

146. Stereoselectivity in Reactions of Metal Complexes

Part X¹⁾

Kinetics and Stereoselectivity of the Inner-sphere Electron-Transfer Reaction between $[\text{Co}(\text{bamap})\text{H}_2\text{O}]^+$ (bamap = 2,6-Bis(3-carboxy-1,2-dimethyl-2-azapropyl)pyridine) and Optically Active Iron(II) Complexes

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The kinetics of the electron-transfer reaction between racemic or optically active $[\text{Co}(\text{bamap})\text{H}_2\text{O}]^+$ and optically active Fe^{2+} complexes of the three new pentadentate ligands bamap, alamp, and valmp has been investigated. All the reacting species show C_2 symmetry. With respect to aquo- Fe^{2+} , the reaction rate for the Fe^{2+} complexes is enhanced by a factor of 10^4 to 10^5 , and the observed k_{AA}/k_{AA} ratio is 1.0, 1.9, and 1.2, respectively. In all cases where stereoselectivity is observed, the reaction is faster between the complexes of opposite absolute configurations (AA or AD) than between species with the same configuration (AA or AD). The stereoselectivity effects are discussed on the basis of the structure of the transition state and the interatomic distances between the two metal centers at the moment of electron transfer.

1. Introduction. – It has been argued, that the stereoselectivity – even when the observed effects are small – may be an important argument in the discussion of mechanistic features in electron-transfer reactions [2–4]. However, only a few other examples have been described [6–14] since the publication of the first example of an electron-transfer reaction, for which stereoselectivity was unambiguously demonstrated [5]. All these examples deal with reactions following an outer-sphere mechanism.

In the present paper, we relate the measurements of electron transfer between a Co(III) and an Fe(II) center, which are known to proceed generally by an inner-sphere mechanism *via* a bridged intermediate [15]. In outer-sphere reactions, stereoselectivity effects can appear in the formation of the precursor complex as well as in the electron transfer itself [7]; this may also be the case for an inner-sphere reaction with respect to the formation of the bridged intermediate or to the electron transfer which follows the pre-equilibrium.

The interpretation of the observed stereoselectivity effects is often difficult for the following reasons: *i*) the effects are, in general, small and represent only a minor fraction of the binding energies of the reactive intermediates, *ii*) several diastereoisomeric struc-

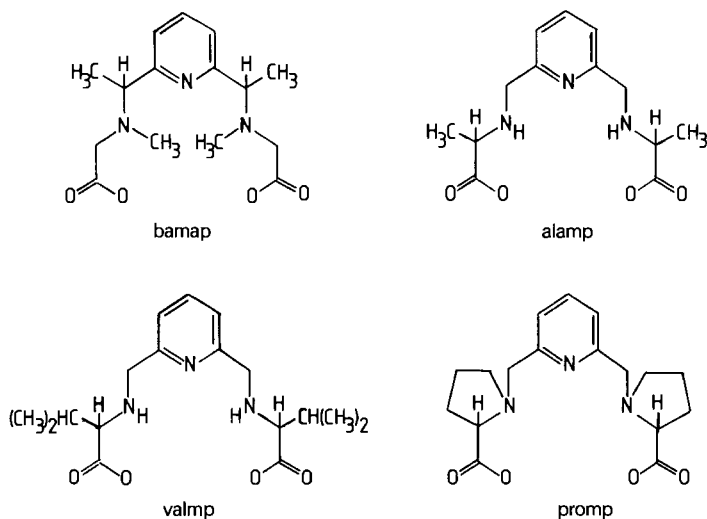
¹⁾ Part IX: [1].

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tures of almost the same stability may be considered for the intermediate so that the real structure of the latter is not known and *iii*) the effects in the pre-equilibrium and in the electron transfer may direct in opposite directions.

To eliminate these factors or at least to diminish their influence, the ligands, constituting the coordination sphere of the reacting compounds, should satisfy several conditions, the most important of which are the following: *i*) the ligand used should occupy all the coordination sites of both metal centers except those occupied by the bridging group, *ii*) the complex formed by the ligand should exist as only one geometrical isomer, *iii*) complex formation with the optically active derivatives of the ligands must be completely diastereoselective, with inert as well as with labile systems, and *iv*) the absolute configuration of both reacting complexes must be known.

In [1], we have shown that linear pentadentate ligands derived from 2,6-bis(3-carboxy-2-azapropyl)pyridine as the basic framework should fulfill the conditions mentioned above, so that only one isomer of the inert Co(III) complexes is obtained, and that the optically active ligand forms complexes with a given absolute configuration. We may, therefore, assume that this will be true for labile complexes too. The ligands used in this work are shown below.



2. Results. – 2.1. *Absolute Configuration.* A tentative proposal for the absolute configuration of the isomers of the $[\text{Co}(\text{bamap})\text{H}_2\text{O}]^+$ and $[\text{Co}(\text{valmp})\text{H}_2\text{O}]^+$ ions has been given on the basis of their CD and $^1\text{H-NMR}$ spectra [1]. To ensure this attribution of configuration, the new compound $[\text{Co}((S,S)\text{-promp})(\text{py})]\text{ClO}_4$ was synthesized. By means of the cyclic structure of the pyrrolidine moieties, this ligand can coordinate as a pentadentate only, if the substituent on the α -C-atom in the aminocarboxylate chelate ring is in the *exo*-position. Together with the C_2 -symmetric arrangement, the absolute configuration of the complex is unambiguously determined on the basis of the chirality of the amino-acid moiety (Fig. 1).

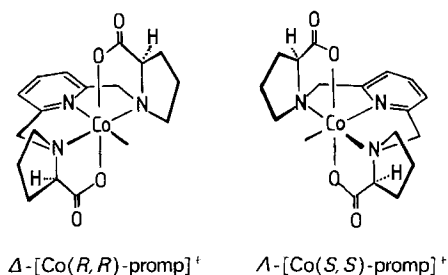


Fig. 1. Absolute configuration of the [Co(*(R,R)*-promp)]⁺ and [Co(*(S,S)*-promp)]⁺ complexes

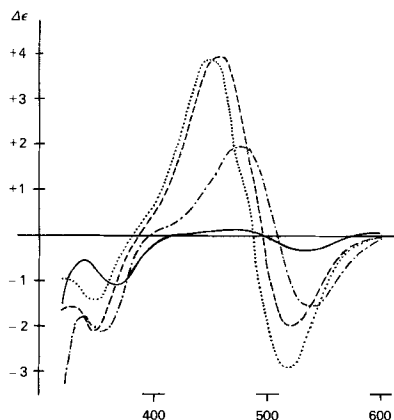


Fig. 2. CD spectra of (—) $(-)\text{[Co(bamap)(H}_2\text{O)]ClO}_4$; (---) $(-)\text{[Co(bamap)(H}_2\text{O)]ClO}_4$; (·····) [Co(*(S,S)*-alamp)(py)]ClO₄; (— · — ·) [Co(*(S,S)*-valmp)(py)]PF₆; and (— · — · — ·) [Co(*(S,S)*-promp)(py)]ClO₄

The comparison of the CD spectra (Fig. 2) shows that the complexes derived from (*S*)-amino acids exhibit Λ -configuration, and that this is also the configuration of $(-)\text{[Co(bamap)(H}_2\text{O)]}^+$. The structure of the latter is known from the X-ray diffraction analysis [16], indicating that (*S*)-chirality of the asymmetric C-atoms leads to the Λ -configuration for the complex. Furthermore, the pentacoordination of the ligand in [Co(*(S,S)*-promp)(py)]⁺ is confirmed by the NMR spectra, which is typical for an arrangement with C₂ symmetry.

2.2. Kinetics of Electron Transfer. When [Co(bamap)H₂O]⁺ reacts with Fe²⁺ under pseudo-first-order conditions (presence of ascorbic acid) and in slightly acidic solution, strong auto-catalysis of the reaction is observed (Fig. 3a). It can be attributed to the complexation of Fe²⁺ by the ligand which is set free during the reduction of the Co(III) complex. This ligand can bind to the different metal ions present in the solution (Fe²⁺, Co²⁺), depending upon their stability constants (cf. Table 1). If a redox-inactive metal ion is present in excess, e.g. Zn²⁺, the free ligand is trapped, and auto-catalysis disappears (Fig. 3a). The reaction rate, then, corresponds to the reduction by the aquo-Fe²⁺, allowing the determination of the corresponding rate constant.

When these rate constants are measured as a function of pH (Fig. 3b), a proportional increase of the reaction rate is observed in slightly acidic solution, whereas, in more acidic solutions, the rate seems to reach a limiting value. This behaviour is in agreement with the rate law (Eqn. 1):

$$k_{\text{obs}} = [\text{Fe}^{2+}] \left\{ k_1 + K_{\text{H}}(k_2 - k_1) / (K_{\text{H}} + [\text{H}^+]) \right\} \quad (1)$$

K_{H} being the acid dissociation constant of either the Co(III) complex or the aqua-Fe²⁺ ion, and k_1 and k_2 the rate constants for the reaction with the pH-independent and the pH-dependent reacting species, respectively. In the presence of ascorbic acid and for the pH range studied, $[\text{Fe}^{2+}] = c_{\text{Fe}^{2+}}$, $K_{\text{H}} \ll [\text{H}^+]$ and $k_1 \ll k_2$, Eqn. 1, then, becomes:

$$k_{\text{obs}} = (k_1 + k_2 K_{\text{H}} / [\text{H}^+]) c_{\text{Fe}^{2+}} \quad (2)$$

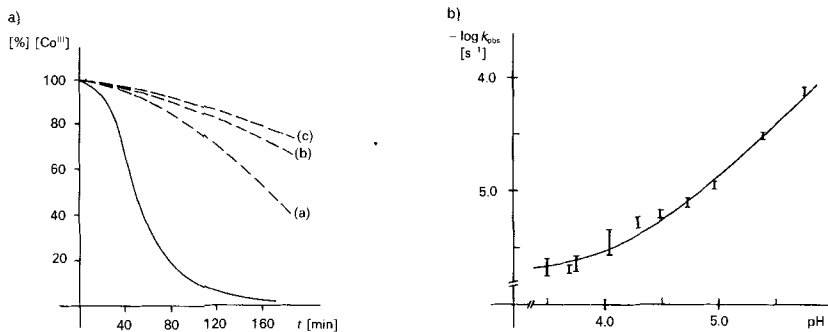


Fig. 3. a) Electron transfer between $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$ and Fe^{2+} without (—) and in the presence of Zn^{2+} (---). Reaction conditions: $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$: $2.5 \cdot 10^{-3}$ M; Fe^{2+} : $2.6 \cdot 10^{-3}$ M; ascorbic acid: 0.02 M; Zn^{2+} : 0.01 M (a); 0.02 M (b); 0.03 M (c); pH = 4.0 (acetate buffer 0.1 M); $T = 25^\circ$. b) Observed rate constants of the reaction between $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$ and Fe^{2+} in the presence of Zn^{2+} as a function of pH. Reaction conditions: $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$: $2.5 \cdot 10^{-3}$ M; Fe^{2+} : $2 \cdot 10^{-3}$ M; Zn^{2+} : 0.1 M; ascorbic acid: 0.02 M; acetate buffer 0.1 M; $T = 25^\circ$.

The curve in Fig. 3b represents the calculated values obtained by using $k_1 = 9.0 \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_2 = 12.0 \text{ M}^{-1} \cdot \text{s}^{-1}$, and $K_{\text{H}} = 5.0 \cdot 10^{-9}$ [1].

When free H_2bamap is added to the solution, a strong increase in the rate of electron transfer due to the formation of $[\text{Fe}(\text{bamap})]$ is observed. The concentration of the latter can be varied in two different ways: by changing the total concentration of $\text{Fe}(\text{II})$ and ligand, or by changing the pH of the solution. As is seen from the results given in Fig. 4, the values for the observed rate constants in both cases fall within the same straight line with a slope close to unity, indicating that the reaction rate depends on the pH value only, since a pH change modifies the concentration of $[\text{Fe}(\text{bamap})]$. The values indicated in Fig. 4 represent a variation of this concentration from 0.5 to 93% with respect to the total Fe^{2+} -bamap concentration. It seems, therefore, that in contrast to the case of aqua- Fe^{2+} , the electron transfer between the two complexed species takes place through the $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$; the reaction with the corresponding OH complex is not observed under the

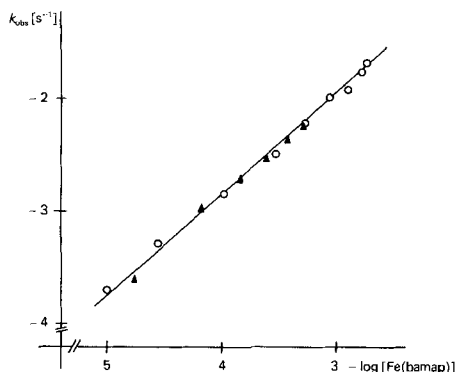


Fig. 4. Observed rate constants of electron transfer between $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$ and $[\text{Fe}(\text{bamap})]$. Reaction conditions: $[\text{Co}(\text{bamap})(\text{H}_2\text{O})]^+$: $2.5 \cdot 10^{-3}$ M; ascorbic acid: 0.02 M; acetate buffer 0.1 M; $-\blacktriangle-\blacktriangle-$: $c_{\text{Fe}^{2+}} = 0.72 \cdot c_{\text{bamap}}$, varied from $1 \cdot 10^{-3}$ M to $6 \cdot 10^{-3}$ M. $-\circ-\circ-$: $c_{\text{Fe}^{2+}} = c_{\text{bamap}} = 2 \cdot 10^{-3}$ M, pH varied from 3.5 to 5.8.

Table 1. Equilibrium Constants of the Systems $M^{2+}-L^{2-}$ ($M = Fe$ and Co) and Second-Order Rate Constants of Electron Transfer between $[Co(bamap)(H_2O)]^+$ and Optically Active FeL Complexes

L^{2-}	$pK_a^a)$	$pK_a^a)$	$\log K_{ML}^a)$		$k^{TE\ b)}$ [$M^{-1} \cdot s^{-1}$]	$k^{TE}(FeL)/k^{TE}(Fe^{2+})^c)$
			Fe^{2+}	Co^{2+}		
bamap	8.91	9.61	11.93	13.72	13	$1.5 \cdot 10^4$
alamp	8.23	9.02	9.62	11.70	61	$6.8 \cdot 10^4$
valmp	8.02	9.28	10.44	11.80	10	$1.1 \cdot 10^4$

^{a)} $T = 25^\circ$; $\mu = 0.1$.

^{b)} Reaction conditions as indicated in Fig. 3a.

^{c)} For exact signification of $k^{TE}(Fe^{2+})$, see text.

prevailing reaction conditions ($pH < 6$). $Fe(bamap)$ concentrations are calculated using the equilibrium constants reported in Table 1. These equilibrium constants, as well as the corresponding values of the optically active ligands (*S,S*)-alamp²⁻ and (*S,S*)-valmp²⁻, were obtained by acidimetric titrations.

From the known concentrations of the three $Fe(II)$ complexes, the pH-independent second-order rate constants of the overall electron-transfer reactions can be obtained.

2.3. *Stereoselectivity*. To demonstrate diastereoselectivity in the reaction between a kinetically inert $Co(III)$ and a labile $Fe(II)$ complex, there are two *Methods*: a) one enantiomer of the optically active $Fe(II)$ complex is reacted with the racemic $Co(III)$ complex; the stereoselectivity is, then, determined by the appearance of an excess of one of the two $Co(III)$ enantiomers during the reaction; b) one enantiomer of one of the reacting complexes is measured individually with both enantiomers of the other complex.

The advantage of *Method a* consists in the fact that both enantiomers of the inert $Co(III)$ complex react under completely identical conditions. Any – even very small – enantiomeric excess arising during the reaction gives, therefore, unequivocal evidence for the stereoselectivity of the reaction. *Method b* is useful, when the determination of enantiomeric excess is complicated by the presence of other optically active species. Its application is limited by the precision of the determination of reaction rates, and it is

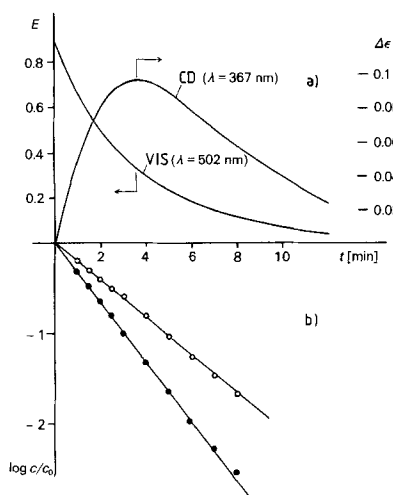


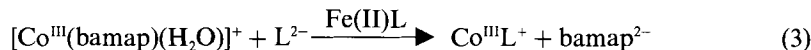
Fig. 5. Stereoselectivity in the electron transfer reaction between $(\pm)-[Co(bamap)(H_2O)]^+$ and $[Fe((S,S)\text{-alamp})]$. a) Change of VIS and CD intensity. b) First-order rate plots of each enantiomer; concentration change calculated from VIS and CD variation. Reaction conditions: $(\pm)-[Co(bamap)(H_2O)]^+$: $2.5 \cdot 10^{-3}$ M; Fe^{2+} : $2.5 \cdot 10^{-3}$ M; (*S,S*)-alamp: 10^{-2} M; ascorbic acid: 0.1 M; $pH = 4.0$ (acetate buffer 0.1 M); $T = 25^\circ$. $-\circ-\circ-\circ-$: $(-)-[Co(bamap)(H_2O)]^+$ ($k_{obs} = 3.2 \cdot 10^{-3} s^{-1}$). $-●-●-●-$: $(+)-[Co(bamap)(H_2O)]^+$ ($k_{obs} = 5.5 \cdot 10^{-3} s^{-1}$).

necessary that optical enantiomers of both complexes be available. In the present work, we applied both methods.

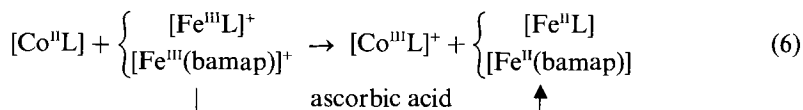
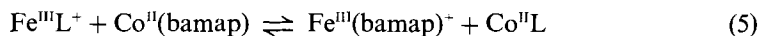
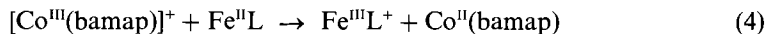
As an example for *Method a*, *Fig. 5a* shows the change of CD ($\lambda = 367$ nm) and VIS-absorption ($\lambda = 502$ nm) intensity as a function of time for the reaction between $[\text{Co}(\pm)\text{-bamap}(\text{H}_2\text{O})]^+$ and $\text{Fe}((S,S)\text{-alamp})$. The sign of the CD signal corresponds to $\Lambda(-)_{436}\text{-}[\text{Co}((S,S)\text{-bamap})(\text{H}_2\text{O})]^+$, which must, therefore, be the enantiomer with the smaller reaction rate.

From the known CD and VIS spectra of the optically pure compounds, the relative concentrations of both antipodes can be obtained separately as a function of time. The corresponding first-order rate plot is given in *Fig. 5b*. In this representation, the net stereoselectivity of the reaction appears clearly.

If the reaction is followed by measuring the intensity of the CD signal at constant wavelength ($\lambda = 365$ nm), an interesting observation is made. At low concentrations of ascorbic acid ($c < 0.02\text{M}$), the CD signal does not return to a value near zero at the end of the reaction, but reaches a final and constant value, which depends on the amount of ascorbic acid present as well as on the concentrations of $\text{Fe}(\text{II})$ and $(S,S)\text{-alamp}$. The CD spectra of the final solution corresponds to the spectrum of $[\text{Co}((S,S)\text{-alamp})(\text{H}_2\text{O})]^+$, indicating that a certain amount of this compound has been formed during the reaction, corresponding to an apparent ligand exchange following *Eqn. 3*:



This apparent ligand exchange must be brought about by the action of the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ couple, no reaction is observed between $[\text{Co}(\pm)\text{-bamap}(\text{H}_2\text{O})]^+$ and Co^{2+} in the presence of $(S,S)\text{-alamp}$ during the time-scale used. The redox-mediated formation of $[\text{Co}((S,S)\text{-alamp})(\text{H}_2\text{O})]^+$ may, therefore, be explained by the following reaction sequence:



$\text{L} = \text{alamp}^{2-}$

The Co^{II} , Fe^{II} , and Fe^{III} species are labile, the amount of the different complexes are under the control of the corresponding equilibrium constants, and the free metal ions may, therefore, also interfere in the reaction sequence too.

The amount of optically active $\text{Co}(\text{III})$ complex formed depends on the concentration of ascorbic acid because of the competition in the reduction of the Fe^{III} -species by the Co^{II} complexes and the ascorbic acid. At the end of the reaction, all the iron present is in the Fe^{2+} form and the amount of $[\text{Co}((S,S)\text{-alamp})(\text{H}_2\text{O})]^+$ remains constant, indicating that this compound is not reduced by Fe^{2+} under the prevailing conditions. A detailed study of this reaction will be published in a following paper.

When $[\text{Co}(\pm)\text{-bamap}(\text{H}_2\text{O})]^+$ reacts with Fe^{2+} in the presence of $(S,S)\text{-valmp}$, the third ligand described in this work, only a small stereoselectivity effect is observed, and

Table 2. *Stereoselectivity in the Electron Transfer between [Co(bamap)(H₂O)]⁺ and Optically Active FeL Complexes*

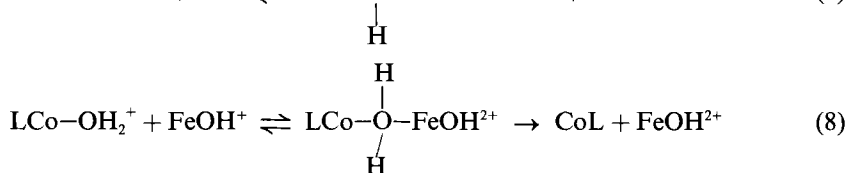
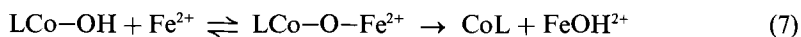
L	pH	Method ^{a)}	k _{AA} /k _{AA'} ^{b)}	ΔΔG [‡] (kJ·M ⁻¹)
bamap	3.5	<i>a</i>	1	0
alamp	4.0	<i>a</i>	1.7	1.3
	4.0	<i>b</i>	1.9	1.6
valmp	4.0	<i>b</i>	1.2	0.45

^{a)} *a*) Variation of ee during the reaction from CD measurements; *b*) kinetics of two diastereoisomeric couples.

^{b)} Mean values of at least five runs; for reaction conditions, see Fig. 5.

the formation of [Co((*S,S*)-valmp)(H₂O)]⁺ is even more important than in the case of (*S,S*)-alamp. For these reasons, the stereoselectivity of the reaction was determined by separate measurements of the reaction between both enantiomers of the optically active Co(III) complexes and [Fe((*S,S*)-valmp)]. The results obtained for the three optically active ligands are reported in Table 2.

3. Discussion. – When [Co(bamap)(H₂O)]⁺ reacts with aqua-Fe²⁺, two reaction paths can be observed: one pH-independent and the other pH-dependent. For the latter, two different intermediates can theoretically exist (Eqns. 7 and 8).



A distinction between these two possibilities can be achieved by the effect of ionic strength on the reaction rate. Whereas in Eqn. 7 the charge product of the reacting species is zero, it is +1 in Eqn. 8. Reaction rate should, therefore, be independent of the ionic strength in the former case, but increase with increasing ionic strength in the latter. In a range from 0.1 to 0.5, the corresponding measurements showed no influence of ionic strength on the reaction rate, indicating that the reaction proceeds by the OH⁻-bridged intermediate. This seems reasonable by the fact that the OH⁻ ion is known to be a much better bridging group than H₂O, also for electrostatic reasons.

Assuming the proposed mechanism, it is seen from the obtained data, that [Co(bamap)(OH)] reacts about 1.3 · 10⁴ times faster with the aqua-Fe²⁺ than [Co(bamap)(H₂O)]⁺.

The question on the reaction mechanism between the two aqua complexes then arises. The H₂O molecule being, if at all, considered as a weak bridging group, it may be inferred that the reaction should be of the outer-sphere type, or that the bridging of the two metal centers take place by an other group, e.g. one of the coordinated COO groups.

On the other hand, the observed stereoselectivity in the overall electron-transfer reaction with the optically active Fe²⁺ complexes implies a rather close approach of the two chiral faces of the reacting complexes. From X-ray data [16] and from model considerations, it is possible to estimate the distances between the two metal centers at which steric interactions between the Me groups of the [Co(bamap)] moiety and the substituents of the optically active Fe²⁺ complexes begin to occur, when the coordination sphere of one metal center of the binuclear intermediate is rotated around the Co-X-Fe

axis. It follows that neither an outer-sphere mechanism nor bridging by a COO group can explain the observed relative stereoselectivities, and we conclude, therefore, that the reaction takes place by an inner-sphere mechanism through a H₂O-bridged binuclear transition state (Fig. 6).

As a further argument for the proposed mechanism, it may be mentioned that the reaction between [Co(bamap)Cl] and Fe(alamp) shows a higher reaction rate, due to the better bridging ability of Cl⁻, and a stereoselectivity with the same geometrical orientation and the same order of magnitude as the aquo-complex, indicating that the reaction takes place by a similar mechanism [17].

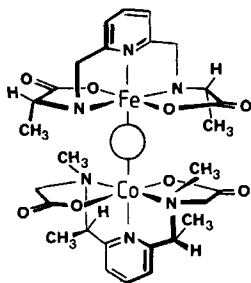


Fig. 6. Proposed structure of binuclear transition state in the reaction between Δ -[Co((R,R)-bamap)(H₂O)]⁺ and Λ -[Fe((S,S)-alamp)]

From Fig. 6, it can be recognized that the chiral faces of the two reacting complexes fit better, when they exhibit opposite chirality. In all the reactions of [Co(bamap)(H₂O)]⁺ or [Co(bamap)Cl] studied so far with the different Fe²⁺ complexes described in this paper, and for which stereoselectivity could be observed, the Δ - Λ couple reacts faster than the Δ - Δ or Λ - Λ couple, in accordance with the model.

When the second-order rate constants of the electron transfer between [Co(bamap)-(H₂O)]⁺ and the aqua-Fe²⁺ are compared with the analogous reactions involving the different Fe²⁺ complexes, a 10⁴ to 10⁵ fold increase is observed. This acceleration can be a consequence of the reduction of the positive charge of the reducing agent as well as a reduction of the *Franck-Condon* rearrangement term, which contributes to the free activation energy.

On the other hand, it can not be decided, if the reaction involves the formation of a precursor complex, and whether the observed stereoselectivity is a consequence of a difference in the stability of the precursor complex or of the rate of the intramolecular electron transfer following the formation of the binuclear precursor.

Experimental Part

1. *General.* Optical rotations were measured on a *Perkin-Elmer 241* polarimeter, UV and VIS spectra on a *Uvikon 820* spectrophotometer, and CD measurements were obtained from a *JASCO J-500* spectropolarimeter. ¹H-NMR: recorded on a *Bruker WP 200* at 200 MHz.

2. *Syntheses.* 2.1. *Aqua[2,6-bis(3-carboxy-1,2-dimethyl-2-azapropyl)pyridine]cobalt(III) Perchlorate* ([Co(bamap)H₂O][ClO₄ · 2 H₂O]). The racemic and the two optically active complexes were prepared as described in [1] and isolated as perchlorate salts by crystallization from 10% aq. NaClO₄.

2.2. *2,6-Bis[(3R,3S)-3-carboxy-1,2-dimethyl-2-azapropyl]pyridine ((R,S)-bamap).* When bamap is prepared as described in [1], a mixture of the *meso* and the racemic isomer, which could be separated only as their Co(III)

complexes, is obtained. The pure racemic ligand was, therefore, obtained by decomposition of the corresponding Co(III) complex: *rac*-[Co(bamap)(H₂O)]ClO₄ · 2 H₂O (1 g, 1.92 mmol) is heated to 50° with KCN (1.3 g, 20 mmol) in 50 ml of H₂O during 6 h. H₂O₂ (1 ml; 30%) is then added to the yellow soln., and the temp. maintained at 50°. After 1 h, AcOH (5 ml) is added and the free HCN eliminated in the hood by bubbling a stream of air through the warm soln. under slightly reduced pressure. After cooling, the soln. is introduced into a small cation-exchange column (*Dowex 50, H⁺*), and the hexacyanocobaltate and other products washed out with H₂O. Elution with 0.2N NaOH and evaporation to dryness of the neutral fractions containing the ligand yields *rac*-H₂bamap as a colourless oil. All attempts to crystallize the product failed. It was characterized by potentiometric titration and the NMR spectrum, which is very similar to the one obtained for the mixture of the two diastereoisomers [1]. ¹H-NMR (D₂O): 1.7 (*d*, 6 H); 3.0 (*s*, 6 H); 3.6 (*s*, 4 H); 4.8–4.9 (*m* unresolved, 2 H); 7.6 (*d*, 2 H); 8.1 (*t*, 1 H).

2.3. *2,6-Bis[(3S)-3-carboxy-1,2-dimethyl-2-azapropyl]pyridine* ((*S,S*)-bamap). The compound was isolated by the procedure indicated under 2.2 from (–)₄₃₆-[Co(bamap)(H₂O)]ClO₄ · 2 H₂O ($[\alpha]_D^{25}(\lambda) = -1000^\circ$ (436)). As for the racemic product, the optically active ligand could not be obtained in a crystalline form. $[\alpha]_D^{25}(\lambda): -185^\circ$ (436); -82° (589) (*c* = 0.46, H₂O, pH 4).

2.4. *2,6-Bis[(3S)-3-carboxy-2-azabutyl]pyridine* ((*S,S*)-alamp). Sodium (*S*)-alaninate (10.1 g, 0.1 mol), obtained by neutralization of (*S*)-alanin with a stoichiometric amount of NaOH, dissolved in MeOH (30 ml), is introduced in a 250-ml flask and heated to 50°. 2,6-Bis(bromomethyl)pyridine (5.4 g, 20 mmol) dissolved in MeOH (150 ml) is slowly added under stirring. After complete addition, the mixture is heated to 60° during 6 h, and the pH is kept constant at 9.6 by addition of NaOH/MeOH. After cooling, 2.13 g of unreacted alanin are filtered off and the filtrate is evaporated to dryness. The residue is redissolved in H₂O and the soln. is introduced in a cation-exchange column (*Dowex 50 X-8, H⁺*). The column is washed to neutrality with H₂O and the product eluted with 0.1M NaOH. Unreacted (*S*)-alanine is eluted first followed by a fraction containing a mixture of (*S*)-alanine and (*S,S*)-alamp. The effluent is analyzed by TLC (silica gel; BuOH/AcOH/H₂O 12:6:5) and by UV and polarimetric measurements. The fraction containing the (*S,S*)-alamp is evaporated to dryness and the residue washed with MeOH. After repeated recrystallization from H₂O/EtOH or H₂O/acetone, 2.25 g (39%) of the product, showing no more trace of alanine by TLC, is obtained. F 265°, $[\alpha]_D^{25}(\lambda): +45.2^\circ$ (365), $+26.1^\circ$ (436) (*c* = 0.26, H₂O). ¹H-NMR (D₂O, 200 MHz): 1.68 (*d*, 6 H); 3.80 (*q*, 2 H); 4.46 (*s*, 4 H); 7.47 (*d*, 2 H); 7.94 (*t*, 1 H). Anal. calc. for C₁₃H₁₉N₃O₄ (281.3): C 55.51, H 6.81, N 14.94; found: C 55.07, H 6.73, N 14.69.

2.5. *2,6-Bis[(3R)-3-carboxy-2-azabutyl]pyridine* ((*R,R*)-alamp). Prepared as the (*S,S*)-enantiomer. 2,6-Bis(bromomethyl)pyridine (77.6 g, 0.7 mol) and sodium (*R*)-alaninate (60.1 g, 0.227 mol) gave 17.3 g (27.1%) of the pure product, after separation and crystallization. $[\alpha]_D^{25}(\lambda): -47.9^\circ$ (365), -26.9° (436) (*c* = 0.2, H₂O).

2.6. *2,6-Bis[(3S)-3-carboxy-4-methyl-2-azapentyl]pyridine* ((*S,S*)-valmp). The procedure from [1] was modified as follows: 2,6-bis(bromomethyl)pyridine (10 g, 0.038 mol) in MeOH (150 ml) is added slowly to a vigorously stirred soln. of sodium (*S*)-valinate (27.5 g, 0.198 mol) in MeOH (50 ml). During the addition, a certain amount of valine precipitates. A methanolic soln. of 1.5 g of NaOH is added in order to maintain the pH of the mixture at 10–11. After 7 h, at 60°, the mixture is cooled, filtered, and the filtrate evaporated to dryness. The residue is redissolved in H₂O, and the (*S,S*)-valmp is purified on *Dowex 50 (H⁺)* and isolated in the same manner as indicated in 2.4 for (*S,S*)-alamp. After five recrystallizations from H₂O/acetone, 4.3 g (34%) of the pure product is obtained. $[\alpha]_D^{25}(\lambda): +19.4^\circ$ (365), $+11.9^\circ$ (436), $+5.4^\circ$ (589) (*c* = 0.45, H₂O). ¹H-NMR (D₂O, 200 MHz): 1.07 (*t*, 12 H); 2.32 (*m*, 2 H); 3.55 (*d*, 2 H); 4.45 (*s*, 4 H); 7.5 (*d*, 2 H); 7.96 (*t*, 1 H). Anal. calc. for C₁₇H₂₇N₃O₄ (337.4): C 60.51, H 8.07, N 12.45; found: C 60.43, H 8.08, N 12.40.

2.7. *2,6-Bis[(S)-(2-carboxypyrrolidin-1-yl)methyl]pyridine* ((*S,S*)-promp). Synthesized in a way similar to that described in 2.4, by reacting sodium (*S*)-prolinate (25 g, 0.182 mol) with 2,6-bis(bromomethyl)pyridine (10 g, 0.038 mol). When the reaction mixture is fixed on *Dowex 50 (H⁺)*, the unreacted proline can be eluted with H₂O. The column is washed with H₂O, as long as the effluent shows any optical activity. The (*S,S*)-promp, which is then eluted with 0.1M NaOH, could not be obtained in a crystalline form. The neutral soln. containing the product, identified by its UV absorption and its optical activity, was, therefore, directly used without further purification for the synthesis of the Co(III) complex.

2.8. *Pyridino(2,6-bis[(3S)-3-carboxy-2-azabutyl]pyridine)cobalt(III) Perchlorate* ([Co((*S,S*)-alamp)(py)]ClO₄ · H₂O). (*S,S*)-alamp (0.158 g, 0.562 mmol) is added to [Co(py)₄Cl₂]Cl dissolved in H₂O (50 ml). By heating to 40–50° during several min, the soln. turns from green to red. After 2 h, the soln. is introduced into a cation-exchange column (*Sephadex SP C25, Na⁺*) which fixes the complex quantitatively. Elution with 0.2% NaClO₄ yields two orange-red bands, the second containing a small quantity of the aqua-complex. Concentration of the soln. containing the main band yields the perchlorate salt of the mixed complex with a coordinated pyridine. The red crystals are filtered and recrystallized from H₂O. ¹H-NMR (DMSO, 200 MHz): 0.67 (*d*, 6 CH₃); 3.43 (unresolved, 2 CH); 4.63 (*d*, CH₂); 5.1 (*q*, CH₂); 7.53 (*d*, 2 NH, exchange with D₂O); 7.75, 7.94, 8.3, 8.9 (8 arom. H).

Anal. calc. for $[\text{Co}(\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_4)\text{C}_5\text{H}_5\text{N}][\text{ClO}_4] \cdot \text{H}_2\text{O}$ (535): C 40.40, H 4.53, N 10.48; found: C 40.26, H 4.35, N 10.64.

2.9. *Pyridino(2,6-bis[(3S)-3-carboxy-4-methyl-2-azapentyl]pyridine)cobalt(III) Hexafluorophosphate* ($[\text{Co}((S,S)\text{-valmp}(\text{py}))][\text{PF}_6]$). (*S,S*)-valmp (0.95 g, 2.7 mmol) is added to a soln. of $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$ (1.3 g, 2.7 mmol) in H_2O . On standing at r.t., the colour of the soln. rapidly turns to red. After heating to 30–40° during 1 h, the soln. is introduced into a cation-exchange column (*Sephadex SP C25*, Na^+). Elution of the complex, which is quantitatively fixed on the column with 0.1% NaCl, yields a single band. UV and CD of samples from the head and the end of the band were perfectly identical, showing that a single compound is formed in the reaction. The soln. containing the product is concentrated, and the hexafluorophosphate is precipitated as a yellow-orange crystalline powder by addition of NH_4PF_6 . Recrystallized from H_2O . $[\alpha]^{25}(\lambda)$: -1037° (436), -540° (546), -370° (589) ($c = 0.1$, H_2O). $^1\text{H-NMR}$ (DMSO, 200 MHz): 0.08 (*d*, 2 CH_3); 0.88 (*d*, 2 CH_3); 1.97 (*m*, 2 $(\text{CH}_3)_2\text{CH}$); 3.24 (unresolved, $\text{CHCH}(\text{CH}_3)_2$); 4.4 (*d*); 6.94 (*s*, 2 NH, exchange with D_2O); 7.85, 8.25, 8.93 (*m*, 8 arom. H). Anal. calc. for $[\text{Co}(\text{C}_{17}\text{H}_{25}\text{N}_3\text{O}_4)\text{C}_{15}\text{H}_5\text{N}][\text{PF}_6]$ (618): C 42.58, H 4.88, N 9.03; found: C 40.81, H 5.08, N 8.66.

2.10. *Pyridino(2,6-bis[(S)-(2-carboxypyrrolidin-1-yl)methyl]pyridine)cobalt(III) Perchlorate* ($[\text{Co}((S)\text{-promp}(\text{py}))][\text{ClO}_4]$). One (theoretical) equiv. of $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$ (18.3 g) is added to the soln. of (*S,S*)-promp obtained as described in 2.7. The mixture is heated to 40° during 1 h, filtered, and introduced into a cation-exchange column (*Sephadex SP C25*, Na^+) and thoroughly washed with H_2O . On elution with 0.1% NaCl, several bands develop. The red coloured main fraction is concentrated, and after elimination of NaCl by elution on *Sephadex G10*, the product is purified by a second chromatographic elution with 0.2% NaClO_4 on the cation-exchange column. Concentration of the effluent yields 8.5 g (47%) of red crystals of the perchlorate salt. Recrystallized twice from H_2O . $[\alpha]^{25}(\lambda)$: -1000° (436), $+35^\circ$ (546), -385° (589) ($c = 0.1$, H_2O). $^1\text{H-NMR}$ (NO_3^- salt in D_2O , 200 MHz): 0.4 (*m*, CH_2 of pyrrolidine); 1.85 (*m*, 2 CH_2 of pyrrolidine); 2.4 (*m*, CH_2 of pyrrolidine); 3.28 (*m*, CH_2 of pyrrolidine); 3.9 (*q*, H-C(2) of pyrrolidine); 4.64 (*d*, CH_2); 5.15 (*d*, CH_2); 7.95, 8.4, 8.8 (*m*, 8 arom. H). Anal. calc. for $[\text{Co}(\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_4)\text{C}_5\text{H}_5\text{N}][\text{ClO}_4]$ (569): C 46.45, H 4.16, N 9.85; found: C 46.27, H 4.52, N 9.99.

3. *Solutions*. All the reagents used were of anal. grade. Solns. for kinetic measurements were prepared under N_2 , and a N_2 atmosphere was maintained during the reactions. Solns. of Fe(II) salt and ascorbic acid were freshly prepared each day. The reaction temp. was controlled within 0.1°.

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