

THE CRYSTAL AND MOLECULAR STRUCTURE  
OF CONFIGURATIONALLY CHIRAL *unsym-fac*-[N-(2-AMINOETHYL)-  
-1,3-DIAMINOPROPANE-(S)-ASPARTATO]COBALT(III)  
PERCHLORATE WITH DOMINATING VICINAL EFFECT  
IN ITS CIRCULAR DICHROISM

Jan ONDRÁČEK<sup>a</sup>, Jaroslav MAIXNER<sup>a</sup>, Bohumil KRATOCHVÍL<sup>a</sup>,  
Jana ONDRÁČKOVÁ<sup>b</sup> and František JURŠÍK<sup>b</sup>

<sup>a</sup> Department of Solid State Chemistry,  
Prague Institute of Chemical Technology, 166 28 Prague 6 and

<sup>b</sup> Department of Inorganic Chemistry,  
Prague Institute of Chemical Technology, 166 28 Prague 6

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The crystal and molecular structure of *unsym<sub>1</sub>-fac-A-( $\delta$ , chair)-(S)-[Co(aepn)(S)-Asp] ClO<sub>4</sub>* (*trans*-6,6) was solved by the heavy atom method. The positions of the non-hydrogen atoms and their anisotropic temperature parameters were refined on the basis of 1 935 observed reflections, yielding values of  $R = 0.121$  and  $wR = 0.117$ , affected by the undetermined position of the oxygen atoms in the ClO<sub>4</sub><sup>-</sup> anion. The substance crystallizes in the orthorhombic system with space group  $P2_12_12_1$ ;  $Z = 4$ ,  $a = 9.664(1)$ ,  $b = 11.805(1)$ ,  $c = 13.966(2)$  Å. The secondary atom of the triamine has *S* configuration, the conformation of the five-membered chelate ring approaches that of the asymmetrical  $\delta$  envelope and the six-membered ring has chair configuration. Both conformations are deformed. The donor atoms deviate from the defined planes and thus form further sources of chirality ( $\lambda$ ) contributing to the optical activity of the isomer. These deviations lead to the similarity of the CD spectra of the isomers.

Previous studies<sup>1-3</sup> have shown that the octahedral complexes of linear triamines forming fused chelate rings differ from the diamine complexes primarily in the marked dependence of the CD curves pattern and rotatory strength in the  $^1A_{1g} \rightarrow ^1T_{1g}$  spectral region on the ligand structure. For example, methylation of the secondary nitrogen atom of diethylenetriamine (Medien) limits the formation of isomers of the [Co(Medien)(S)-Asp]<sup>+</sup> complex to symmetrical form and further forces the five-membered chelate ring to assume the enantiomeric envelope conformation, so that its CD spectrum exhibits only the contribution from the (S)-aspartic acid<sup>1</sup>. Similarly, the vicinal contribution to unsymmetrical isomers of the [Co(dpt)-(S)-Asp]<sup>+</sup> (dpt = dipropylenetriamine) complex predominates; here, the linear triamine is coordinated to form two six-membered fused chelate rings, even though these isomers have configurational chirality<sup>2</sup>. This phenomenon, where the diastereoisomers exhibit identical CD curves pattern and the configurational contribution to

the rotatory strength in the region of  $d-d$  transition is smaller than the vicinal, is unique\* among octahedral chiral complexes and apparently specific for systems with condensed chelate rings in which the ligands behave as nonchelating as a result of deviations of the coordinating donor atoms from the Cartesian coordinates, and thus make only a small contribution to their circular dichroism<sup>2</sup>. Consequently, and especially because the reasons for the chirality of complexes of nonlinear polydentate ligands cannot be found in helicity of the chelate rings, analysis permitting correlation of the chiroptical properties and the configuration is an important step in determining their molecular structure by X-ray structural analysis. Thus, this work describes the structure of one of two unsymmetrical isomers, *unsym*<sub>1</sub>-*fac*-[Co(aepn)(S)-Asp]ClO<sub>4</sub> (aepn = N-(2-aminoethyl)-1,3-diaminopropane and Asp = aspartic acid), whose optical activity is the superposition of several contributions with predominance of the vicinal contribution<sup>3</sup>.

## EXPERIMENTAL

*Unsym*<sub>1</sub>-*fac*-*A*-(S)-[Co(aepn)(S)-Asp]ClO<sub>4</sub> was prepared<sup>5</sup> by the method of Legg and Cook with chromatographic separation of the reaction mixture. Crystals for X-ray structural analysis were prepared by recrystallization from water. For C<sub>9</sub>H<sub>20</sub>ClCoN<sub>4</sub>O<sub>8</sub> (406.7) calculated 26.58% C, 4.95% H, 13.77% N; found 26.60% C, 4.97% H and 13.48% N.

A four-circle CAD4 diffractometer (Enraf-Nonius) was used to measure the lattice parameters, determine the space group and find the reflection intensities. Measurements were carried out using a single crystal with dimensions of 0.10 × 0.15 × 0.20 mm. Systematic extinctions  $h00$ ;  $h = 2n + 1$ ,  $0k0$ ;  $k = 2n + 1$  and  $00l$ ;  $l = 2n + 1$ , were found from the complete data set. The lattice parameters were refined on the basis of 25 high-angle reflections. The  $\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$  radiation employed was monochromatized using a graphite monochromator. Reflections were measured in the interval  $0 < 2\theta < 60^\circ$  ( $0 \leq h \leq 13$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 19$ ) by the  $\theta/2\theta$  scanning technique with automatic adjustment of the scan rate in the range  $1.28-16.48^\circ \text{ min}^{-1}$ . A total of 2731 reflections were measured and the intensities of three standard reflections were controlled after measuring 200 reflections. The change in the intensities of the standard reflections during the measurement corresponded to a decrease of only 0.3% of the original value. Only 1935 reflections that fulfilled the condition  $I > 1.96\sigma(I)$  were considered as observed.

The phase problem was solved by the heavy atom method. The position of the cobalt atom was determined by evaluation of the Patterson map and the positions of the remaining non-hydrogen atoms were found from Fourier maps. The positions of the oxygen atoms in the perchlorate anions were not found, and the maxima around the chlorine atom did not correspond to a chemically acceptable model for this ion. The structural parameters were refined by minimization of the function  $\sum w(|F_o| - |F_c|)^2$  using the weighting scheme  $w = 1.5810/(\sigma^2(F_o) + 0.0009F_o^2)$ . A total of 172 parameters were refined in two block-diagonal cycles: the scale factors

\* A decrease in the rotatory strength of the transition in the region of the  $T_{1g}$  absorption band has also been observed in the circular dichroism spectrum of the octahedral complex with three 6-membered isolated chelate rings<sup>4</sup>. So far, however, no complex with two six-membered diamine chelate rings, whose optical activity consisted of both configurational chirality and a vicinal contribution, has been described.

and the positional and anisotropic temperature parameters of the non-hydrogen atoms. The disordered oxygen atoms of the  $\text{ClO}_4^-$  anions were not included in the refinement. The positions of the hydrogen atoms could not be found because of this disordering. The highest maximum in the final Fourier map was found in the vicinity of the chlorine atom (Table I). The maximal value in the final refinement cycle was  $(\Delta/\sigma)_{\max} = 0.0005$ . The final values of the reliability factors, which are strongly affected by the lack of the four oxygen atoms, are  $R = 0.121$  and  $wR = 0.117$ . The values of the atomic scattering factors for cobalt, which are not included in the SHELX-76 program, were taken from the tables<sup>6</sup>. All the calculations were carried out using the SHELXS-86 (ref.<sup>7</sup>), SHELX-76 (ref.<sup>8</sup>), PARST (ref.<sup>9</sup>) and XANADU (ref.<sup>10</sup>) programs on the EC 1033 computer and the data reduction programs, ORTEP and PLUTO of the SDP system on the PDP11/73 computer (ref.<sup>11</sup>).

The basic crystallographic data for the  $unsym_1\text{-fac-[Co(aepn)(S)-Asp].ClO}_4$  system are given in Table II. Table III contains the final atomic coordinates and their equivalent temperature parameters.

## RESULTS AND DISCUSSION

The coordination of N-(2-aminoethyl)-1,3-diaminopropane and (S)-aspartic acid around Co(III) leads theoretically to six possible isomers (conformational isomers are neglected), of which three have been found experimentally and have been tentatively identified<sup>3</sup> on the basis of their electronic absorption and circular dichroism spectra as *sym-fac*, *A-(S)-unsym<sub>1</sub>-fac*, and  $\Delta\text{-(R)-unsym}_2\text{-fac-[Co(aepn)-(S)-Asp]}^+$  (the symbols in parenthesis refer to the configuration of the secondary nitrogen atom). The limited isomer formation is a result of the stereospecific isomerization  $mer\text{-[Co(aepn)Cl}_3] \rightarrow fac\text{-[Co(aepn)(S)-Asp]}^+$  in which only the part of the triamine forming the six-membered chelate ring, are in motion<sup>3</sup> (unsymmetrical trigonal bipyramid intermediates). In addition, the isomerization is also controlled by the steric conditions around the C—N(H)—C bonds, preventing formation of the *endo* isomer<sup>3</sup>. Comparison of the chiroptical properties indicates that the chromato-

TABLE I

The highest maxima on the final Fourier map and their distances from the chlorine atoms

Distance Å	Maximum $e \text{ \AA}^{-3}$	Distance Å	Maximum $e \text{ \AA}^{-3}$
1.54	3.62	2.23	1.43
1.40	2.33	1.32	1.43
1.50	2.01	1.26	1.34
1.81	1.74	1.24	1.20
1.62	1.70	1.29	1.09
1.48	1.68		

graphic behaviour on ion-exchangers of all the unsymmetrical isomers of [Co(ABA).(*S*)-Asp]<sup>+</sup> type (ABA = linear triamine) can be correlated with their structures. The curves CD spectra patterns of *unsym*<sub>1</sub>-*fac*-[Co(dien)(*S*)-Asp]<sup>+</sup> (dien = diethylenetriamine) (ref.<sup>12</sup>), -[Co(aepn)(*S*)-Asp]<sup>+</sup> (ref.<sup>3</sup>) and -[Co(dpt)(*S*)-Asp]<sup>+</sup> (ref.<sup>2</sup>) isomers exhibit a positive and negative maximum for this reason irregardless

TABLE II

Basic crystallographic data for the studied compound

$a = 9.664(1) \text{ \AA}$	$\rho_c = 1.695 \text{ kg m}^{-3}$
$b = 11.805(1) \text{ \AA}$	space group: $P2_12_12_1$
$c = 13.966(2) \text{ \AA}$	$\mu(\text{Mo K}\alpha) = 1.70 \text{ mm}^{-1}$
$V = 1593.3(3) \text{ \AA}^3$	$F(000) = 840$
$Z = 4$	

TABLE III

Relative coordinates of the non-hydrogen atoms ( $\cdot 10^4$ ) and their equivalent temperature parameters ( $\cdot 10^3$ ).  $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Atom	$x$	$y$	$z$	$U_{eq}, \text{ \AA}^2$
Co	1 838(2)	8 342(2)	8 482(1)	17(1)
Cl	5 092(15)	8 365(8)	5 576(6)	160(9)
O1	18(11)	8 180(9)	9 046(7)	27(5)
O2	-2 239(12)	7 979(11)	9 071(9)	37(6)
O3	34(14)	10 702(9)	7 020(9)	38(7)
O4	1 478(11)	9 816(9)	7 967(8)	27(5)
N1	2 287(15)	9 039(11)	9 704(10)	32(7)
N2	3 762(15)	8 391(13)	8 054(11)	38(7)
N3	2 245(13)	6 796(10)	8 911(9)	25(6)
N4	1 109(14)	7 831(10)	7 246(8)	23(6)
C1	3 327(21)	10 046(16)	9 733(14)	47(11)
C2	4 747(23)	9 647(18)	9 298(17)	55(12)
C3	4 643(21)	9 456(20)	8 292(18)	55(13)
C4	4 475(17)	7 308(15)	8 337(21)	52(11)
C5	3 429(19)	6 390(13)	8 349(14)	41(10)
C6	-1 145(14)	8 174(13)	8 609(12)	28(8)
C7	-1 305(19)	8 306(14)	7 554(10)	32(8)
C8	63(19)	8 621(12)	7 048(11)	28(8)
C9	561(16)	9 839(12)	7 357(10)	23(7)

of the rotatory strength of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition (in the latter two cases, the calculated curves correspond to configurational chirality) and thus the isomers have the same configuration as a result of the change in  $\text{sign}^2$  of the components of the transition in dependence on the magnitude of the  $\text{NH}_2\text{—Co—N(H)}$  angle. The arrangement of the chelate rings of the first of the two isolated unsymmetrical isomers and the configuration of the secondary nitrogen atom proposed on the basis of its CD spectrum (the calculated  $\Delta\epsilon$  values corresponding to configurational chirality<sup>3</sup>:  $\Delta\epsilon_{540} = +0.47$ ;  $\Delta\epsilon_{480} = -0.44$ ), in which vicinal chirality predominates similarly as for the *unsym-fac*-[Co(dpt)(*S*)-Asp]<sup>+</sup> isomers, were confirmed by determination of the molecular structure (perspective drawing together with the atom-numbering scheme, is given in Fig. 1), which can be considered as a model for all the *unsym<sub>1</sub>-fac* isomers.

The crystal structure of the complex studied (the interatomic distances and bonding angles are given in Table IV) consists of the [Co(aepn)(*S*)-Asp]<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> ions. In this structure, the [Co(aepn)(*S*)-Asp]<sup>+</sup> cations are interconnected by NH...O bridges (Table V). The participation of the carbonyl oxygen atoms of the carboxylic groups in the formation of hydrogen bonding is evident in equalization of the C—O and C=O interatomic distances, which is especially apparent for the five-membered ring of aspartic acid. The arrangement of the chelate rings (*trans*-6,6) depicted in Fig. 1, which due to the nonlinear character of Asp does not permit the chirality to be determined by ring pairing, corresponds to the *unsym<sub>1</sub>-fac*-[Co(dien)(*R*)-Asp]<sup>+</sup> isomer (considering the opposite chirality of aspartic acid), which was assigned configuration *A* on the basis of analysis of the CD spectra<sup>5</sup>. The same

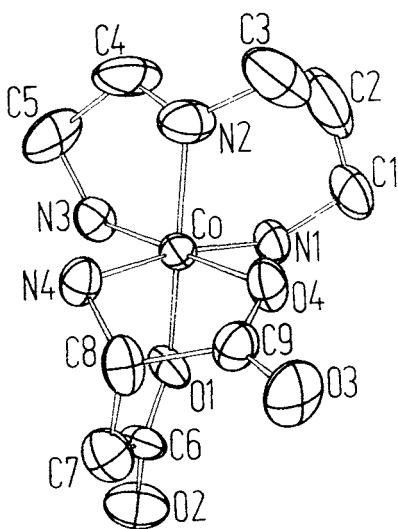


FIG. 1  
A perspective view of the *unsym<sub>1</sub>-fac*-(*S*)-[Co(aepn)(*S*)-Asp]<sup>+</sup> cation

TABLE IV

The intramolecular interatomic distances and bonding and torsion angles in the *unsym*<sub>1</sub>-*fac*-[Co(aepn)(*S*)-Asp]ClO<sub>4</sub> isomer

Interatomic distances (Å)			
Co—O1	1.937(11)	N2—C3	1.554(27)
Co—O4	1.915(11)	N2—C4	1.505(24)
Co—N1	1.944(14)	N3—C5	1.468(22)
Co—N2	1.954(15)	N4—C8	1.403(21)
Co—N3	1.961(12)	C1—C2	1.573(30)
Co—N4	1.960(12)	C2—C3	1.427(35)
O1—C6	1.279(18)	C4—C5	1.482(24)
O2—C6	1.260(19)	C6—C7	1.490(22)
O3—C9	1.232(18)	C7—C8	1.545(25)
O4—C9	1.230(18)	C8—C9	1.577(21)
N1—C1	1.557(24)		
Bonding angles (°)			
N3—Co—N4	93.1(5)	Co—N2—C3	118.7(12)
N2—Co—N4	94.7(6)	C3—N2—C4	112.3(14)
N2—Co—N3	86.0(6)	Co—N3—C5	107.3(10)
N1—Co—N4	169.8(6)	Co—N4—C8	103.2(9)
N1—Co—N3	94.6(5)	N1—C1—C2	108.9(15)
N1—Co—N2	92.5(6)	C1—C2—C3	111.5(18)
O4—Co—N4	83.3(5)	N2—C3—C2	112.2(18)
O4—Co—N3	175.7(5)	N2—C4—C5	108.2(14)
O4—Co—N2	91.8(6)	N3—C5—C4	107.4(14)
O4—Co—N1	89.2(5)	O1—C6—O2	119.6(14)
O1—Co—N4	90.1(5)	O2—C6—C7	116.0(13)
O1—Co—N3	88.1(5)	O1—C6—C7	124.2(13)
O1—Co—N2	172.6(6)	C6—C7—C8	112.9(12)
O1—Co—N1	83.5(5)	N4—C8—C7	111.5(12)
O1—Co—O4	94.5(5)	C7—C8—C9	110.8(13)
Co—O1—C6	127.2(10)	N4—C8—C9	109.4(13)
Co—O4—C9	114.3(10)	O4—C9—C8	112.9(13)
Co—N1—C1	119.4(11)	O3—C9—C8	121.6(14)
Co—N2—C4	109.3(11)	O3—C9—O4	125.5(14)
Torsion angles (°)			
N2—Co—N1—C1	41.7(13)	Co—N3—C5—C4	45.7(16)
N3—Co—N2—C4	-3.7(12)	Co—N4—C8—C9	39.6(13)
Co—O1—C6—C7	-0.6(21)	N1—C1—C2—C3	69.3(21)
Co—O4—C9—C8	-8.3(16)	C1—C2—C3—N2	-70.3(23)
Co—N1—C1—C2	-58.6(18)	N2—C4—C5—N3	-49.7(19)
Co—N2—C4—C5	30.0(18)	O1—C6—C7—C8	-8.1(22)
Co—N2—C3—C2	59.7(21)	N4—C8—C9—O4	-22.9(18)

chirality follows from the CD curves calculated for configurational chirality<sup>3</sup> of *unsym*<sub>1</sub>-*fac*-[Co(aepn)(S)-Asp]<sup>+</sup>. The configuration of the secondary nitrogen atom defined by the positions of the five- and six-membered chelate rings aepn is *S*. This configuration corresponds to the *exo* position the N—H bond.

The CoN<sub>2</sub>O<sub>4</sub> octahedron is considerably deformed, more than for the *sym-fac* isomer. The greatest deviation from ideal octahedral geometry is exhibited by the N1 and N4 donor atoms, which deviate from the perpendicular line passing through the equatorial plane by about 12.2°. The longest bonds are Co—N3 and Co—N4 and the shortest are Co—O1 and Co—O4. The bond lengths exhibit the same trend as for the *sym-fac* isomer. The N—C and C—C interatomic distances are longer in the six-membered aepn ring than in the five-membered one. The lengths of the C—C bonds in the six-membered aepn ring are not equivalent and are not much longer than the distances calculated for the isolated six-membered ring<sup>13</sup>. The Co—N bonds were found to be shortened. The Co—sec. N interatomic distance, which changes in dependence on the structure of the linear triamine, is shorter for the *sym-fac* isomer. Its length, which reflects the greater steric strain in the dpt complex, decreases in the order: *sym-fac*-[Co(dpt)(S)-Asp]<sup>+</sup> (ref.<sup>14</sup>) > *unsym*<sub>1</sub>-*fac* > *sym-fac*-[Co(aepn)(S)-Asp]<sup>+</sup> (ref.<sup>15</sup>). It follows from comparison of the interatomic distances of the atoms constituting the aepn ring that the length of the N—C bonds in both rings in both the *unsym*<sub>1</sub>-*fac* and *sym-fac* isomers is different and this asymmetry is greater in the *sym-fac* isomer. In addition, the C1—C2 and C2—C3 interatomic distances are also different in the six-membered ring. As these bond lengths are not significantly different in the *sym-fac*-[Co(dpt)(S)-Asp]<sup>+</sup> isomer (ref.<sup>13</sup>), the condensed five-membered chelate ring apparently affects the length of the C—C bonds.

Except for the O1—Co—N4 angle, the bonding angles of the donor atoms with the cobalt atom differ from 90°. The greatest deviations are exhibited by the N2—Co—N4, N1—Co—N3, O4—Co—N4, O1—Co—N1 and O1—C—O4 angles. The endocyclic angles in the aepn chelate rings remain almost the same as in the *sym-fac* isomer except for the six-membered ring, where the N1—Co—N2 angle is close to 90°, i.e. the theoretical value for an isolated six-membered ring<sup>13</sup>. In contrast, the sum of the internal angles of the five-membered ring is 6° less than for the

TABLE V

Probable hydrogen bonds (in Å). Symmetry code: *i*) 1/2 + *x*, 1/2 - *y* + 1, -*z* + 2; *ii*) -*x*, 1/2 + *y* - 1, 1/2 - *z* + 1

N1...O2 <sup><i>i</i></sup>	2.969(19)	N3...O2 <sup><i>i</i></sup>	2.874(18)
N3...O3 <sup><i>ii</i></sup>	2.865(18)	N4...O3 <sup><i>ii</i></sup>	2.931(17)

*sym-fac* isomer, which could be one of the reasons for the different thermodynamic stabilities of the two isomers. Compared to the *sym-fac* isomer, the Co—N1—C1 and Co—N2—C3 angles, with an average value of 119.5(11)°, are closer to the value of 120° calculated<sup>13</sup> for an isolated six-membered ring.

The conformation of the chelate rings depends both on their size and stability. It follows from the deviations given in Table VI that the six-membered aepn ring assumes the energetically favourable chair conformation with the Co and C2 atoms deviating by 0.776(20) and -0.747(22) Å from the plane formed by the N1N2C1C3 atoms, where the C2 atom is oriented away from the five-membered ring of aspartic acid, thus decreasing the probability of interligand interaction. It follows from the values of the Co—N1—C1 and Co—N2—C3 angles that the chair is somewhat

TABLE VI

Deviations of the atoms in the *unsym*<sub>1</sub>-*fac*-[Co(aepn)(*S*)-Asp]ClO<sub>4</sub> isomer from the defined planes. The planes are fitted through the atoms designated by an asterisk

Atom	Deviation Å	Atom	Deviation Å
Plane 1 <sup>a</sup>		Plane 3 <sup>c</sup>	
Co*	-0.002(2)	Co*	0.002(20)
O1*	-0.074(11)	O4*	0.040(11)
N1*	0.148(13)	N1*	-0.122(14)
N2*	-0.133(15)	N3*	0.042(13)
N4*	0.112(12)	N4*	-0.106(13)
Plane 2 <sup>b</sup>		Plane 4 <sup>d</sup>	
Co*	-0.000(20)	N1*	-0.004(14)
O1*	-0.042(10)	N2*	0.005(15)
O4*	0.051(11)	C1*	0.010(20)
N2*	-0.102(15)	C3*	-0.016(23)
N3*	0.071(13)	C2	-0.747(22)
Plane 5 <sup>e</sup>		Co	0.776(2)
Co*	0.0	N2*	0.0
N3*	0.0	C4	0.092(27)
		C5	-0.555(19)

<sup>a</sup> -0.199(4) X + 0.930(2) Y - 0.310(4) Z = 5.14(7),  $\chi^2 = 341.9$ ; <sup>b</sup> -0.320(4) X - 0.391(4) Y - 0.863(2) Z = -14.642(22),  $\chi^2 = 161.7$ ; <sup>c</sup> 8.937(2) X + 0.067(5) Y - 0.343(5) Z = -1.74(8),  $\chi^2 = 116.3$ ; <sup>d</sup> -0.614(7) X + 0.550(9) Y - 0.566(5) Z = -3.16(16),  $\chi^2 = 0.839$ ; <sup>e</sup> 0.276(7) X + 0.353(6) Y + 0.894(4) Z = 14.56(3).



flattened. In addition, the C1—C2 and C2—C3 interatomic distances indicate that it is also partly deformed. The degree of this deformation is particularly apparent, when Co—N1—C1—C2 ( $-58.6(18^\circ)$ ) and Co—N2—C3—C2 ( $59.66(21)^\circ$ ) torsion angles are compared. In the five-membered ring, the deviations of the C4 and C5 atoms from the line connecting the N2 and N3 atoms define the  $\delta$  conformation, which approaches an asymmetrical envelope. As follows from the Dreiding model, this conformation is preferable as, in the  $\lambda$  conformation of the five-membered ring, the hydrogen atoms on the C3 and C4 atoms are in mutual interaction (the model gives an H $\cdots$ H distance of  $\sim 1.5$  Å). These interactions are however, absent in the  $\delta$  conformation. The unsymmetrical distribution of the C4 and C5 atoms (Table VI) with respect to the N2—Co—N4 axis is very closely connected with the presence of the six-membered ring and its conformation. The N2—C4—C5—N3 torsion angle, with a value of  $-49.7(19)^\circ$ , indicates that the degree of puckering of the five-membered ring is only slightly greater than for the *sym-fac* isomer ( $48.3^\circ$ ). (ref.<sup>15</sup>). However, compared to the isolated five-membered ring (see ref.<sup>16</sup>), the value of the torsion angle is decreased as fused chelate rings are involved.

Finally, as follows from Table VI, the donor atoms deviate from the mean planes and their positions with respect to these planes define a helical system around the cobalt atom, similarly as for the *sym-fac*-[Co(dpt)(S)-Asp]<sup>+</sup> isomer<sup>14</sup> ( $\lambda$ ,  $\delta$ ,  $\lambda$ -planes 1, 2 and 3 in Table VI — net result  $\lambda$ ). Thus, in addition to the other contributions, the *unsym<sub>1</sub>-fac* isomer also has a contribution to circular dichroism. The determined deviations from the planes not only lead to the very complex CD spectra of the complexes with fused chelate rings, but also result in the measured CD spectra not reflecting the chirality following from the distribution of the chelate rings around the cobalt atom<sup>2</sup>. The donor atom helicity can greatly contribute to the CD sign in complexes where the primary source of the optical activity lies in vicinal or conformational chirality (refs<sup>17,18</sup>).

Except for the C6—C7 and O4—C9 distances and the Co—O1—C6 and O4—C9—C8 angles, the chelate rings of aspartic acid in the *unsym<sub>1</sub>-fac* isomer do not greatly differ from the values found for the *sym-fac* isomer<sup>15</sup>. The five-membered chelate ring of aspartic acid assumes an asymmetric  $\delta$  envelope and the six-membered ring a skew boat conformation. The contributions of the aspartic acid to the optical activity of the complex are the same in all the isomers of [Co(ABA)(S)-Asp]<sup>+</sup>.

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