STERIC AND HYDROPHOBIC EFFECTS ON STEREOSELECTIVITY IN TERNARY COBALT(III) COMPLEXES OF AMINO ACID DERIVATIVES

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The preparation, separation, and characterization of mixed ligand cobalt(III) complexes containing either the new asymmetric linear tetradentate ligand, ethylenebis-(*S*)-phenylalanine ((*SS*)-EBPhe), or known asymmetric linear tetradentate ligand, ethylenebis-(*S*)-valine ((*SS*)-EBV), and an aromatic or aliphatic diamine (dam) respectively are reported. The absolute configuration of these complexes are assigned by considering the electronic absorption, circular dichroism, infrared, ^{1}H and ^{13}C NMR spectra, and the known configuration of the ligands. The optically active tetradentate ligands coordinate stereospecifically because only *Δ* diastereoisomers are formed. The factors determining stereoselectivity in these complexes are mainly the steric and intramolecular hydrophobic ligand–ligand interactions. These intramolecular hydrophobic interactions have been confirmed by ^{1}H NMR shift measurements in water.

One of the most important properties expected for ternary complexes are through--space and through-metal ligand–ligand interactions in complex molecules. Substrate specificity and efficiency of enzymatic reactions around the central metal ion depend much on a various non-covalent interactions[1], and ligand–ligand interactions are particularly intriguing in view of their structural and functional relevance to biological phenomena and chemical properties associated with them[2].

In order to elucidate some aspects of the stereoselectivity and stereospecificity* in metal complexes, we have recently postulated[3] the stereospecific coordination of amino acid derivatives with substituents at asymmetric C(α) atom greater than C_2H_5. This assumption was supported experimentally from the studies of stereochemistry of the mixed ligand cobalt(III) complexes of EBAA** with en (refs[4–6]).

* Both terms stereospecificity and stereoselectivity are often confused. Here stereoselectivity will be defined as a nonstatistical formation of stereoisomers. Stereospecificity will be considered in the relation to the optical activity of complexes, e.g., coordination is stereospecific when only one of two possible enantiomers is formed.

** Abbreviations used: EBAA, ethylenebis(amino acidate); en, ethylenediamine; phen, 1,10-phenanthroline (*o*-phenanthroline); BHBOP, N,N′-bis(*o*-hydroxybenzyl)-*o*-phenylenediamine.

In all cases the coordination of these ligands occurred stereospecifically. As a part of our continuing study of the stereospecificity and stereoselectivity in mixed ligand complexes of amino acid derivatives, we have investigated the question of whether or not the intramolecular ligand–ligand interactions can induce stereoselectivity in these complexes.

EXPERIMENTAL

Reagents

(*S*)-Phenylalanine was kindly supplied as sample without price from Fluka AG (Buchs). (*S*)-Valine, 1,2-dibromoethane, and 1,2-diaminoethane were purchased from Merck. All other chemicals used were commercial reagent grade.

Preparation of Compounds

BHBOP. An amount of 5·4 g (0·05 mol) of *o*-phenylenediamine was dissolved in 50 ml of benzene. The solution was heated to boil and 12·2 g (0·10 mol) of salicylaldehyde dissolved in 25 ml of benzene was added portionwise under stirring. The heating under reflux of benzene was continued for 1 h and during next 1 h the water was removed by azeotropic distillation. Condensation product was suspended in 150 ml of methanol and 1·2 g of $NaBH_4$ was added portionwise; after adding the reaction mixture was poured under vigorous stirring into 600 ml of water. After a short standing the white flakes precipitated. The raw product was washed with water to pH 7. The substance was purified by recrystallization from methanol. Yield 80%, m.p. 118°C. For $C_{20}H_{20}N_2O_2$ (320·4) calculated: 74·97% C, 6·29% H, 8·74% N; found: 74·60% C, 6·30% H, 8·61% N.

The optically active ligands, (*SS*)-EBVH_2 (ref.[7]) as well as [Co((*SS*)-EBV)(en)]ClO_4 isomers[4], were prepared by the methods previously reported.

(*SS*)-EBPheH_2. To a slurry of (*S*)-phenylalanine (1·7 g, 10 mmol) in 10 ml of water was added a solution of NaOH (0·4 g, 10 mmol) in 4 ml of water under stirring and water cooling. The solution was heated to boil under reflux condenser, and 0·95 g (5 mmol) of 1,2-dibromoethane and 0·7 g (5 mmol) of K_2CO_3 were added portionwise so as to hold the pH in the range of 10—11. The heating was continued for 20 h. After cooling down, the KBr separated and unreacted K_2CO_3 were filtered off, and the filtrate was acidified with conc. HCl. At pH 8, a white substance separated. It was purified by repeated conversion to the sodium salt and precipitation with HCl. After cooling, the product was washed with water and dried in vacuum at 50°C. Yield 0·86 g (48%), m.p. 276—278°C. For $C_{20}H_{24}N_2O_4$ (356·5) calculated: 67·40% C, 6·79% H, 7·86% N; found: 66·86% C, 6·73% H, 7·65% N.

(Ethylenebis(amino acidato)-carbonato)cobaltate(III) complexes. The "green solution" (ref.[8]) prepared from 5 mmol (1·19 g) of $CoCl_2.6\,H_2O$ with added EBAA (5 mmol, e.g., 1·3 g of (*SS*)-EBVH_2 or 1·78 g of (*SS*)-EBPheH_2, respectively) and 5 ml of water is stirred at 50°C for 20 min. The resulting wine-red solution was used as "starting material" for syntheses of other mixed ligand complexes.

Mixed ligand $[Co(EBAA)(dam)]^+$ complexes. A typical preparation is given for [Co((*SS*)-EBV)(phen)]NO_3. A solution of 0·9 g (5 mmol) of phen in 5 ml of ethanol and 1·5 ml of conc. HNO_3 was added slowly to "starting material" K[Co((*SS*)-EBV)(CO_3)]. The solution was mixed with 0·2 g of charcoal at 60°C for 3 h. The resulting orange solution was filtered and

cooled to room temperature. After adding some ethanol, the mixture was kept cold overnight in order to precipitate some KNO_3 and K_2CO_3. After filtration, one part A of filtrate was chromatographed on a cation-exchange cellulose Ostsorb SHP (Na^+-cycle). After sweeping the column with water, the adsorbed band was eluted with 0·1M-KNO_3, yielding only a single fraction. The product was evaporated to dryness on a rotary evaporator and then extracted with absolute ethanol in order to remove KNO_3. The residual KNO_3 was removed by gel permeation chromatography on a column packed with Sephadex G-10. Eluate was concentrated to a small volume and with the second (unchromatographed) part B was left to stand in refrigerator overnight. The precipitated orange crystals were washed with cold ethanol and acetone and filtered off. No differences in the elemental analysis and spectroscopic properties we observed between the compounds obtained from both A and B parts. Yield 0·8 g. For $C_{24}H_{30}CoN_5O_7$ (559·5) calculated: 51·56% C, 5·41% H, 12·52% N; found: 51·18% C, 5·49% H, 12·34% N.

Ethylenebis-(*S*)-valinato-(N,N′-bis(*o*-hydroxybenzyl-*o*-phenylenediamine)cobalt(III) chloride ([Co((*SS*)-EBV)(BHBOP)]Cl). The synthesis of this complex was identical with that used for corresponding phen complex except that 1·6 g (5 mmol) of BHBOP in 10 ml of 50% dioxane and 3 ml of conc. HCl were used. The dark rose product was precipitated by evaporation to 5 ml, filtered and washed with cold acetone. Yield 0·7 g. For $C_{32}H_{42}ClCoN_4O_6$ (673·1) calculated: 33·29% C, 9·78% H, 12·94% N; found: 33·10% C, 9·56% H, 12·78% N.

Ethylenebis-(*S*)-phenylalaninato-)(1,10-phenanthroline)cobalt(III) chloride ([Co((*SS*)-EBPhe)(phen)]Cl). Instead of (*SS*)-$EBVH_2$ to prepare corresponding mixed ligand complex, 1·78 g (5 mmol) of (*SS*)-$EBPheH_2$ and 5 ml of conc. HCl were used. When the evolution of carbon dioxide was completed, the red solution was filtered and, upon cooling, 1·05 g of complex was isolated. For $C_{32}H_{30}ClCoN_4O_4$ (629·0) calculated: 64·11% C, 4·81% H, 8·91% N; found: 60·76% C, 4·84% H, 8·74% N.

In all above described procedures only one isomer, *cis*-α, was formed.

Ethylenebis-(*S*)-phenylalaninato-(ethylenediamine)cobalt(III) perchlorate ([Co((*SS*)-EBPhe)-(en)]ClO_4). To a suspension of 0·7 g (1·9 mmol) of (*SS*)-$EBPheH_2$ in 3 ml of water added a suspension of 0·2 g (1·9 mmol) of $CoCO_3$ in 15 ml of water, 0·1 g of charcoal, 0·3 ml of 65% HNO_3 diluted to 2 ml, and 0·13 ml (1·9 mmol) of en diluted to 8 ml. The mixture was heated to about 60°C, and 0·5 ml of 30% H_2O_2 was added dropwise. Heating was continued with vigorous stirring for 6 h. The resulting wine-red solution was filtered to remove the charcoal and a trace of unreacted $CoCO_3$. It was then loaded on an ion-exchange column of Ostsorb SHP cation-exchange cellulose in the Na^+ form. The mixture of complexes formed a compact band at the top. Washing with water removed a purplish material that was not adsorbed on the column. The complex was eluted with 0·5M-$NaClO_4$ at the rate ca 0·1 ml min^{-1}. Two bands were collected and concentrated to near dryness on a rotary evaporator, and excess of $NaClO_4$ was filtered off. After removing most of $NaClO_4$ by extraction into absolute ethanol, final desalting was carried out by gel permeation chromatography on a column of Sephadex G-10. Solid, brick-like-red, crystalline products were obtained by slow evaporation. The yields were 0·37 g of *cis*-α (*trans*-O) isomer from band *I* and 0·13 g of *cis*-β (*cis*-O) isomer from band *II*. For $C_{22}H_{30}ClCoN_4O_8$ (514·0) calculated: 46·12% C, 5·28% H, 9·78% N; found (*cis*-α): 45·34% C, 5·29% H, 9·76% N; found (*cis*-β): 45·58% C, 5·26% H, 9·72% N.

Measurements

Infrared spectra of the solid samples were recorded using KBr discs on a Perkin–Elmer 337 spectrophotometer. Electronic absorption spectra were recorded on a Specord UV-VIS spectrophotometer. Solutions (10^{-3} mol l^{-1}) were prepared and 1 cm cells were used. Circular dichroism spectra were measured on a Jobin–Yvon dichrograph III using 5 mm cells and water as the

solvent at the concentration of the order 10^{-4} mol l^{-1}. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer using *p*-dioxane as the internal standard. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer using $(CH_3)_3COD$ as the internal standard. Generally, D_2O solutions were 10% (w/w) where possible and KOD was used for adjusting of pH. A pH-meter PHM-4 Radiometer with glass and SCE electrodes was used. Elemental analyses were carried out on an Elemental Analyzer M 1102, Carlo Erba.

RESULTS AND DISCUSSION

The linear tetradentate ligands used in this work were prepared from optically active parent amino acids of known absolute configuration. The absolute configuration of the ligands is as shown in Fig. 1. The C(α) carbon atom is asymmetric and, because the formation of the ligands does not involve this atom, it is assumed that no racemization occurred during the preparation. Therefore, they should have, similarly as parent amino acids, the *S* absolute configuration. The new ligand (*SS*)-EBPheH$_2$ has been characterized by the IR, CD, ^{1}H and ^{13}C NMR spectra. The latter one indicated that there were no carbon-containing impurities.

Separation and Distribution of Isomers

For the $[Co(EBAA)(X)_2]^n$ complexes three geometrical isomers are possible (Fig. 2) and further there are two optical isomers *Λ* and *Δ* for both *cis*-α and *cis*-β forms. To date the *trans* configuration for EBAA has been formed only in Pt system[10]. The relative lack of abundance of *trans* configuration can be rationalized in terms of bond angle strain[11] when EBAA is considered in a strictly planar fashion. Similarly, considering C—N—C bond angle strain[11], it would appear that the *cis*-β configuration would be more favorable than the *trans*, with the *cis*-α configuration being the most favorable. In the case of the $[Co(EBAA)(1,2\text{-dam})]^+$ species the number

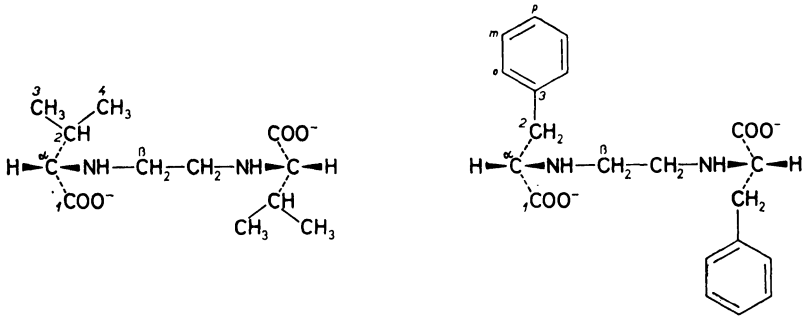

FIG. 1

The configuration of (*SS*)-EBV (left) and (*SS*)-EBPhe (right), showing the numbering system

of possible geometrical isomers (Fig. 2) is reduced to two, because a 1,2-dam is unable to span the *trans* position. The conformation of central chelate *E* ring is given by the configuration of the secondary nitrogen atoms. A chelate ring joining an equatorial and polar coordination site seems sufficiently flexible to make λ and δ conformation possible, independently of the configuration of the nitrogen atoms.

The order of elution of complexes followed the expected order in that the *cis*-α isomer, with small dipole moment, was eluted before the *cis*-β isomer.

Identification and Characterization of Isomers

Although IR spectroscopy is not the most reliable method of differentiation between diastereoisomers, it brings valuable information about the order of strength of the coordinate bonds by comparing the magnitudes of the band shifts. Both $EBAAH_2$ ligands, similarly to parent amino acids, exist in solid state in the form of dipolar ions–$NH_2^+CH(R)COO^-$. This fact is confirmed by their vibrational spectra (Table I). These spectra have a large stretching ν(NH) band at ca 3 400 cm^{-1}. In spectra of the obtained complexes there are essential changes with reference to spectra of $EBAAH_2$, especially in the ranges 3 500–2 800 cm^{-1} and 1 750–1 300 cm^{-1}. Formation of the Co—N bond and hydrogen bond result in enhanced polarity of the N—H bond, thus causing greater band intensity. Both these factors cause also lowering frequencies of the band. This effect will be greater, the stronger the Co—N bond is and in the same order the covalence of the Co—N bond increases. As the difference, $\Delta\nu(COO^-)$, is greater for the covalently complexed carboxylate anion than in the uncomplexed anion, an unidentate Co—OCO bond could be proposed[4] in the case of prepared complexes.

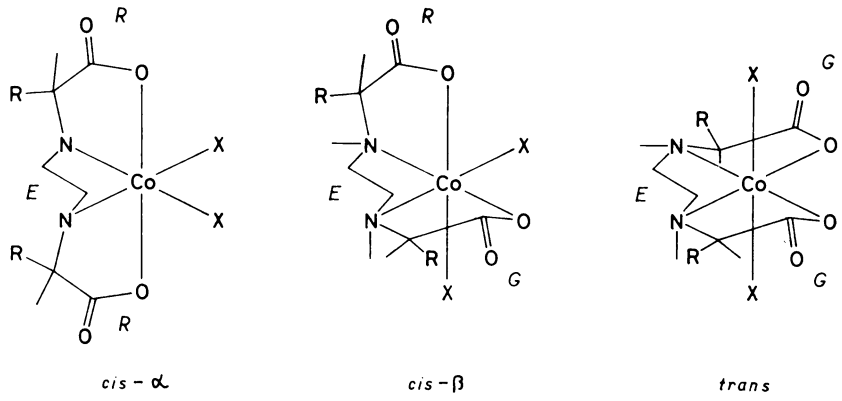

FIG. 2

Three possible geometrical isomers for a $[Co(EBAA)(X)_2]^n$ complex. (*R* out-of-plane or "relaxed" ring, *G* in-plane or "girdling" ring, *E* central "ethylenediamine" ring.)[9]

The absorption and CD data of complexes are listed in Table II. Since both geometrical isomers are essentially *cis*-CoN_4O_2, the absorption spectra are not particularly helpful in distinguishing the geometrical isomers. It is noted here, however, that the absorption maxima of the *cis*-β isomer occur at slightly higher energy than the corresponding maxima of the *cis*-α isomer. Under tetragonal symmetry the $T_{1g}(O_h)$ level is split into levels with A_2 and E symmetry. It is predicted[13] that the E level will be lower than the A_2 level for these complexes. Such a splitting of the first absorption band which manifests as a shoulder is seen for *cis*-α isomers (Table II). Thus, unambiguous distinguishing the geometrical isomers can be made. Marked blue shift of the absorption maxima of the $[Co(EBAA)(phen)]^+$ complexes corresponds to the position of phen in the spectrochemical series (see values of 10 *Dq* in Table II). Rather covalent character of both Co—N and Co—O bonds in all studied mixed ligand complexes, yielding from IR spectra, is also supported by the value of the nephelauxetic ratio, β, indicating relatively large electron cloud expansion.

The *cis*-α and *cis*-β isomers have been clearly distinguished by their ^{13}C NMR spectra (Table III). Comparison of the measured spectra indicated that the cis-α isomer (C_2 symmetry) has a simple spectrum with the same number of the peaks as the ligand alone. As the *cis*-β isomer contains three different chelate rings, its symmetry is lower (C_1) and some splitted signals are observed in the spectrum.

The absolute configuration of the isomers was determined by measuring the CD spectra on the basis of the Cotton effect observed for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. It was confirmed on the basis of correlation of the stereochemical data for these

TABLE I

Infrared data for the prepared compounds (cm^{-1})

Compound	$\tilde{\nu}$(NH)	$\tilde{\nu}_{as}(COO^-)$	$\tilde{\nu}_s(COO^-)$	$\Delta\tilde{\nu} = \tilde{\nu}_{as} - \tilde{\nu}_s$
(*SS*)-$EBVH_2$[a]	3 400	1 590	1 395	195
Δ-cis-α-[Co((*SS*)-EBV)(en)]$^+$[a]	3 250	1 640	1 374	266
Δ-cis-β-[Co((*SS*)-EBV)(en)]$^+$[a]	3 290	1 627	1 382	245
Δ-cis-α-[Co((*SS*)-EBV)(phen)]$^+$	3 240	1 610	1 383	227
Δ-cis-α-[Co((*SS*)-EBV)(BHBOP)]$^+$	3 360	1 600	1 370	230
(*SS*)-$EBPheH_2$	3 430	1 574	1 388	186
Δ-cis-α-[Co((*SS*)-EBPhe)(en)]$^+$	3 280	1 643	1 405	238
Δ-cis-β-[Co((*SS*)-EBPhe)(en)]$^+$	3 144	1 636	1 400	236
Δ-cis-α-[Co((*SS*)-EBPhe)(phen)]$^+$	3 310	1 580	1 390	190

[a] Data taken from ref.[4].

TABLE II

Spectral data for the aqueous solutions of the $[Co(EBAA)(dam)]^+$ complexes

Compound	Absorption		CD		$10Dq^c$	B^c	β^c
	$10^{-3}\tilde{\nu}^a$	ε^b	$10^{-3}\tilde{\nu}^a$	$\Delta\varepsilon^b$			
Δ-cis-α-[Co((*SS*)-EBV)(en)]$^{+d}$	18·47	122	18·30	−1·13	20·36	773	0·690
	28·07	176	21·91	+0·34			
			25·96	−0·12			
Δ-cis-β-[Co((*SS*)-EBV)(en)]$^{+d}$	18·96	46	17·72	−1·08	20·89	758	0·677
	28·55	124	20·86	+0·70			
Δ-cis-α-[Co((*SS*)-EBV)(phen)]$^+$	22·12	80	18·66	−0·35	23·25	366	0·327
	25·19 sh		27·93	−0·05			
	27·47	150					
Δ-cis-α-[Co((*SS*)-EBV)(BHBOP)]$^+$	18·38	76	16·84	−0·71	20·23	696	0·621
	22·99 sh		25·77	−0·31			
	27·40	170					
Δ-cis-α-[Co((*SS*)-EBPhe)(en)]$^+$	18·90	104	18·66	−1·59	21·32	560	0·500
	21·60 sh		22·22	+0·42			
	27·93	194					
Δ-cis-β-[Co((*SS*)-EBPhe)(en)]$^+$	20·12	118	20·75	−1·32	21·73	600	0·536
	23·42 sh		27·78	+0·56			
	28·17	183					
Δ-cis-α-[Co((*SS*)-EBPhe)(phen)]$^+$	21·05	148	20·00	−1·48	22·63	573	0·512
	23·67 sh		21·74	+0·59			
	28·90	194	27·03	−0·16			

[a] $\tilde{\nu}$ (The position of a maximum in the absorption spectrum, or a maximum or minimum in the CD spectrum) in cm^{-1}; [b] ε (the molar absorptivity) and $\Delta\varepsilon$ in l mol^{-1} cm^{-1}; [c] calculated according to procedure in ref.[12]; [d] data taken from ref.[4].

TABLE III

^{13}C NMR spectra of the EBAA and their ternary complexes[a]

Compound	C(1)	C(α)	C(β)	C(dam)	C(2)	C(3)	C(4)	C(*o*, *m*, *p*)
(*SS*)-EBV[b]	182·67	72·69	49·68		33·55	21·67	21·35	
Δ-cis-β-[Co(*SS*-EBV)(en)]$^+$								
Δ-cis-α-[Co((*SS*)-EBV)(phen)]$^+$	184·72	72·75	49·72	154·39, 154·26 150·61, 149·55 143·47, 142·42 133·85, 133·36 130·73, 130·54 129·59, 128·62	33·60	21·70	21·37	
Δ-cis-α-[Co((*SS*)-EBV). .(**BHBOP**)]$^+$	188·29	74·63	49·46	173·96, 141·95 135·83, 135·10 130·86, 123·45 122·55, 120·04 119·32, 56·95	33·54	22·00	21·93	
(*SS*)-EBPhe[b]	181·89	66·05	47·28		39·85	139·12		130·17, 129·35, 127·37
Δ-cis-vα-[Co((*SS*-EBPhe)(en)]$^+$	186·57	69·39	45·89	54·30	37·74	136·14		130·00, 128·83, 128·18
Δ-cis-β-[Co((*SS*)-EBPhe)(en)]$^+$	178·15 176·60	67·75 67·36	45·99	54·30	37·80 37·33	136·29 136·20		130·29, 130·00, 129·59
Δ-cis-α-[Co((*SS*)-EBPhe). .(phen)]$^+$	184·22	68·30	49·45	154·07, 153·86 150·43, 148·75 143·56, 141·22 132·29, 132·26 131·58, 131·33 129·52, 129·37	41·57	140·86		131·04, 129·57, 129·23

[a] Chemical shifts were measured to *p*-dioxane and converted to the TMS scale using δ(dioxane) = 67·4 ppm; [b] pH = 12·5.

complexes with the X-ray diffraction data[11,14] that the negative Cotton effect corresponds to the *Δ* absolute configuration and the positive effect to the *Λ* configuration. A strong negative CD $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic absorption band, belonging to the tetragonal $^1A_{1g} \rightarrow {}^1E$ component, has been observed for all complexes indicating the *Δ* absolute configuration[15]. Thus the chirality of the ligand controls stereospecifically the absolute configuration of the complex forming only the *Δ* diastereoisomers.

Hydrophobic Interactions and Stereoselectivity

In view of the possible importance of the hydrophobic interactions involving an aromatic or aliphatic moiety, evaluation of the extent of such interactions would offer a key to the mechanism of protein structure stabilization[16,17] and similar biological phenomena. These interactions have been studied extensively by Sigel[18] and Yamauchi[2,19]. A valuable method to more directly establish hydrophobic interactions for mixed-ligand complexes involves the use of ^{1}H NMR shift measurements. Generally, protonation or coordination of a metal ion shifts the signals of the ligand hydrogens close to the binding site downfield. However, in a complex in which the aliphatic side chain of the EBAA is located above or below the plane of an aromatic ring system (Fig. 3), the signals of the aliphatic hydrogens should be shifted upfield, relative to those of the free EBAA ligand, due to the ring current of the aromatic system.

^{1}H NMR shift measurements (Table IV) of the mentioned systems in the absence and presence of Co(III) confirmed that such hydrophobic ligand–ligand interactions exist and that they are promoted by the formation of a metal–ion-bridge between the two ligands. The greater the aromatic-ring system of the dam, the larger is the upfield shift of the terminal methyl groups of the (*SS*)-EBV, resulting from the interaction between these groups and the aromatic-ring system of BHBOP or phen within the ternary complexes. The same is true for aromatic-ring stacking interaction within the $[Co((SS)\text{-EBPhe})(phen)]^+$ ternary complex. A possible structures of these complexes are shown in Fig. 3. Such upfield movement associated with aromatic systems is due to the magnetic anisotropy of the ring system and indicates that the proton moving upfield is experiencing the ring current of the "face" of another aromatic system. The formation of "closed" form can enhance stability of *cis*-α isomer relative to *cis*-β isomer and together with steric factors favorized formation of the *cis*-α isomer in solution.

The predominance of the *cis*-α isomer indicates that the synthesis is also influenced by kinetic effects. These are particularly pronounced in the case of the *Δ*-*cis*-β isomer which for steric reasons is thermodynamically less stable than the *Λ*-*cis*-β isomer[20]. The steric factors are also responsible for unsuccessful synthesis of $[Co((SS)\text{-EBPhe}).(BHBOP)]^+$ complex. According to molecular models, steric hindrances of the both ligands are to pronounced to coordination may proceed.

TABLE IV

Chemical shift (ppm) of the terminal methyl groups (the midpoint of the multiplets) for coordinated (*SS*)-EBV or phenyl protons (the midpoint of the multiplets) for coordinated (*SS*)--EBPhe, respectively, relative to the resonance position of the uncoordinated EBAA anion at pH 11·2

Compound	δ	$\Delta\delta^a$
(*SS*)-EBV	0·945	0
Co(en)[b]	1·170	−0·225
Co(BHBOP)	0·940	0·005
Co(phen)	0·930	0·015
(*SS*)-EBPhe	7·380	0
Co(en)[b]	7·572	−0·192
Co(phen)	7·318	0·062

[a] $\Delta\delta = \delta_{\text{ligand}} - \delta_{\text{complex}}$; [b] data for *cis*-α isomer.

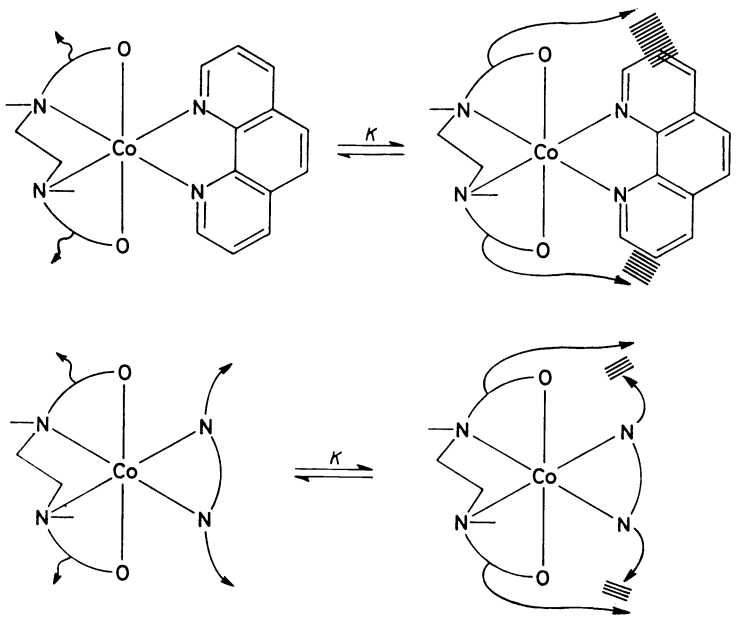

FIG. 3

Possible structures of ternary *cis*-α-[Co(EBAA)(phen)]$^+$ (top) or *cis*-α-[Co((*SS*)-EBV).(BHBOP)]$^+$ (below) complexes. K = ["closed" form]/["open" form]

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