OPTICAL ACTIVITY AND STEREOCHEMISTRY OF (S)-ASPARTATO-DIPROPYLENETRIAMINECOBALT(III) ISOMERS

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The sym-fac-, unsym₁-fac-(Λ)-and unsym₂-fac-(Δ)-[Co(dpt)(S)-Asp]⁺ isomers, where dpt is dipropylenetriamine and (S)-Asp is (S)-aspartate, which are formed in the ratio 60 : 18 : 22, show very similar circular dichorism spectra due to similar distortions of the triamine nitrogen atoms from the Cartesian coordinates and domination by the vicinal effect from (S)-aspartic acid. Absolute configurations of the unsymmetrical iosmers have been tentatively assigned using the calculated configurational contributions of the very low rotatory strength, which depends on the magnitude of NH_2–Co–N(H) triamine bond angles. Distorted chair conformations of one of the two dipropylenetriamine chelate rings provide chirally displaced nitrogen donor atoms which are thought to be responsible for the CD similarity in the isolated isomers. The isomer population is discussed in terms of trigonal bipyramid intermediates with the coordinated oxygen atoms of (S)-Asp preferentially in the trigonal plane and the differences in acidity of α- and β-chain carboxylates.

Recently[1,2], the comparative stereochemistries of the $[Co(dien)(S)\text{-}Asp]^+$, $[Co(medien)(S)\text{-}Asp]^+$, and $[Co(NH_3)_3(S)\text{-}Asp]^+$ systems were reported, where dien is diethylenetriamine or 1,4,7-triazaheptane and medien is 4-methyl-1,4,7-triaza-heptane. The stereochemical conclusions were primarily based on circular dichrosim (CD) spectra and the molecular structure[3] of the sym-fac-$[Co(aepn)(S)\text{-}Asp]^+$ isomer, where aepn is 1,4,8-triazaoctane. Methylation of the secondary nitrogen atom of the linear triamine was found to restrict the formation of isomers with the aspartic acid NH_2 group cis to the N–CH₃ group due to the steric requirements of the N–CH₃ group. Only the sym-fac-$[Co(medien)(S)\text{-}Asp]^+$ isomer, which has the NH_2 trans to the N–CH₃ group, was obtained. Furthermore, as a result of the steric crowding between the N–CH₃ group and the adjacent CH₂ group of the triamine, which forces medien to adopt λ, δ or δ, λ (essentially meso) envelope conformations, the CD spectrum of the sym-fac-$[Co(medien)(S)\text{-}Asp]^+$ isomer exhibits only avicinal contribution from (S)-Asp. This is contrary to the analogous dien species, which can have λ, λ or δ, δ truly asymmetric conformations — thus providing a richer CD spectrum. Six-membered chelate rings in this type of complex can also strongly

influence the isomer populations and their chiroptical properties. To further elucidate the effect of the ring size of linear triamine structural diversity on the overall stereochemistry of their octahedral metal complexes, we describe herein the synthesis and characterization of $[Co(dpt)(S)\text{-}Asp]^+$ isomers (dpt means dipropylenetriamine) as well as a correlation of the CD spectra with the established structure of one of the isomers.

EXPERIMENTAL

Reagents and Synthesis

Aspartic acid was purchased from Fluka. Dipropylenetriamine and diethylenetriamine were obtained from Aldrich. $[Co(dpt)(S)\text{-}Asp]ClO_4 . H_2O$ was prepared according to the literature[4] starting from $[Co(dpt)Cl_3]$ and $Ag_2(S)$-aspartate. The reaction mixture which was obtained (0·03 mole scale) was filtered and separated on a Dowex 50WX8 (100—200 mesh, Na^+ form.) Elution with water afforded a violet eluant containing the $[Co((S)\text{-}Asp)_2]^-$ isomers, whereas elution with 0·15M $NaClO_4$ resulted in the separation of three bands, which are the desired $[Co(dpt)(S)\text{-}Asp]^+$ isomers. Individual eluants were concentrated in vacuo. From the first eluant, a crystalline compound, assigned as *sym-fac*, was deposited. The crystals which were obtained were washed with water and dried in air.

For $C_{10}H_{24}ClCoN_4O_9$ (438·7) calculated: 27·38% C, 5·51% H, 12·77% N; found: 27·41% C, 5·58% H, 12·70% N.

The two remaining eluants were evaporated to dryness and the contaminating $NaClO_4$ was extracted with absolute ethanol. For $C_{10}H_{24}ClCoN_4O_9$ calculated: as above; found (2nd elutedisomer): 27·28% C, 5·60% H, 12·60% N; found (3rd eluted isomer): 27·44% C, 5·61% H, 12·70% N.

The isomer ratios were obtained from cobalt analyses (AAS).

$[Co(dien)(S)\text{-}Asp]ClO_4$ isomers were obtained as described in the literature[4].

Apparatus

The circular dichroism spectra were obtained on a Cary 60 optical rotatory dispersion spectrometer with circular dichroism and end-on photomultiplier attachments. The ^{13}C NMR spectra were obtained with a Bruker AM 400 spectrometer in the D_2O (decoupled mode) with sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the internal standard.

RESULTS AND DISCUSSION

Synthesis

The preparation of $[Co(dpt)(S)\text{-}Asp]^+$ from $[Co(dpt)Cl_3]$ and $Ag_2(S)$-Asp at 60° and 25 min in the presence of charcoal results in the formation of three isomers which were separated using ion-exchange chromatography and assigned according to the order of elution in conformity with Legg and Cooke[4] as *sym-fac*, *unsym₁-fac* and *unsym₂-fac* (Fig. 1). The proportions obtained under the conditions mentioned above (60 : 18 : 22) parallel those of $[Co(dien)(R)\text{-}Asp]^+$ (68 : 6 : 26, calculated

from the results of Legg and Cooke.[4] Attempts to reach equilibrium were compli-cated by increasing $[\text{Co}((S)\text{-Asp})_2]^-$ concentration. Thus, some dpt lidang dissoci-ation occurs.

The *sym-fac* isomer undergoes charcoal catalyzed isomerization giving an isomer ratio *sym-fac* : *unsym₁-fac* : *unsym₂-fac* of 65 : 18 : 17. For comparison, the analo-gous *sym-fac*-[Co(dien)(S)-Asp]⁺ isomerizes to a 66 : 9 : 25 mixture. Duplicate de-terminations agree within $1-2\%$.
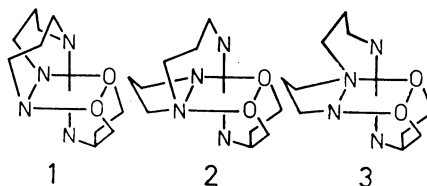
Absorption and CD Spectra

The electronic absorption spectra of the isolated isomers (Table I) are similar in shape and correspond to the spectra of cobalt(III) complexes with *cis*-N_4O_2 chromophores. The features of the absorption spectra are very similar to those of the known [Co-(dien)(R)-Asp]⁺ isomers[4], which allows the *sym-fac* isomer to be distinguished from

TABLE I

Electronic absorption (cm⁻¹) and CD spectra of [Co(dpt)(S)-Asp]⁺ isomers

Isomer	Absorption ε, mol⁻¹ l⁻¹ cm⁻¹		CD $\Delta\varepsilon$ (λ_{max}, cm⁻¹)
	T_{1g}	T_{2g}	
sym-fac	19 600 (100)	27 140 (95)	+0·78 (18 181)
			−0·22 (21 008)
			+0·37 (27 777)
unsym₁-fac	19 250 (98)	27 140 (91)	+0·77 (17 921)
			−0·33 (20 816)
			+0·11 (26 315)
unsym₂-fac	19 250 (97)	27 140 (91)	+0·70 (17 921)
			−0·27 (20 408)
			+0·12 (26 315)

FIG. 1

[Co(dpt)(S)-Asp]⁺ isomers: 1 *sym-fac*, 2 *unsym₁-fac-Λ*, 3 *unsym₂-fac-Δ*

the *unsym-fac* isomers. The observed differences in the absorption maxima positions for the respective isomers are due to the reduced ligand field strength of dpt.

The CD spectra of all three $[Co(dpt)(S)\text{-}Asp]^+$ isomers (Fig. 2 and Table I), do not distinguish any chirality differences between the isomers. In the $^1A_{1g} \rightarrow {}^1T_{1g}$ spectral region, all three isomers show a positive band at lower energy and a negative band of lower intensity at higher energy. The CD band maxima, which show the same trends as in the case of the $[Co(dien)(R)\text{-}Asp]^+$ isomers[4], support our assignments of *sym-fac* and *unsym-fac* isomers, cf. Fig. 1.

The observed similarity in the CD spectral patterns for these $[Co(dpt)(S)\text{-}Asp]^+$ isomers strongly contrasts with the $[Co(dien)(R)\text{-}Asp]^+$ system (in which the linear triamine forms 5-membered rings) and undoubtedly can be ascribed to the coordination of the angle-expanding dpt ligand. Actually, a number of reports have appeared describing changes in CD spectra of structurally related octahedral complexes to differences in the chelate ring size; cf. ref.[5]. It was argued[6] that metal-ligand bond amgles of greater (or less) than 90° affect both the energies and the signs of electronic states and that the cumulative effect of the individual distortions (which may give rise to a twisted crystal field) rather than ring strain controls the rotatory strength of metal *d–d* transitions. Possibly the cumulative effect of the individual distortions resulting from the coordination of two 6-membered fused chelate rings is greater than in the case of isolated 6-membered or fused 5-membered chelate rings. The CD spectral pattern, which does not differentiate between the *sym-fac* and *unsym-fac* isomers of opposite chirality, supports this assumption. The common chiroptical properties of the isomers prepared can be attributed to the small distortion of the dpt nitrogen atoms from the Cartesian coordinate[7]; thus, the dpt molecule makes only a small contribution to the symmetry aspects of the CD spectrum and all three isomers show very similar CD spectra. That is, the dpt ligand provides an environment in all of the $[Co(dpt)(S)\text{-}Asp]^+$ isomers which is similar to non-chelating amine isomers. This is quite evident when the CD curves (Fig. 2) are compared. From this comparison, the close corre-
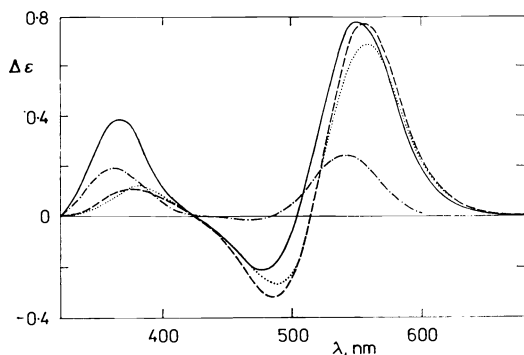

FIG. 2

CD spectra of $[Co(dpt)(S)\text{-}Asp]^+$ isomers: *sym-fac* (———), *unsym$_1$-fac* (— — —), *unsym$_2$-fac* (······). CD of $[Co(NH_3)_3(S)\text{-}Asp]^+$ (–··–··–)

spondence between the CD spectra of the three $[Co(dpt)(S)\text{-Asp}]^+$ isomers and $[Co(NH_3)_3 (S)\text{-Asp}]^+$ is apparent. Neglecting the small CD frequency shifts due to slightly different ligand field strengths, the primary difference is the greater rotatory strength for both the T_{1g} and T_{2g} transitions for the $[Co(dpt)(S)\text{-Asp}]^+$ isomers. This fact, together with the small variations in CD intensities and wavelengths for the three $[Co(dpt)(S)\text{-Asp}]^+$ isomers, suggests that in addition to the (S)-aspartic acid vicinal effect, other effects, such as configuration and conformational ones or dissymmetric displacement of the ligating atoms from their regular octahedral position (cf., ref.[7]), also contribute to the T_{1g} and T_{2g} rotatory strengths.

The optical activity of a specific isomer is generally governed by several contributions. These are additive, as detailed by Legg and Cooke[4] for the $Co(dien)(R)\text{-}$ $\text{-Asp}]^+$ complexes. To determine the configurational contributions, which are not readily apparent in the observed CD spectra, the following considerations were made According to the additivity concept, the observed CD spectra for the $unsym_1\text{-}fac.$ and $unsym_2\text{-}fac$ diastereomers are as follows:

$$\Delta\varepsilon(unsym_1\text{-}fac) = X + C(S) \tag{1}$$

$$\Delta\varepsilon(unsym_2\text{-}fac) = Y + C(S), \tag{2}$$

where X and Y are the contributions corresponding to octahedral chiralities and $C(S)$ is the vicinal effect for (S)-aspartic acid (at this point, conformational contributions are not included). The chirality effect of the chelate rings with a cancelled vicinal effect by substituting Eq. (2) in Eq. (1) and Eq. (1) in Eq. (2) and assuming inverse octahedral chiralities $(X = -Y)$ produces

$$X = [\Delta\varepsilon(unsym_1\text{-}fac) - \Delta\varepsilon(unsym_2\text{-}fac)]/2 \tag{3}$$

$$Y = [\Delta\varepsilon(unsym_2\text{-}fac) - \Delta\varepsilon(unsym_1\text{-}fac)]/2 \tag{4}$$

The calculated configurational CD spectra which bear enantiomeric character (Fig. 3) show two bands of alternating signs in the T_{1g} spectral region. For the complexes of the $[Co(ABA)(Asp)]^+$ type (where ABA means a linear triamine) with a $cis\text{-}N_4O_2$ chromophore (neglecting the chelate rings), the T_{1g} CD band is split (approximately C_2 symmetry) into one component with A symmetry and two components with B symmetry[8]. For the $[Co(dien)(R)\text{-Asp}]^+$ isomers, which possess two 5-membered triamine chelate rings, Legg and Cooke[4] used the sign of the symmetry determined A_2 component, which has the same orbital construction[9] as the dominant $E_a(D_3)$ transition in $[Co(en)_3]^{3+}$, to assign the absolute configuration of unsymetrical isomers. Experimentally, the sign of the transition with $E_a(D_3)$ parentage is positive for $\Lambda\text{-}$ $\text{-}[Co(en)_3]^{3+}$ and negative for the Δ-isomer (cf., ref.[9]). However, it should be noted

that the energy of the $E_a(D_3)$ transition depends on the distortions of the ligand atoms from the exact O_h symmetry[10-13]. For the $[Co(tn)_3]^{3+}$ ion with 6-membered chelate rings, but with the same chromophore as in $[Co(en)_3]^{3+}$, Judkins and Royer[14] suggested that the energy of the $^1A \rightarrow {}^1E_a$ transition is the higher component, unlike the ethylenediamine complex. Since the N–Co–N bond angles subtended by the dpt ligand in the isolated sym-fac-$[Co(dpt)(S)\text{-Asp}]^+$ isomer are greater than 90° (ref.[7]), consideration of Piper's model for the sign of the Cotton effect seems to be the appropriate approach. Applying the same arguments as Legg and Cooke[4], and taking the opposite raltionship of the E_a transition into account, we tentatively assign the absolute Λ configuration to the *unsym$_1$-fac* isomer with the negative higher energy CD band, and the Δ configuration to the *unsym$_2$-fac* isomer with the positive higher energy band.

The optical activity data obtained for the unsymmetrical isomers presented in Table II show that the CD band intensities for the configurational components of the $[Co(dpt)(S)\text{-Asp}]^+$ isomers are significantly lower than the others and that the configurational components depend generally on the chelate ring size of the linear triamine coordinated to the cobalt(III) center. As can be seen from Table II, the CD band intensities of the configurational component are reduced in the order $[Co\text{-}(dien)(R)\text{-Asp}]^+ > [Co(aepn)(S)\text{-Asp}]^+ > [Co(dpt)(S)\text{-Asp}]^+$, suggesting that the rotatory strength contribution to the configurational effect of the complexes containing linear triamines depends on the magnitude of the NH_2–Co–N(H) bond angle. As
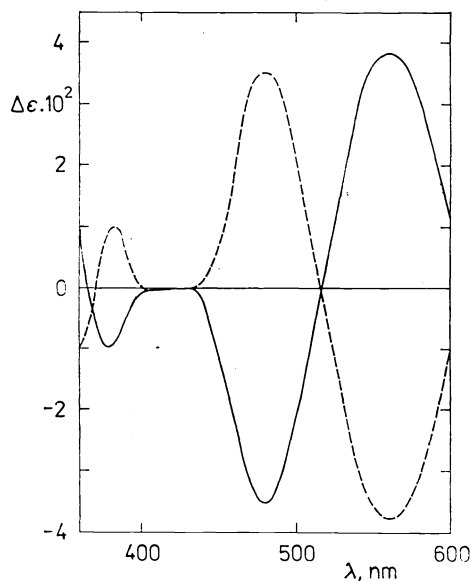

FIG. 3

Calculated configurational CD spectra of *unsym$_1$-fac*-(———) and *unsym$_2$-fac*-(— — —) $[Co(dpt)(S)\text{-Asp}]^+$ isomers

this bond angle increases (assuming that NH_2–Co–N(H) angles of the unsymmetrical isomers are similar to those of the *sym-fac* isomers), rotatory strength decreases.

The interpretation of the CD spectra based primarily on the (*S*)-aspartic acid vicinal effect, together with minor conformational and other contributions, coincides well with the ^{13}C NMR spectral patters of the individual isomers. The NMR results (summarized in Table III) show that there are no substantial differences in the carbon atom resonances in the isomers. As was suggested for the CD spectral similarities, this phenomenon can be ascribed to the small deviations of the donor atoms from the Cartesian coordinates. To differentiate between the C—NH_2, the —CH_2— and the C—NH carbon atoms in the individual isomers, their stereochemical relationships together with the shielding and deshielding characteristics of the neighboring atoms were taken into account. For example, from symmetry considerations three resonances are possible in the methylene region for the *sym-fac* isomer while the two remaining unsymmetrical isomers could exhibit six resonances. As can be seen from Table III, the dpt C—NH carbon resonances appear strictly equivalent in all three isomers with only one resonance. Two resonances which can be attributed to the —CH_2— and two which can be attributed to the C—NH_2 carbon atoms is a common feature for all three isomers, which indicates differences in chelate ring geometry rather than the existence of another ring conformational form. This is in accord with the crystal structure of the *sym-fac* isomer[7], which shows that both chelate rings assume chair conformations, but that one of the two conformers is more distorted. A flattened

TABLE II

Configurational chiralities of unsymmetrical-*fac*-[Co(ABA)(*S*)-Asp]$^+$ isomers

Isomer	$\Delta\varepsilon_1\,T_{1g}$ region (λ, (cm^{-1}))		Angle^a
[Co(dpt)(*S*)-Asp]$^+$			95·7°^{b}
unsym$_1$-fac-Λ	−0·038 (17 857)	+0·035 (20 408)	
unsym$_2$-fac-Δ	+0·038	−0·035	
[Co(aepn)(*S*)-Asp]$^+$			90·7°^{c}
unsym$_1$-fac-Λ	+0·47 (17 857)	−0·44 (20 833)	
unsym$_2$-fac-Δ	−0·47	+0·44	
[Co(dien)(*S*)-Asp]$^+$			85·2°^{d}
unsym$_1$-fac-Λ	−1·20 (18 181)	+0·23 (20 618)	
unsym$_2$-fac-Δ	+1·20	−0·23	

^{a} Mean NH_2CoN(H) angle taken from the data obtained for: ^{b} *sym-fac*-[Co(dpt)(*S*)-Asp]$^+$ (ref.[7]), ^{c} *sym-fac*-[Co(aepn)(*S*)-Asp]$^+$ (ref.[3]) ^{d} *sym-fac*-[Co(dien)(dpt)]$^+$ (ref.[15]).

chair together with a distorted chair appear to be the favorable conformations of facially coordinated dpt, and we feel there are no reasons to suppose that the chelate rings in the unsymmetric facial isomers would adopt boat or skew-boat conformations. This is indirectly supported by the study of Dreiding models, which show intraligand interactions which tend to exclude the boat and skew-boat conformations.

Stereochemical Considerations

As mentioned above, the complex $[Co(dpt)(S)\text{-}Asp]ClO_4 . H_2O$ obtained from the reaction of $[Co(dpt)\text{-}Cl_3]$ with silver aspartate consists of three isomers with a formation ratio of 60 : 18 : 22. In the absence of any stereoselectivity the isomeric ratio

TABLE III
^{13}C NMR data (ppm) for $[Co(dpt)(S)\text{-}Asp]^+$ isomers

C atom	Isomer		
	sym-fac	*unsym₁-fac*	*unsym₂-fac*
$-CH_2-$	22·9	23·8	23·6
	24·3	24·0	24·6
$-C-NH_2$	37·3	37·3	37·2
	38·1	38·9	38·8
$\beta\text{-}CH_2$	38·3	38·2	39·0
$-C-NH-$	48·3	48·3	48·5
$\alpha\text{-}CH-$	56·7	56·8	56·8
$\beta\text{-}COO$	177·5	177·5	175·6
$\alpha\text{-}COO$	185·1	185·3	185·1

Ia   Ib   Ic   Id

II
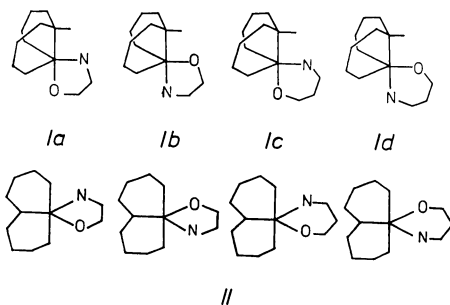
FIG. 4

Possible symmetrical (*I*) and unsymmetrical (*II*) dissociative intermediates which could control the steric pathways of the [Co(dpt). .Cl₃] + Ag₂(*S*)-Asp substitution reaction. The arm of Asp which completes the octahedron in the last step to the product is not shown to keep the diagrams simple. *Ib* and *Id* yield *sym-fac*, *Ia* yields *Δ-unsym-fac*, and *Ic* yields *Λ-unsym-fac* isomers

is expected to be close to the statistical 50 : 25 : 25 ratio. To explain the experimentally observed isomeric ratio, two possible mechanisms of $[Co(ABA)(S)\text{-}Asp]^+$ isomer formation can be considered. In the first one, bidentate coordination of the aspartate ion (in place of 2 chloride ions) followed by an edge displacement or a retentive dissociation of the third chloride or water by the uncoodinated $\alpha\text{-}COO^-$ or $\beta\text{-}COO^-$ arm of the aspartic acid (facilitated by charcoal) results in a product composition of 50 : 25 : 25, just like the statistical distribution. Alternatively, an S_N1 mechanism starting from two types of trigonal bipyramids, symmetrical (I) or unsymmetrical (II), can be considered, but regardless of which bipyramid is considered, both yield the same formation ratio of 50 : 25 : 25. However, since the unsymmetrical set of intermediates is not a direct precursor to the product, as both ligands have to move to form the products, only the symmetrical (I) set of intermediates is considered any further (see Fig. 4).

In the absence of stereoselective effects the two unsymmetrical facial isomers: $\Lambda\text{-}(S)$ $(unsym_1\text{-}fac)$ and $\Delta\text{-}(S)$ $(unsym_2\text{-}fac)$ isomers are expected to be present in equal amounts. However, experimentally obtained isomer populations are somewhat different from the statistical ratio. In the synthesis, the $\Delta\text{-}(S)$ isomer is slightly favored over the $\Lambda\text{-}(S)$ one $(56\%\Delta : 44\%\Lambda)$. It should be noted that the same ratio was obtained regardless of the reaction time. An analysis of the interligand interactions (via Dreiding models) did not reveal any serious differences which would explain why the $\Delta\text{-}(S)$ isomer should be favored. The same situation, i.e., the absence of any discriminating nonbonding interactions, also exists between the corresponding isomers of the $[Co(dien)(R \text{ or } S)\text{-}Asp]^+$ ions, where the ratio is also distorted from unity[4], which demonstrates a similarity with the dpt system. One plausible explanation for the difference in the rate of formation of the two unsymmetrical isomers is the greater acidity (lower basicity) of the amino acid α-chain carboxylate. Thus the β-chain is more often protonated by water than is the carboxylate of the α-chain on a statistical basis. A deprotonated anionic carboxylate is a much superior nucleophile relative to a protonated neutral carboxylate. Therefore, intermediate Ia should occur more often than Ic in agreement with the data. The predominance of $sym\text{-}fac$ over the 50% level predicted from statistics agrees with the projected dominance of Ib and Id relative to Ia and Ic, respectively, because Ib and Id have the more π-donating anionic oxygen in the trigonal plane, which is a common feature of 5-coordinated complexes[16]. Furthermore, the predominance of Ib and Id in comparison with the remaining two trigonal bipyramids follows also from the fact, that in the $mer\text{-}[Co(ABA)(S)\text{-}AB(X)]^+$ ions, where AB is an amino acid anion, only isomers with the amino acid NH_2 group $trans$ to the sec-N of dien (or dpt) are formed[17,18].

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