(gly)₂]⁺ isolated as hydrogen tartrates are related by the symmetry of a mirror plane.

The present investigation has revealed an unusual difference between the stereochemistry of the two enantiomers of the [Co(en)₂gly]²⁺ ion when they are precipitated as [Sb₂(tart)₂]²⁻ salts. To investigate whether these differences in stereochemistry are accompanied by variations of the molecular geometry, the bond lengths and angles listed in Table

6 have been analyzed. Full-normal probability plots have been calculated for both bond lengths and bond angles between the two enantiomers. These plots confirm the intuitive conclusion that appears from the inspection of Table 6, that the [Co(en)₂gly]²⁺ ion is significantly different in the two structures. The full-normal probability plot for the bond lengths does not deviate significantly from the expected appearance with an intercept of 0.1 and a slope of 1.2 if the Co-N(5) bond is omitted. In the similar plot for bond angles the observed differences are so large that they cannot be explained by the experimental errors, and it seems meaningless to define a slope and an intercept for the distribution of points. The largest normal deviations are associated with the angles involving the glycinato ligand and the ethylenediamine group which is not related by mirror-image symmetry. These results have been compared with those obtained in other glycinato-cobalt(III) complexes. The Co-N(5) distance in the less soluble isomer, 1.943 (3) Å, is similar to the Co-N(glycinato) distances observed in the two enantiomers of the [Co(en)(gly)₂]⁺ ion (Kuramoto, 1979), which are in the range 1.947 (5)-1.964 (6) Å. All these distances appear slightly shorter than the Co-N(5) distance of 1.971 (3) Å found in the more soluble salt. The remaining distances agree well with those found in the related amino acid complexes bis(ethylenediamine)alaninatocobalt(III) (Anderson, Buckingham, Gainsford, Robertson & Sargeson, 1975) and bis(ethylenediamine)-glutaminatocobalt(III) (Gillard, Payne & Robertson, 1970).

If it is assumed that the contribution to the conformational energy of an octahedral complex from a glycinato ligand is similar to the contribution from an ethylenediamine ligand it should be possible to estimate the relative energy of the two conformers of the cation from the force-field calculations that Niketic & Rasmussen (1978) performed for the [Co(en)₃]³⁺ ion. They found that the energies of the conformers follow $(\text{lel})_3 < (\text{lel})_2\text{ob} < (\text{ob})_2\text{lel} < (\text{ob})_3$. For a [Co(en)₃]³⁺ complex with the absolute configuration Λ , this corresponds to isomers classified as $\Lambda(\delta\delta\delta) < \Lambda(\delta\delta\lambda) < \Lambda(\delta\lambda\lambda) < \Lambda(\lambda\lambda\lambda)$. Based on structural data for [M(en)₃]^{m+} cations Cramer & Huncke (1978) postulated the following energies of the conformers $\Lambda(\delta\delta\lambda) < \Lambda(\delta\delta\delta) \leq \Lambda(\delta\lambda\lambda) < \Lambda(\lambda\lambda\lambda)$. By analogy with these results $\Lambda(\lambda\lambda\lambda)$, which is observed in the more soluble salt, has a higher energy than the cation with the $\Delta(\lambda\delta\lambda)$ conformation precipitated in the least soluble salt. The differences in energy between the conformers of octahedral complexes are in the range 2-4 kJ mol⁻¹ (Niketic & Rasmussen, 1978).

In an attempt to explain why the cation takes different conformations in the two structures the intermolecular interactions have been examined. They are all slightly longer than the sum of the van der Waals radii (Bondi, 1964) so the cation seems to adopt

conformations that minimize the energy of the steric interactions. To investigate this in detail an artificial structure was designed which is based on the more soluble salt. Instead of the cation of the observed $\Lambda(\lambda\lambda\lambda)$ conformation it contains the mirror image of the cation in the less soluble salt in a $\Lambda(\delta\lambda\delta)$ conformation. The shifts in positions for some of the atoms in this structure compared to those in the more soluble salt are quite significant. C(6) of the glycinato ligand moves 0.91 Å, and the two C atoms C(1) and C(2) are shifted 0.61 Å and 0.67 Å respectively. There are some very short interatomic distances in this structure. C(2) and its H atoms are very close to O(22) of the anion, C(2)-O(22) = 2.57 Å; C(6) of the glycinato ligand has a distance of 2.29 Å to one of the water molecules, O(34). Because of this it seems likely that the cations in the most soluble salt are found with the conformation that corresponds to a higher energy to avoid these very short contacts.

Thermodynamic properties

As part of an investigation of the binary and ternary solubility phase diagrams for different salts of racemic and optically active $[\text{Co}(\text{en})_2\text{gly}]^{2+}$, Kaki, Yamanari & Shimura (1982) determined the solubilities for the two diastereoisomeric salts structurally investigated in this paper at different temperatures in the range 5 to 55 °C (278–328 K). These numbers have been used to plot $\ln(m_\Delta)$ and $\ln(m_\Lambda)$ as a function of $1/T$, as shown in Fig. 5. m_Δ and m_Λ designate the solubilities of the two salts. Within the experimental error, van't

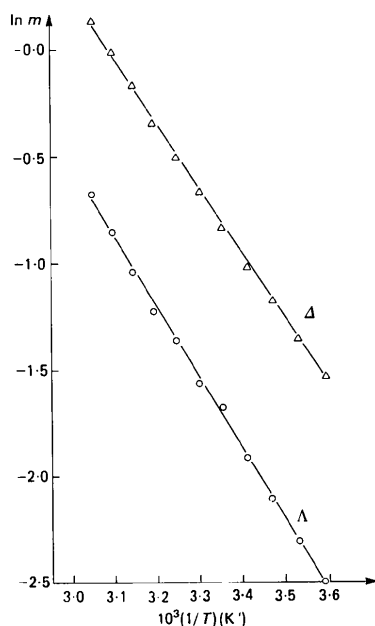


Fig. 5. The variation of the solubility (m) with temperature for the two diastereoisomeric salts; $\ln m$ is shown as a function of $1/T$.

Hoff's equation is obeyed for the dissolution processes of the two salts. The slopes obtained by linear regression are $\alpha_\Delta = -3.3099 \times 10^3 \text{ K}$ and $\alpha_\Lambda = -3.0645 \times 10^3 \text{ K}$.

If it is assumed that the diastereoisomeric salts are fully dissociated into the independent divalent ions this would correspond to the dissolution enthalpies, $\Delta H_\Lambda^\ominus = 50.96 \text{ kJ mol}^{-1}$ and $\Delta H_\Delta^\ominus = 55.04 \text{ kJ mol}^{-1}$. From the solubilities at 298 K (Table 1), $\Delta G_\Delta^\ominus = 29.97 \text{ kJ mol}^{-1}$ and $\Delta G_\Lambda^\ominus = 25.80 \text{ kJ mol}^{-1}$, the following entropies at 298 K, $\Delta S_\Delta^\ominus = 84.09 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_\Lambda^\ominus = 84.36 \text{ J K}^{-1} \text{ mol}^{-1}$ can be calculated. The ΔS values associated with the dissociation processes for the two salts are very similar in magnitude, and the difference in solubility between the two diastereoisomeric salts seems to be due largely to the different ΔH^\ominus values for the dissolution of the two diastereoisomeric salts. The compounds were dissolved in water, and to a first approximation one would expect the resulting solutions to have almost identical enthalpy. Thus the difference in the enthalpies of dissolution arises because the two crystalline diastereoisomeric salts differ in their enthalpies. Accordingly the difference in solubility for the two diastereoisomeric salts will mainly be caused by the difference in enthalpies for the two salts. However, this result is based on the assumption that outer-sphere complex formation between the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ and $[\text{Sb}_2(\text{tart})_2]^{2-}$ ions in the aqueous solution can be neglected.

The ion-pair association constants for the two enantiomers (Λ and Δ) of the $[\text{Co}(\text{en})_3]^{3+}$ ion with the $[\text{Sb}_2(\text{tart})_2]^{2-}$ ion have been determined by Taura, Nakazawa & Yoneda (1977). K_Δ was found to be ca 26 and K_Λ to be 47 in this system at an ionic strength of 0.1 mol dm^{-3} . With the other chiral anions the two association constants are more similar in magnitude (Tatehata, Iiyoshi & Kotsuji, 1981). An estimate of the ratio between the association constants for the enantiomers of the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion with $[\text{Sb}_2(\text{tart})_2]^{2-}$ has been deduced from the separation of the two enantiomers by ion exchange eluting with $\text{Na}_2[\text{Sb}_2(\text{tart})_2]$ (Larsen, 1985). From these experiments K_Λ/K_Δ was estimated as ca 1.4. This result shows that the Λ isomer associates more strongly than the Δ isomer with $[\text{Sb}_2(\text{tart})_2]^{2-}$ as observed in the crystal, and that ion-pair association cannot be completely neglected. If the difference in ion-pair association alone should account for the difference in solubilities this would lead to the result that the Λ isomer forms the more soluble salt. However, even if association constants as large as 100 are assumed, a rough calculation shows that the difference in the ion-association equilibria alone cannot be responsible for the observed difference in solubilities. It is necessary to include a difference in Gibbs free energy and enthalpy between the two diastereoisomeric salts to explain the experimental solubilities.

The crystal structure determinations showed that the two salts differ mainly by containing the cation as different conformers in the two structures. Both the sign and the magnitude ($2\text{--}4\text{ kJ mol}^{-1}$) of the difference in conformational energy between the enantiomers are consistent with the difference in energies estimated from the solubilities.

The two salts have also been examined by thermogravimetry.* The less soluble isomer starts to lose the water of crystallization at 343 K and reaches a plateau at 357 K, when it has lost weight corresponding to four water molecules per formula unit. The more soluble Λ isomer begins to lose H_2O at a slightly lower temperature, 336 K. It reaches a plateau at 364 K with a weight loss equivalent to three water molecules per formula unit. When the temperature is increased above 383 K the compound loses weight and gradually becomes completely dehydrated at 463 K. It decomposes at 507 K.

Table 4 has been examined for differences in the surroundings of the water molecules in order to explain the different thermogravimetric results. In the less soluble salt, the water molecules seem more tightly bound. Three of the molecules are involved in four hydrogen bonds and one molecule is participating in three. In the more soluble salt two water molecules form four hydrogen bonds, and the remaining two forms three hydrogen bonds. This is in agreement with the observation that the water molecules will be lost at a higher temperature for the less soluble than for the more soluble. It is remarkable that O(31), which is not involved in hydrogen bonding with other water molecules, apparently is lost with the other water molecules.

Conclusion

The two salts formed by the enantiomers of the $[\text{Co}(\text{en})_2\text{gly}]^{3+}$ ion with $[\text{Sb}_2(\text{tart})_2]^{2-}$ ion differ from other similar systems of diastereoisomeric salts by precipitating the Δ isomer as the less soluble salt. This isomer is both in solution and in the crystalline state involved in weaker interactions with the $[\text{Sb}_2(\text{tart})_2]^{2-}$ ion than the Λ isomer which precipitates as the more soluble salt.

Chiral discrimination has previously been attributed to close contacts between the two different chiral ions in the salts (Okazaki, Sakaguchi & Yoneda, 1983). The present structure analysis has shown that a difference in the conformational energy of two chiral

ions that precipitate in the diastereoisomeric salts may also contribute to the chiral discrimination expressed as different solubilities of the salts.

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* The graphs have been deposited. See previous footnote.