

**SYNTHESIS OF THE *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> ISOMER AND ITS STEREOCHEMICAL COMPARISON WITH OTHER TERNARY COBALT(III) COMPLEXES CONTAINING (*S*)-ASPARTIC ACID AND LINEAR TRIAMINE\***

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The *sym-fac*-[Co(medien)(*S*)-Asp]ClO<sub>4</sub> (medien = 4-methyl-1,4,7-triazaheptane) isomer was prepared from [Co(medien)Cl<sub>3</sub>] and Ag<sub>2</sub>(*S*)-Asp in the presence of charcoal. Since *sym-fac* isomer does not isomerize when equilibrated with charcoal, its formation is of thermodynamic origin. The *sym-fac* configuration was assigned from electronic, NMR, and circular dichroism spectra. The *d-d* circular dichroism spectrum which is very similar both in shape and relative intensity to that of the [Co(NH<sub>3</sub>)<sub>3</sub>(*S*)-Asp]<sup>+</sup> ion exhibits vicinal contribution from *S* centre, conformational contributions either from aspartic acid ( $\lambda$ ,  $\delta$ -twist boat) either from medien rings ( $\lambda$ ,  $\delta$  or  $\delta$ ,  $\lambda$  asymmetric envelope). The last contributions are canceled. NMR parameters are consistent with symmetrical conformation which is favoured due to the staggered placement of N—CH<sub>3</sub> group with respect to oxygen atoms of aspartic acid. The preferred formation of *sym-fac* isomer over *unsym-fac* ones is discussed in relation to the nonbonded interactions of N—CH<sub>3</sub> group with H<sub>ax</sub> of adjacent NH<sub>2</sub> group of aspartic acid in each of the two *unsym-fac* isomers.

Systematic studies of stereochemistry of cobalt(III) complexes imposed by structural-related ligands have largely included the use of quadridentate ligands. Contrary to this, limited amount of work has been devoted to metal complexes of terdentate ligands. The most widely studied is [Co(AAA)<sub>2</sub>]<sup>3+</sup> system (AAA = linear terdentate ligand). However, as far as mixed ligand cobalt(III) complexes are concerned, work has concentrated to the study of [Co(dien)(ONO)]<sup>+</sup> (dien = diethylenetriamine, ONO = aminodicarboxylate) isomers<sup>1-3</sup>. Since this system include chelation of terdentate ligand forming two fused five-membered chelate rings, question concerning the relationship between the structure of closely related linear triamines and stereochemistry of cobalt(III) complexes arises. In this paper stereochemistry of [Co(AAA)-(*S*)-Asp]<sup>+</sup> isomers adopted by homologous terdentate ligand AAA *i.e.* 4-methyl-diethylenetriamine (4-methyl-1,4,7-triazaheptane) is described.

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## EXPERIMENTAL

4-Methyldiethylenetriamine (medien) was prepared by the procedure described in the literature<sup>4</sup>. (S)-aspartic acid was purchased from Reanal ( $[\alpha]_{589} = +24^\circ$  in 1M-HCl).

*Preparation of sym-fac*-[Co(medien)(S)-Asp]ClO<sub>4</sub>. This complex was prepared according to the method of Legg and Cooke<sup>2</sup> by the reaction of [Co(medien)Cl<sub>3</sub>] with Ag<sub>2</sub>(S)-Asp (scale 0.03 mol of [Co(medien)Cl<sub>3</sub>]) in the presence of charcoal. Because the evaporation of reaction mixture in air did not afford solid material, the reaction mixture was diluted and poured into a column of Dowex 50WX8 (3 × 60 cm, 100–200 mesh, Na<sup>+</sup> cycle) cation resin and eluted with water. Further elution with 0.2M-NaClO<sub>4</sub> solution gave only one broad orange band. The eluate was divided into fractions of 15 ml and optical rotation together with absorption spectra were measured. Since all fractions contained only one isomer, they were collected all together and concentrated *in vacuo* at 40°C. NaClO<sub>4</sub> deposited was continuously filtered off and filtrate was evaporated. Dry solid was extracted with acetone which dissolved NaClO<sub>4</sub>. Orange solid remained was dissolved in minimum amount of water and passed through a Sephadex G-10 column (2 × 30 cm). The eluate was evaporated. For C<sub>9</sub>H<sub>18</sub>ClCoN<sub>4</sub>O<sub>8</sub> (405.8) calculated: 26.70% C, 4.95% H, 13.80% N; found: 26.69% C, 5.22% H, 13.81% N.

*sym-fac*-[Co(dien)(S)-Asp]ClO<sub>4</sub> was obtained by the method of Legg and Cooke<sup>2</sup>. For the preparation of [Co(NH<sub>3</sub>)<sub>3</sub>(S)-Asp]ClO<sub>4</sub> direct oxidation of reaction mixture was used<sup>5</sup>.

*Physical measurements.* Electronic absorption spectra were recorded on Specord UV-VIS spectrophotometer. CD spectra were collected on Jouan Dichrograph Model II. <sup>1</sup>H NMR spectra were obtained on either Varian XL100 or Tesla apparatus both operating at 100 MHz. Spectra were obtained in D<sub>2</sub>O using DSS as internal standard. For the <sup>13</sup>C NMR spectra measurements Tesla instrument operating at 20 MHz was used. <sup>13</sup>C NMR spectra in <sup>2</sup>H<sub>2</sub>O were referenced to dioxane. Optical rotations were measured on Perkin-Elmer 241 spectropolarimeter.

## RESULTS AND DISCUSSION

The complex [Co(medien)(S)-Asp]ClO<sub>4</sub> was prepared by a procedure analogous to that used to prepare [Co(dien)(S)-Asp]<sup>+</sup>, *i.e.* by the reaction of *mer*-[Co(medien).Cl<sub>3</sub>] with Ag<sub>2</sub>(S)-Asp in the presence of charcoal. Although three isomers can be theoretically expected (Fig. 1), chromatography of reaction mixture on cation ex-

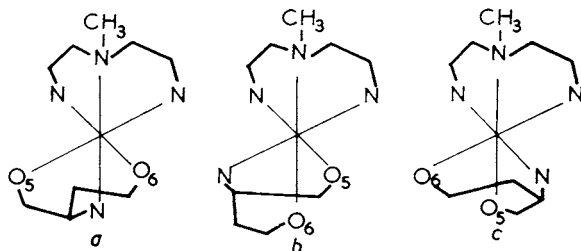


FIG. 1

Possible isomers of [Co(medien)(S)-Asp]<sup>+</sup> a *sym-fac*; b *unsym<sub>1</sub>-fac*; c *unsym<sub>2</sub>-fac*

change resin afforded only one isomer. Elemental analysis is in accord with the above formulation, and the facial structure was confirmed from visible absorption spectral data. The complex isolated belongs to  $\text{CoN}_4\text{O}_2$  chromophore which leads to two different positions of oxygen atoms (Fig. 1). The electronic absorption spectrum of  $[\text{Co}(\text{medien})(S)\text{-Asp}]^+$  isomer in aqueous solution shows two symmetrical visible absorption bands ( $20\,220\text{ cm}^{-1}$ ,  $\epsilon = 84.2\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ;  $27\,920\text{ cm}^{-1}$ ,  $\epsilon = 63.5\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) (Fig. 2) which are similar in shape but their maxima are shifted to lower energy, compared to those of *sym-fac*- $[\text{Co}(\text{dien})(S)\text{-Asp}]^+$  ( $20\,620\text{ cm}^{-1}$ ,  $28\,860\text{ cm}^{-1}$ ) due to the N-methylation. This similarity and absence of splitting confirm facial geometry of isomer prepared. Another means of identification and differentiation between *sym-fac* and *unsym-fac* isomers lies with the CD,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

The isolated optically active product yielded CD curve which can not be explained due to its chiral structure. The great similarity in shape between the CD curves of isomer obtained and  $[\text{Co}(\text{NH}_3)_3(S)\text{-Asp}]^+$  or *sym-fac*- $[\text{Co}(\text{dien})(S)\text{-Asp}]^+$  is obvious in comparison (Fig. 3, Table I), all showing the same pattern and intensity of CD. This indicates clearly that  $[\text{Co}(\text{medien})(S)\text{-Asp}]^+$  isomer has *sym-fac* geometry with vicinal and conformational effects as an only source of optical activity (dissymmetry originating from the unsymmetrical character of Asp should not be neglected<sup>5</sup>). Since aspartic acid coordinates rigidly when chelated as terdentate ligand in  $[\text{Co}(\text{NH}_3)_3(S)\text{-Asp}]^+$ ,  $[\text{Co}(\text{dien})(S)\text{-Asp}]^+$  and  $[\text{Co}(\text{medien})(S)\text{-Asp}]^+$ , making conformational contribution constant, difference between *sym-fac*- $[\text{Co}(\text{medien})(S)\text{-Asp}]^+$  and *sym-fac*- $[\text{Co}(\text{dien})(S)\text{-Asp}]^+$  consists essentially in the confor-

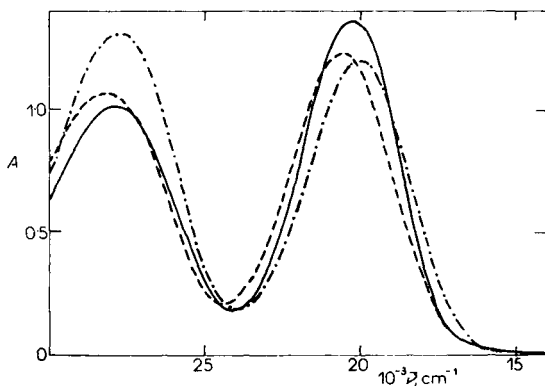


FIG. 2

Absorption spectra of *sym-fac*- $[\text{Co}(\text{medien})(S)\text{-Asp}]^+$  ———, *sym-fac*- $[\text{Co}(\text{dien})(S)\text{-Asp}]^+$  ----, and  $[\text{Co}(\text{NH}_3)_3(S)\text{-Asp}]^+$  -.-.-.

mation of triamine part. Two dien (medien) rings can generally adopt the variety conformations:  $\delta-\delta$ ,  $\delta-\lambda$ ,  $\lambda-\delta$ ,  $\lambda-\lambda$ , including also asymmetric envelope conformations. Whereas the  $\delta-\delta$  and  $\lambda-\lambda$  ones contribute to negative and positive circular dichroism, respectively, symmetric mixed conformation  $\lambda, \delta$  ( $\delta, \lambda$ ) and asymmetric envelope conformation have no effect on the  $d-d$  circular dichroism intensity. The fact that both *sym-fac*-[Co(medien)(S)-Asp]<sup>+</sup> and [Co(NH<sub>3</sub>)<sub>3</sub>(S)-Asp]<sup>+</sup> exhibit similar CD spectra (except of different CD bands energies) both in appearance and intensity, strongly suggests that the conformational contribution to the CD in the former is compensated and hence C-vicinal and other effects<sup>5</sup> from (S)-aspartic acid dominates. Justification for it arises from the application of regional rule for the optical activity of the  $d-d$  transitions of the conformational isomers of octahedral

TABLE I

Circular dichroism data obtained for the mixed cobalt(III) aspartic acid complexes

Complex	$\lambda_{\max}, \text{cm}^{-1}$	$\Delta(\epsilon)$
[Co(NH <sub>3</sub> ) <sub>3</sub> (S)-Asp]ClO <sub>4</sub>	18 656	+0.25
	27 700	+0.20
<i>sym-fac</i> -[Co(dien)(S)-Asp]ClO <sub>4</sub>	20 408	+0.77
	27 700	+0.20
<i>sym-fac</i> -[Co(medien)(S)-Asp]ClO <sub>4</sub>	20 202	+0.28
	27 472	+0.15

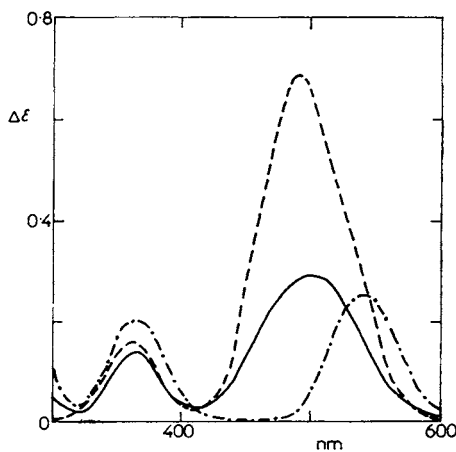


FIG. 3

CD spectra of *sym-fac*-[Co(medien)(S)-Asp]<sup>+</sup> ———, *sym-fac*-[Co(dien)(S)-Asp]<sup>+</sup> - - - - , and [Co(NH<sub>3</sub>)<sub>3</sub>(S)-Asp]<sup>+</sup> - · - · - ·

metal complexes derived by Bosnich and Harowfield<sup>6</sup>. As can be seen from Fig. 4, where  $\lambda$ ,  $\delta$  and  $\delta$ ,  $\lambda$  envelope conformations are depicted, conformation contributions to the  $d-d$  circular dichroism are canceled ( $\text{CH}_2$  groups of medien generate positive and negative circular dichroism) when rings adopt  $\lambda$  and  $\delta$  conformation or exist in  $\lambda$ ,  $\delta$  asymmetric envelope conformations.

In bis- or tris-chelated diamine system N-alkylation usually alter the conformer distribution in favour to one with equatorially disposed alkyl group. N— $\text{CH}_3$  group in *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> has equatorial character regardless of chelate ring conformation. However, N— $\text{CH}_3$  group of medien lies in the space between two oxygen atoms ( $\text{O}_5$  and  $\text{O}_6$ ) of (*S*)-aspartic acid (the opposite direction of N— $\text{CH}_3$  group is due to the serious nonbonded interactions in medien rings sterically excluded) and its orientation toward  $\text{O}_5$  or  $\text{O}_6$  depends on the conformation of coupled chelate rings (molecular models). Steric repulsion imposed by N— $\text{CH}_3$  group can be relieved when this group will be poised just between  $\text{O}_5$  and  $\text{O}_6$  which is realized for  $\lambda$ ,  $\delta$  or  $\delta$ ,  $\lambda$  asymmetric envelope conformations. This causes on the other hand that N— $\text{CH}_3$  group is not oriented away from the node normal to octahedral edge and does not contribute to  $d-d$  circular dichroism. Reduced intensity of low-energy CD band in comparison with that of *sym-fac*-[Co(dien)(*S*)-Asp]<sup>+</sup> suggests that medien rings must adopt either the  $\lambda$  (ring A) and the  $\delta$  (ring B) or  $\delta$ ,  $\lambda$  envelope conformations which place both  $\alpha$ - and  $\beta$ - $\text{CH}_2$  carbons of medien rings A and B symmetrically toward mirror plane bisecting the  $\text{NH}_2\text{—Co—NH}_2$  angle formed by medien molecule. Both conformations which are fixed by the N— $\text{CH}_3$  group may be of similar energy and are capable of interconversion. Broad — $\text{CH}_2\text{—CH}_2\text{—}$  resonances observed in the <sup>1</sup>H NMR spectrum and CD intensity support our assumption.

Further support for *sym-fac* arrangements of geometry is afforded by NMR spectra. As expected because of  $C_1$  symmetry, the <sup>13</sup>C NMR spectrum of *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> isomer should show four resonances corresponding to

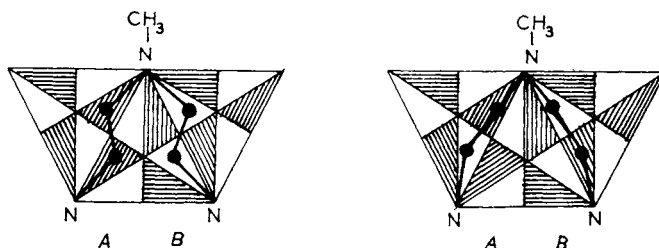


FIG. 4

$\lambda$ ,  $\delta$  and  $\delta$ ,  $\lambda$  asymmetric envelope conformations of medien in *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup>. Sector occupancy of medien C atoms

magnetically different carbon atoms of medien backbone. The resonance separations of the double peaks are larger in *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> than those of *sym-fac*-[Co(dien)(*S*)-Asp]<sup>+</sup> isomer. In addition another resonances corresponding to N—CH<sub>3</sub>, α-CH, β-CH<sub>2</sub>, α- and β-COO carbon atoms should also appear. The results summarized in Table II bear out these expectations. The spectral resonance parameters both for *sym-fac*-[Co(medien)((*S*)-Asp)]<sup>+</sup> and *sym-fac*-[Co(dien)((*S*)-Asp)]<sup>+</sup> were assigned on comparison with the <sup>13</sup>C NMR spectra of [Co(dien)<sub>2</sub>]<sup>3+</sup> (ref.<sup>7</sup>), *sym-fac*-[Co(medien)<sub>2</sub>]<sup>+</sup> (ref.<sup>4</sup>) and [Co(NH<sub>3</sub>)<sub>3</sub>((*S*)-Asp)]<sup>+</sup> (ref.<sup>5</sup>). Two resonance signals which appear in the low field are associated with the carbon atoms of α- and β-COO groups, respectively. The lower field resonance (185 ppm) is in accordance with reference to literature<sup>8</sup> ascribed to α-COO whereas the higher field one (177 ppm) to β-COO.

The 100 MHz <sup>1</sup>H NMR spectra of *sym-fac*-[Co(medien)((*S*)-Asp)]<sup>+</sup>, *sym-fac*-[Co(dien)((*S*)-Asp)]<sup>+</sup> and [Co(NH<sub>3</sub>)<sub>3</sub>(*S*)-Asp]<sup>+</sup> which are consistent with <sup>1</sup>H NMR spectra of bis((*S*)-aspartato)cobaltate(III) isomers<sup>9</sup> are given in Table III. The protons of aspartic acid form an ABX system (resonances arising from methylene protons of medien are not informative and thus are not discussed) and data summarized in Table III show that there are no substantial differences in the coordination of aspartic acid. Fact that triamine part of the complex does not influence significantly the conformation of aspartic acid is readily apparent from the comparable values of *J*<sub>AB</sub>.

As follows from the experimental part, medien contrary to dien tends to give *sym-fac* isomer only. This distinct contrast in coordination suggests that the methyl group of the nitrogen atom of the linear terdentate ligand exerts pronounced effect on the mode of coordination of the second terdentate one. N—CH<sub>3</sub> group is in close proximity to an apical octahedral positions occupied in *unsym-fac* isomers by NH<sub>2</sub> group of aspartic acid. Detailed examinations of Dreiding scale models suggests that both *unsym-fac* isomers (model also excludes mer coordination of aspartic acid) experience nonbonded interactions between N—CH<sub>3</sub> group of medien and N—H<sub>ax</sub> of aspartic acid which prevents probably their formation. Similarly, coordination of medien both in [Co(medien)<sub>2</sub>]<sup>3+</sup> and [Co(dien)(medien)]<sup>3+</sup> ions obtained by the usual air oxidation technique leads only to the *sym-fac* isomer, although substitution reaction between *fac*-[Co(H<sub>2</sub>O)Cl<sub>2</sub>(medien)]<sup>+</sup> and dien afforded also *unsym-fac*-[Co(dien)(medien)]<sup>3+</sup> isomer (ref.<sup>10</sup>). In an effort to determine if the *unsym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> isomer can be obtained through the isomerization of the *sym-fac* one, the aqueous solution of the latter isomer was equilibrated for several hours at 65°C in the presence of charcoal. However, chromatography of the reaction mixture did not revealed the presence of *unsym-fac* isomer. The complex obtained after equilibration exhibited chiroptical properties indistinguishable from the initial *sym-fac*-[Co(medien)(*S*)-Asp]<sup>+</sup> isomer. Both the absence of other isomers in the equilibrium mixture and the fact that equilibration of *sym-fac*-

$-\text{[Co(medien)(S)-Asp]}^+$  is not accompanied with disproportionation and formation of  $[\text{Co(medien)}_2]^{3+}$  and  $[\text{Co}((S)\text{-Asp})_2]^-$  demonstrate that the synthesis of *sym-fac*- $-\text{[Co(medien)(S)-Asp]}^+$  isomer is undoubtedly of thermodynamic origin. Although the stereochemistry of both  $[\text{Co(dien)(medien)}]^{3+}$  and  $[\text{Co(medien)(S)-Asp}]^+$

TABLE II  
 $^{13}\text{C}$  NMR chemical shifts (ppm) of different cobalt(III) complexes containing aspartic acid

$\beta\text{-CH}_2$	$\alpha\text{-CH}$	$\alpha\text{-COO}$	$\beta\text{-COO}$	$^1\text{CH}_2$	$^2\text{CH}_2$	N—CH <sub>3</sub>
<i>sym-fac</i> -[Co(medien)(S)-Asp]ClO <sub>4</sub>						
37·40	56·97	184·79	177·32	42·59 42·15	61·98 61·48	48·20
<i>sym-fac</i> -[Co(dien)(S)-Asp]ClO <sub>4</sub>						
37·63	56·79	185·31	177·62	44·54 44·20	52·05	—
[Co(NH <sub>3</sub> ) <sub>3</sub> (S)-Asp]ClO <sub>4</sub> <sup>a</sup>						
37·29	57·16	185·60	177·68	—	—	—

<sup>a</sup> Ref.<sup>5</sup>, H<sub>2</sub>N—<sup>1</sup>CH<sub>2</sub>—<sup>2</sup>CH<sub>2</sub>—N(CH<sub>3</sub>)—<sup>2</sup>CH<sub>2</sub>—<sup>1</sup>CH<sub>2</sub>—NH<sub>2</sub>.

TABLE III  
 $^1\text{H}$  NMR chemical shifts (ppm) and coupling constants (Hz) of different cobalt(III) complexes containing aspartic acid

N—CH <sub>3</sub>	$\delta_x^a$	$\delta_A^a$	$\delta_B^a$	$J_{AB}$	$J_{AX}$	$J_{BX}$
<i>sym-fac</i> -[Co(medien)(S)-Asp]ClO <sub>4</sub>						
2·70	3·92	2·93	2·74	14	6	4
<i>sym-fac</i> -[Co(dien)(S)-Asp]ClO <sub>4</sub>						
	3·94	2·98	2·82	13·5	5	4
[Co(NH <sub>3</sub> ) <sub>3</sub> (S)-Asp]ClO <sub>4</sub> <sup>b</sup>						
	3·94	2·95	2·84	11·5	5	2

<sup>a</sup> F or designation of A and B protons see ref.<sup>9</sup>; <sup>b</sup> ref.<sup>5</sup>.

complexes should be very similar, they differ from each other in the conformational flexibility of dien rings in comparison with aspartic acid ones. Conformational flexibility allows to dien chelate rings to accommodate more to the steric requirements of N—CH<sub>3</sub> group of medien which in turn makes the formation of *unsym-fac*-[Co(dien)(medien)]<sup>3+</sup> isomer possible. On the other hand aspartic acid five-membered chelate ring is forced to adopt rigid  $\lambda$  conformation which causes the mentioned steric requirements are more exclusive and only one preferred isomer (*sym-fac*) is formed. The same arguments rationalize the exclusive formation<sup>11</sup> of *sym-fac*-[Co(medpt)(S)-Asp]<sup>+</sup> (medpt = 5-methyl-1,5,9-triazanonane) isomer. Furthermore, Kojima<sup>10</sup> and coworkers stated that when medien coordinates to Co(III) ion, the Co—N(CH<sub>3</sub>) bond lengthens (the lengthening of the Co—N(CH<sub>3</sub>) bond accounts for the shift of absorption maximum to lower energy due to the lower ligand field strength for medien) compared with Co—N(H) distance in dien and the angle Co—N—C(H<sub>3</sub>) becomes larger than the normal tetrahedral angle. Although these structural changes can reduce steric repulsion mentioned, *sym-fac* geometry remains the most stable one.

The other factor undoubtedly contributing to the stability of *sym-fac* geometry is related to the conformation of both —CH<sub>2</sub>—CH<sub>2</sub>— and —CH<sub>2</sub>—N(CH<sub>3</sub>)—CH<sub>2</sub>— part of medien. Two five-membered medien rings can adopt several conformations which as mentioned (*vide ultra*) alter somewhat the orientation of N—CH<sub>3</sub> group with regard to aspartic acid donor atoms. In dependence on the orientation of N—CH<sub>3</sub> group different arrangements of H—C—N—CH<sub>3</sub> bonds can take up. These differ from each other in dihedral angle, energetically most stable being structure with eclipsed conformation of H—C—N—CH<sub>3</sub> part of medien corresponding either to  $\lambda$ ,  $\delta$  or  $\delta$ ,  $\lambda$  asymmetric envelope chelate rings conformations. These and other factors including bond stretching, angle bending and torsional stretching contribute to strain energy which is lowest for *sym-fac*-[Co(dien)(medien)]<sup>3+</sup> isomer making *sym-fac* topology more stable<sup>10</sup>. The energy difference between *sym-fac* and *unsym-fac*-[Co(medien)(dien)]<sup>3+</sup> ion was calculated to be 22.06 kJ mol<sup>-1</sup> (ref.<sup>10</sup>) and it is assumed this difference for [Co(medien)(S)-Asp]<sup>+</sup> ion should be, however from the reasons discussed above, greater.

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