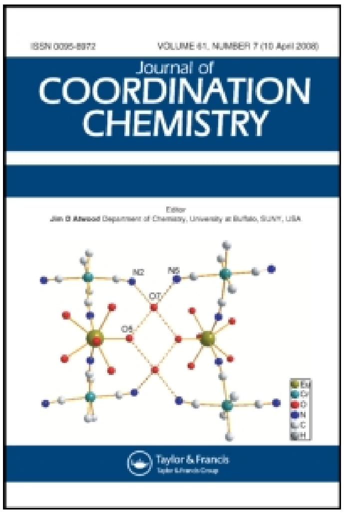

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STEREOSELECTIVITY ON ELECTRON TRANSFER REACTIONS(I); REACTION OF THE Λ-$[Co(EDDS)]^-$ AND *RAC*-$[Co(DIAMINE)_3]^2$ COMPLEXES (DIAMINE = EN, CHXN)

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STEREOSELECTIVITY ON ELECTRON TRANSFER REACTIONS(I); REACTION OF THE Λ-[Co(EDDS)]$^-$ AND RAC-[Co(DIAMINE)$_3$]$^{2+}$ COMPLEXES (DIAMINE = EN, CHXN)

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The absolute configuration of an optically active Λ-[Co(EDDS)]$^-$ (EDDS = ethylenediaminedisuccinate) complex was determined as Λ by the regional rule and spectroscopic data. The stereoselective ionic association between Λ-[Co(EDDS)]$^-$ and *rac*-[Co(en)$_3$]$^{3+}$ occurs preferentially between Λ-[Co(EDDS)]$^-$ and Δ-[Co(en)$_3$]$^{3+}$. The stereoselective electron transfer reaction between Λ-[Co(EDDS)]$^-$ and *rac*-[Co(en)$_3$]$^{2+}$ has been investigated in aqueous solution, DMF and DMSO. Their enantiomeric excesses (e.e.) observed are 14%, 26% and 40% of Δ-[Co(en)$_3$]$^{3+}$, respectively. The electron transfer reaction between Λ-[Co(EDDS)]$^-$ and conformationally restricted [Co(chxn)$_3$]$^{2+}$ has been examined in aqueous and DMSO solution. In aqueous solution, there are four isomers in the product which were determined as *lel$_3$*, *lel$_2$ob*, *lelob$_2$*, and *ob$_3$* of Δ-[Co(chxn)$_3$]$^{3+}$ with optical purities of 22%, 25%, 11% and 10% e.e. respectively. In DMSO, the reaction produces *lel$_3$*-Δ- and *lel$_2$ob*-Δ-[Co(chxn)$_3$]$^{3+}$ with optical purities of 100% and 75% e.e. respectively.

KEYWORDS: optical activity, cobalt(III) complexes, electron transfer

INTRODUCTION

There are numerous reports of stereoselective substitution reactions in which [Co(edta)]$^-$ or a related complex reacts with en (ethylenediamine) to give [Co(en)$_3$]$^{3+}$[1]. In fact, Busch and his coworkers have suggested a mechanism for the stereoselective substitution reaction.[2] Doh, *et al.*, have proposed a modification of Busch's mechanism from the fact that the intermediates and en do not react.[3] There are several reports that the stereoselective substitution reaction may be explained by a Co(II)-catalyzed, stereoselective electron transfer reaction.[1b,4] Lappin, *et al.*, reported that the Δ-[Co(edta)]$^-$ complex reacted with *rac*-[Co(en)$_3$]$^{2+}$ to produce Λ-[Co(en)$_3$]$^{3+}$ with an 11% e.e.[5] The stereoselectivity of this electron transfer

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reaction was explained by preferential ionic association between Δ-$[Co(edta)]^-$ and Λ-$[Co(en)_3]^{3+}$[5]. Taube and coworkers investigated the solvent dependence showing that protic solvents appear to display lower stereoselectivities compared to less protic solvents because formation of hydrogen bonds between the solvent and reactants make hydrogen bonding between reactants less effective.[6]

In this paper, we show that the absolute configuration of stereospecifically synthesized Λ-$[Co(EDDS]^-$ is determined by the regional rule and ring-pair method. Also, studied are the electron transfer reaction between Λ-$[Co(EDDS)]^-$ and *rac*-$[Co(diamine)_3]^{2+}$ [diamine = ethylenediamine(en), *trans*-1,2-diaminocyclohexane(chxn)] in various solvents to investigated the stereoselectivity of electron transfer reactions. The ionic association between reactants, the influence of the inner-sphere on conformational exchange, and the solvent effect on the electron-transfer reactions are also investigated.

EXPERIMENTAL

Synthesis of the Ligand and Complexes

Λ-$[Co(EDDS]^-$, $[Co(en)_3]^{3+}$, $[Co(en)_3]^{2+}$, and $[Co(chxn)_3]^{2+}$ were synthesized according to reported methods.[7,8] Optical resolution of chxn was accomplished by Saito's method.[9] The purities of materials and optical purities of complexes were checked by electronic absorption spectra (Shimadzu UV-2201) and circular dichroism spectra (JASCO J-500C Spectropolarimeter).

Stereoselective Ionic Association Between Λ-$[Co(EDDS)]^-$ and $[Co(en)_3]^{3+}$

Samples of $[Co(en)_3]^{3+}$ were absorbed as a 2 mm band on Sp-Sephadex C-25 cation exchange resin. Those samples were eluted with a 0.1M Λ-$[Co(EDDS)]^-$ solution containing 0.1 M sodium perchlorate. After the band had spread to 4–5 cm, the column was washed by water and the resin containing the cobalt(III) complex was eluted with concentrated NaCl and collected as four sections. After the solvent was stripped under reduced pressure, the CD spectrum of each sample was recorded in aqueous solution.

Stereoselective Electron Transfer Reactions

All reactions were performed at ambient temperatures under a nitrogen atmosphere to prevent air oxidation of the cobalt(II) complexes. The 0.04M Λ-$[Co(EDDS)]^-$ and 0.04M *rac*-$[Co(en)_3]^{2+}$ mixture and 0.6M ethylenediamine solution were purged with deoxygenated nitrogen. After 15 min solutions were mixed. When the distinct purpole-to-yellow color change was completed (*ca* 5 min), the reaction mixture was acidified by adding 20 mL of nitrogen purged 1M HCl, and the solution was diluted with water to 500 mL. This solution was adsorbed onto Dowex 50W-X2 cation resin in the H^+ form. The column was washed with 2M HCl to remove mono- and dications. Finally, the yellow $[Co(en)_3]^{3+}$ complex was eluted with 5M HCl and the elutant evaporated to dryness. The resulting residue was dissolved in water and electronic absorption and circular dichroism spectra were recorded. The reaction between Λ-$[Co(EDDS)]^-$ and $[Co(chxn)_3]^{2+}$ was similarly accomplished following the reaction between Λ-$[Co(EDDS)]^-$ and *rac*-$[Co(en)_3]^{2+}$. In order to separate possible conformational isomers in the resulting residue, the residue was adsorbed onto a Sp-Sephadex C-25 cation exchange resin in the Na^+ form (2.5x10 cm) and then eluted with 0.2M Na_3PO_4 solution. The resin-containing cobalt(III) complex was divided into four sections. Each section was adsobred onto a Sp-Sephadex C-25 column, washed with water to prevent CD induction due to phosphate ion and then eluted with 5M NaCl. Each solution was evaporated to dryness and electronic absorption and circular dichroism spectra were recorded.

RESULTS AND DISCUSSION

It was reported that stereoselectivity of outer-sphere electron transfer reactions is due to the stereoselective ionic association reactants in the transition state.[5] The information on stereoselectivity can be deduced from ion pairing studies for optically active complexes. In this paper, optically active $[Co(EDDS)]^-$ was used as oxidant, and the stereoselectivities of electron transfer reactions with $[Co(en)_3]^{2+}$ or $[Co(chxn)_3]^{2+}$ were studied. In order to study the stereoselectivity of the electron transfer reaction, determination of the absolute configuration of $[Co(EDDS)]^-$ is very important.

Rose and Neal have reported the synthesis and characterization of a novel ligand and its complex.[7] The EDDS ligand, which is an analog of EDTA, exhibits absolute stereospecificity on coordination to Co(III) as has been confirmed by an X-ray crystal structure determination.[10] Although $[Co(EDTA)]^-$ and $[Co(EDDS)]^-$ are structurally similar, the CD spectra are distinctly different and the dominant CD peaks show opposite signs creating difficulty for interpretation of absolute configurations. Applying to the ring pair method, $[Co(EDDS)]^-$ complex shows the helicity consists of ΛΛΔ and the absolute configuration is classified as Λ.

Assuming the absolute configuration of this complex as Λ-$[Co(EDDS)]^-$, we have investigated the regional rule to analyze the CD pattern of Λ-$[Co(EDDS)]^-$. Despite having the same configuration, CD patterns are different with opposite CD signs in the first absorption region. Legg and Douglas interpreted these data as having the same configuration with a dominant negative CD sign for the first absorption region.[11] Legg and Neal reported a difference in CD pattern due to changes in the chelate ring size.[12] The conformation of the EDTA and EDDS ligands for the diamine portion of each complex have the δ-form as shown by X-ray data but the differences for the CD pattern in the EDDS complex is due to the conformation of the aspartic portion of the molecule. Applying these portions to the regional rules for the D_{4h} group, the acetate portions of the EDTA complex are at the edge of octahedral because of planarity whereas the succinate portions of the EDDS complex belongs to a positive section in the D_{4h} group due to the asymmetric carbon branched with a five-membered ring in out-plane. We would expect a positive CD at long wavelength. This expectation agrees with the CD spectrum. Therefore, we can determine the absolute configuration of the $[Co(EDDS)]^-$ complex as Λ.

Stereoselective ionic association between Λ-$[Co(EDDS)]^-$ and *rac*-$[Co(en)_3]^{3+}$ was investigated in order to study the stereoselectivity of electron transfer between Λ-$[Co(EDDS)]^-$ and *rac*-$[Co(en)_3]^{2+}$. Fig. 1 shows CD spectra for each portion of

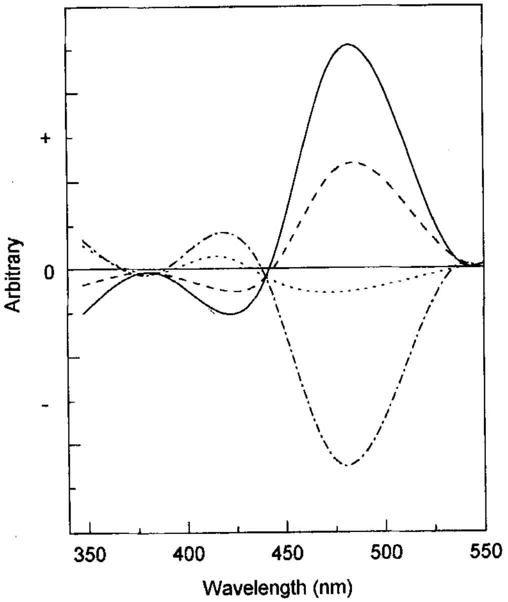

Figure 1 CD spectra of $[Co(en)_3]^{3+}$ after elution by Λ-[Co(EDDS)]$^-$ from a cation exchange resin column. CD of the first to final eluents, from top to bottom at 480 nm.

$[Co(en)_3]^{3+}$ eluted with Λ-[Co(EDDS)]$^-$ solution from a Sp-sephadex C-25 cation exchange resin. The first eluted portion exhibits the negative Cotton effect and is identified as Δ-$[Co(en)_3]^{3+}$. The last portion shows a positive Cotton effect and is identified as Λ-$[Co(en)_3]^{3+}$. This observation supports preferential ionic association between Λ-[Co(EDDS)]$^-$ and Δ-$[Co(en)_3]^{3+}$. We have considered the chirality of each complex in order to interpret the ion pairing mechanism. In the Δ-$[Co(en)_3]^{3+}$ complex, the helicity is composed of $P(C_3)M(C_2)$ {for $P(C_3)$ the helicity is plus along the C_3 axis while $M(C_2)$ is minus along the C_2 axis} similarly Λ-[Co(EDDS)]$^-$ is designated $P(C_3)M(C_2)$. Since homochiral pairwise interactions (PP or MM) are favored,[14] the pair is an effective C_3-C_2 interaction. The ionic association model between two complexes is displayed in Fig. 2 which shows the approach without spatial hinderance through hydrogen bonding between an oxygen of the C_3 axis in Λ-[Co(EDDS)]$^-$ and hydrogen of diamine of the C_2 axis on Δ-$[Co(en)_3]^{3+}$.

The reactivity of [Co(EDTA)]$^-$ with HCl is well-established but that of Λ-[Co(EDDS)]$^-$ with HCl is still unclear. The Λ-[Co(EDDS)]$^-$ complex was treated with HCl but no reaction was observed. It is reported that [Co(EDTA)]$^-$ can be easily reacted with HCl to form [CoCl(HEDTA)]$^-$ for the [Co(EDTA)]$^-$ complex ring opening occurs in the acetate ring from hinderance in the plane composing a diamine portion and the acetate rings which are five-membered rings.[15] Λ-[Co(EDDS)]$^-$ has six-membered rings without in-plane hinderance. The difference in the hinderance on ring size is believed to be closely related to the reactivity. Lack of reactivity of Λ-[Co(EDDS)]$^-$ towards substitution also arises from relaxation of hinderance (ring size). Therefore the Λ-[Co(EDDS)]$^-$ complex is more inert than [Co(EDTA)]$^-$.

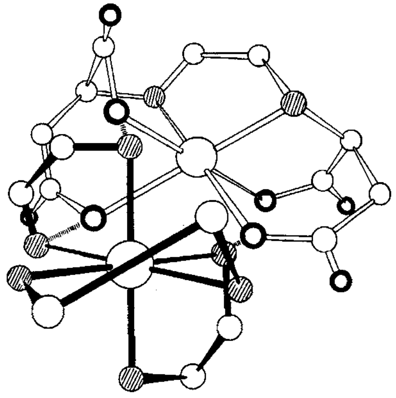

Figure 2 Proposed structure for the favorable ion pair of Δ-$[Co(en)_3]^{3+}$ with Λ-$[Co(EDDS)]^-$. Carbon (○), nitrogen (▨), and oxygen (⭘).

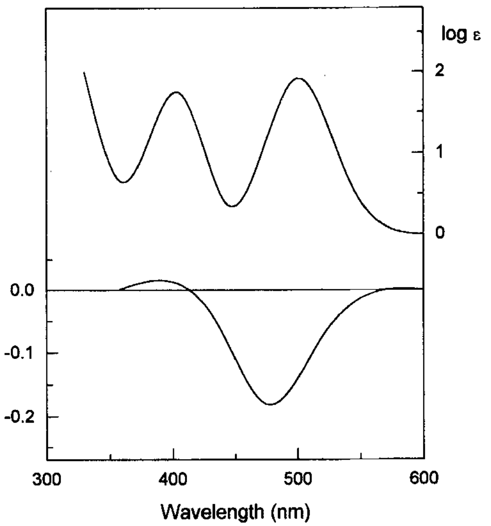

Figure 3 Electronic absorption and CD spectra of $[Co(en)_3]^{3+}$ obtained by a stereoselective electron transfer reaction.

Λ-$[Co(EDDS)]^-$ has been treated with *rac*-$[Co(en)_3]^{2+}$ under nitrogen. The reaction was too fast to obtain kinetic data from the electronic absorption spectrum. The product identified as $[Co(en)_3]^{3+}$ by electronic absorption spectra and elemental analyses. The reaction is thought to be an outer sphere reaction considering that Λ-$[Co(EDDS)]^-$ is more inert than $[Co(EDTA)]^-$ which undergoes outer sphere electron transfer with *rac*-$[Co(en)_3]^{2+}$. That only $[Co(en)_3]^{3+}$ is formed is also consistent with an outer sphere process.

The CD spectrum of $[Co(en)_3]^{3+}$ exhibits a big negative Cotton effect in the first absorption region (Fig. 3). The absolute configuration is determined as Δ. The chiral induction agrees with the result expected from ionic association. In other words, the stereoselective ionic association in the reaction plays an important role in the stereoselectivity of the electron transfer reaction. The enantiomeric excess (e.e.) of the Δ-$[Co(en)_3]^{3+}$ product is found to be 14% ($\Delta\varepsilon = -0.27$). The reason for this low chiral induction can be self-exchange between Δ-$[Co(en)_3]^{3+}$ and *rac*-$[Co(en)_3]^{2+}$ leading to racemization. This is not likely in the current system because the rates of self-electron transfer and racemization of $[Co(en)_3]^{2+/3+}$ were reported to be very slow.[16] Excluding these possibilities, the chiral reduction may arise from conformational exchange of the chelate rings in aqueous solution. The conformational exchange of chelate rings of $[Co(en)_3]^{2+}$ in aqueous solution is possible by simple rotation.[17] The conformational exchange of the $[Co(en)_3]^{2+}$ complex weakens the hydrogen-bonding from ionic association between Λ-$[Co(EDDS)]^-$ and $[Co(en)_3]^{2+}$ to reduce the stereoselectivity of Δ-$[Co(en)_3]^{3+}$.

Based on this assumption, *rac*-$[Co(chxn)_3]^{2+}$ having some restriction in the conformational exchange, has been treated with Λ-$[Co(EDDS)]^-$ to investigate the effect of conformational exchange. The reaction is very fast as observed for *rac*-$[Co(en)_3]^{2+}$. The product is identified as $[Co(chxn)_3]^{3+}$ by the electronic absorption spectrum and elemental analysis. The conformational isomers due to the stereospecific ligand, have been separated by Na_3PO_4 on the SP-sephadex C-25 cation resin as reported in the literature.[18] The four fractions were checked by electronic absorption spectra. From the area ratio of the curve, we have estimated the distribution percentage for formation of each isomer. The fractions are *lel₃*(A), *lel₂ob*[B], *lelob₂*[C], and *ob₃*[D] in the order as reported.[18] The ratio of *lel₃*:*lel₂ob*:*lelob₂*:*ob₃* is estimated as 30:40:22:3. This ratio is different from the general synthetic method[19] 46:34:14:3: e.g. the amount of *lel₃* isomer is reduced and *lel₂ob* isomer is increased a little. This may be because of the relative stability of each isomer according to various conformations, the relative reactivity and the relative ionic association with the Λ-$[Co(EDDS)]^-$ complex.

In order to investigated the absolute configuration and optical purities on isolated isomers, the CD spectra were measured (Fig. 4). All isomers exhibit a negative Cotton effect in the first absorption region of the electronic absorption spectra suggesting all isomers are in the Δ configuration. These stereoselectivities can also be interpreted as Δ-$[Co(en)_3]^{3+}$ finding the preferential ionic association of the Λ-Δ interaction. Their stereoselectivities are 22%, 25%, 11%, and 3% e.e, respectively for *Δ-lel₃, Δ-lel₂ob, Δ-lelob₂* and *Δ-ob₃*. In this result, the primary *Δ-lel₃*, and *Δ-lel₂ob* isomers show high stereoselectivity, whereas the *Δ-lelob₂* and *Δ-ob₃* isomers have low stereoselectivities. This suggests a high probability for reaction with the Λ-$[Co(EDDS)]^-$ complex for the *Δ-lel₃*, and *Δ-lel₂ob* isomers. The stereoselectivities of the dominant isomers are high compared to the Δ-$[Co(en)_3]^{3+}$ case, supporting that $[Co(en)_3]^{3+}$ interconverts the conformation of the ethylenediamine chelate rings by a simple rotation. $[Co(chxn)_3]^{3+}$ cannot convert the ligand conformation of the stereospecific ligand. Since the rigidness of conformational exchange causes effective ionic association with the Λ-$[Co(EDDS)]^-$ complex, the stereoselectivities of electron transfer between Λ-$[Co(EDDS)]^-$ and *rac*-$[Co(chxn)_3]^{2+}$ are higher than between Λ-$[Co(EDDS)]^-$ and $[Co(en)_3]^{2+}$.

The stereoselectivity of electron transfer is thought to depend on stereoselective ionic association between reactants and the conformation of the inner-sphere complex, but the optical purities are still low. If the stereoselectivity arises from

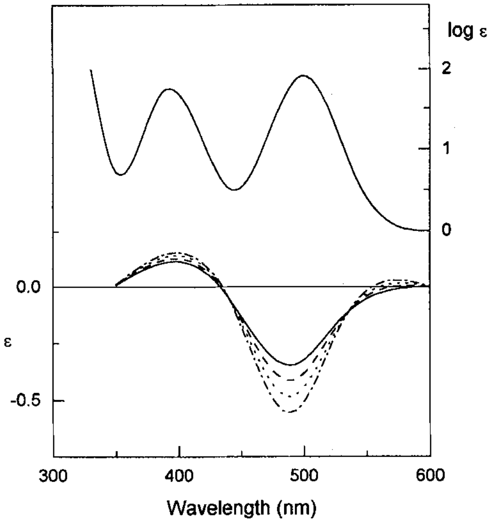

Figure 4 Electronic absorption and CD spectra of optically active Δ-$[Co(chxn)_3]^{3+}$ obtained from the reaction of [Co(±chxn)$_3$]$^{2+}$ and Λ-[Co(EDDS)]$^-$ in aqueous solution; *lelob$_2$* (——), *ob$_3$* (– – –), lel$_3$ (· · · ·), *lel$_2$ob* (–·–·).

ionic association between reactants in aqueous solution, protons in solution may hinder the ionic association.

The electron transfer reactions between Λ-[Co(EDDS)]$^-$ and *rac*-[Co(diamine)$_3$]$^{2+}$ have been accomplished in various solvents (H_2O,DMF,DMSO) to investigate the solvent effect. The reaction between Λ-[Co(EDDS)]$^-$ and *rac*-[Co(en)$_3$]$^{2+}$ in various solvents produces Δ-[Co(en)$_3$]$^{3+}$ in enantiomeric exesses 14% e.e in water, 26% e.e in DMF, 40% e.e in DMSO, respectively (Fig. 5). The increase in stereoselectivity according to solvent (H_2O<DMF<DMSO) agrees with an order for the decrease of protons in the solvent. A proton oriented between reactants would hinder ionic association. A remarkable dependence of stereoselectivity on solvent indicates the importance of protons in ionic association.

The reaction between Λ-[Co(EDDS)]$^-$ and *rac*-[Co(chxn)$_3$]$^{2+}$ in DMSO has been accomplished to investigate in one experiment the effect of solvent and inner-sphere on the rigid conformation. The products are two [Co(chxn)$_3$]$^{3+}$ isomers (*lel$_3$* and *lel$_2$ob*) unlike the reaction in aqueous solution. The distribution percentage for formation on each isomer, obtained from the elution curve, as 60% and 40%, respectively, for *lel$_3$* and *lel$_2$ob*. For the electron transfer reaction there is more probability that the primary isomers *lel$_3$* and *lel$_2$ob* can be associated and reacted with Λ-[Co(EDDS)]$^-$. The minor *lelob$_2$* and *ob$_3$* isomers have less probability for interaction with Λ-[Co(EDDS)]$^-$ because they have obstacles for ionic association with Λ-[Co(EDDS)]$^-$ due to the oblique conformation of [Co(chxn)$_3$]$^{2+}$ which prevents the electron transfer reaction. The absolute configuration of each isomer is identified as the Δ form, and the stereoselectivities are shown to be 100% e.e and 73% e.e respectively for *Δ-lel$_3$*, *Δ-lel$_2$ob* (Fig. 6). Considering the facts, it is reasonable to assume that the high stereosensitivty for *Δ-lel$_3$*-[Co(chxn)$_3$]$^{3+}$ is due to more effective ionic association with Λ-[Co(EDDS)]$^-$ than for the *Δ-lel$_2$ob*

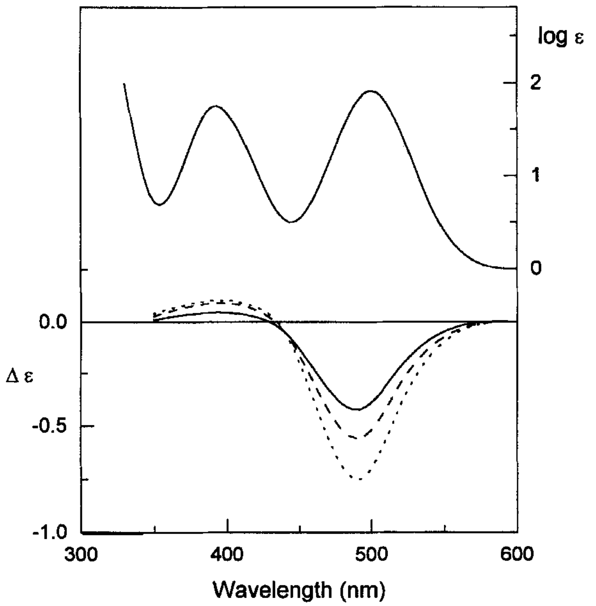

Figure 5 Electronic absorption and CD spectra of the Δ-$[Co(en)_3]^{3+}$ obtained from the reaction of $[Co(en)_3]^{2+}$ and Λ-$[Co(EDDS)]^-$ in various solvents; water (—), DMF(----) and DMSO (····).

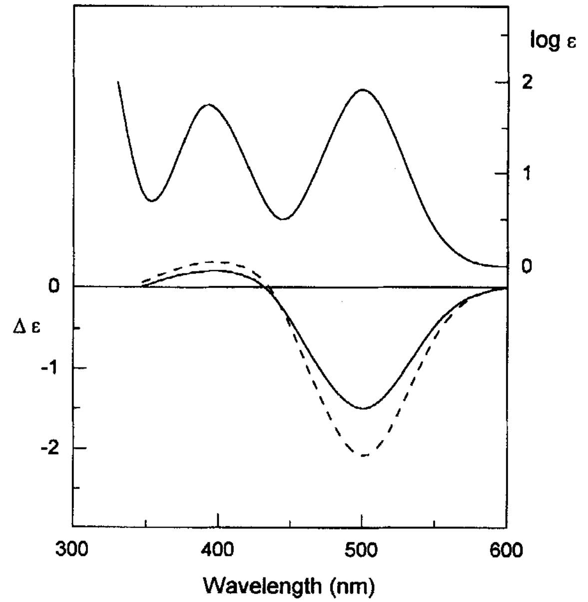

Figure 6 Electronic absorption and CD spectra of optically active Δ-$[Co(chxn)_3]^{3+}$ obtained from the reaction of $[Co(\pm chxn)_3]^{2+}$ and Λ-$[Co(EDDS)]^-$ in DMSO; *lelob*$_2$, (—), lel$_3$ (----).

isomer, the rigidness in conformational change, and the solvent effect without interference from protons in the ionic association. The stereoselectivity of electron transfer is more dependant on solvent effects than on the conformational rigidness of the inner-sphere. This conclusion is based on the facts that the stereoselectivity of Δ-$[Co(chxn)_3]^{3+}$ in DMSO is highest and that the stereoselectivity of Δ-$[Co(chxn)_3]^{3+}$ in water is higher than the that of Δ-$[Co(en)_3]^{3+}$ in water.

Acknowledgments

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