imine nitrogens in the cases of tetraazacyclic ligands when the central metal ion is Co(III). In the case of d^3 systems, the energy of the longest wavelength d–d band is known to give a direct measure of the field strength of the ligands.[33b] The data given in Table II suggest that as the number of imino nitrogens increases, the field strength of macrocycles bonded to Cr(III) decreases. A detailed discussion of the field strength of related macrocycles as a function of intraligand ring size, steric strain, symmetrical nature (or otherwise), etc. was presented by Swisher et al.[10] Following their arguments,[10] it may be suggested that the steric strain associated with symmetrical [14]-membered macrocycles in forming trans complexes contributed to the observed order of field strength for the ligands, Me_6[14]ane > Me_6[14]diene > Me_4[14]tetraene. Since the C=N bond is shorter than the C—N bond, as the number of C=N bonds increases, the intraligand ring size of [14]-membered macrocycles is expected to decrease, thereby increasing the steric strain. At least in the case of $Cr(Me_4[14]tetraene)(H_2O)_2^{3+}$, considerable steric strain may be inferred on the basis of the electronic spectrum.

When the strain due to the mismatch of the intraligand ring size and the size of the metal ion is large, displacement of the central metal ion from the plane of the ring donor atoms (as in $Cr(salen)(H_2O)_2^+$) or ring opening of the macrocycles as in the cases of Me_6[14]diene and Me_4[14]tetraene cannot be ruled out. Recently, an X-ray structural study[42,43] of a methoxy-bridged Cr(III) dimer prepared from Cr(II) and Me_4[14]tetraene in methanolic media proved conclusively that Me_4[14]tetraene undergoes breakdown at the time of synthesis.[42] Therefore, in cases where the synthesis of diaquo complexes of the formulation $Cr(Me_6[14]diene)(H_2O)_2^{3+}$ or $Cr(Me_4[14]\text{-tetraene})(H_2O)_2^{3+}$ is possible, substantial steric strain in the trivalent state of the metal ion may be anticipated.

Summarizing the results of this study, it is now possible to synthesize Cr(III) complexes of symmetrical [14]-membered tetraaza macrocycles (with trans structures) in spite of steric strain. The field strength of these macrocycles also seems to be influenced by the cavity sizes. The implication of our results in this study is that there is a possibility of stabilizing the tetravalent state of chromium by way of both destabilizing Cr(III) with respect to Cr(IV) by the choice of macrocyclic ligand and increasing the Franck–Condon barriers for the conversion of octahedral Cr(IV) to tetrahedral Cr(V) through equatorially coordinated macrocyclic ligands.[44,45]

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Optical Resolution and Racemization Reaction of Tris(bathophenanthrolinedisulfonato)iron(II): Absence of an Intramolecular Racemization Path in Aqueous Solution

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Tris(bathophenanthrolinedisulfonato)iron(II) ($Fe(BPS)_3^{4-}$) was resolved on a chromatographic column of Λ-tris(1,10-phenanthroline)ruthenium(II)–montmorillonite. The Δ-enantiomer of $Fe(BPS)_3^{4-}$ exhibited higher affinity toward the column than the Λ-enantiomer. The ligand dissociation rate (k_D) and racemization rate (k_R) of $Fe(BPS)_3^{4-}$ were obtained in a mixed solvent of methanol and water. In water, k_R was identical with k_D with the same activation parameters: $\Delta H^{*} = 130$ kJ mol^{-1}, $\Delta S^{*} = 90$ J mol^{-1} K^{-1}. The results indicate that the complex racemizes by the dissociation path exclusively.

Introduction

Racemization of tris(1,10-phenanthroline)metal(II) ($M(phen)_3^{2+}$) in water has been a subject of many investigators.[1-3] One interesting aspect on this topic is that $M(phen)_3^{2+}$ follows different paths in racemization, depending on the electronic properties of the central metal ion. For example, the racemization rate (k_R) of $Ni(phen)_3^{2+}$ in water has been compared with the dissociation rate of a ligand (k_D). k_R is identical with k_D over wide ranges of temperature and pressure.[3] The results are interpreted in terms of the mechanism that $Ni(phen)_3^{2+}$ racemizes by dissociating one of its ligands

$$\Delta\text{-}M(phen)_3^{2+} \rightleftharpoons M(phen)_2^{2+} \rightleftharpoons \Lambda\text{-}M(phen)_3^{2+} \qquad (1)$$

in which a dissociation intermediate, $M(phen)_2^{2+}$, is optically inactive, losing the memory of the configuration of an initial $M(phen)_3^{2+}$.[1]

On the contrary, in the case of $Fe(phen)_3^{2+}$, k_R is about 1 order of magntidue larger than k_D in water.[2] It is concluded that $Fe(phen)_3^{2+}$ racemizes by way of two parallel paths; one is a dissociation path (1) and the other an intramolecular path (2).

$$\Delta\text{-}M(phen)_3^{2+} \rightleftharpoons M(phen)_3^{2+*} \rightleftharpoons \Lambda\text{-}M(phen)_3^{2+} \qquad (2)$$

In the activated state, the complex, $M(phen)_3^{2+*}$, undergoes an intramolecular configuration change without producing any free ligand.[1] In $M(phen)_3^{2+*}$, the significant lengthening of metal–ligand bonds occurs to satisfy the steric requirement for the change of the coordination positions. The stabilization of such an expanded state due to the contribution of the high-spin state ($(t_{2g})^4(e_g)^2$) is considered to be the main reason that $Fe(phen)_3^{2+}$ racemizes dominantly by wasy of the intramolecular path.[1]

Recently the present author has developed the method of optical resolution by use of an optically active clay–chelate adduct as a resolving agent.[4-6] The method is based on the stereoselective

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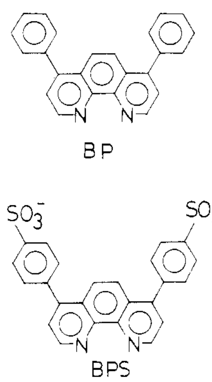

Figure 1. Structures of investigated ligands: BP = bathophenanthroline (4,7-diphenyl-1,10-phenanthroline); BPS = bathophenanthrolinedisulfonate (4,7-diphenyl-1,10-phenanthrolinedisulfonate).

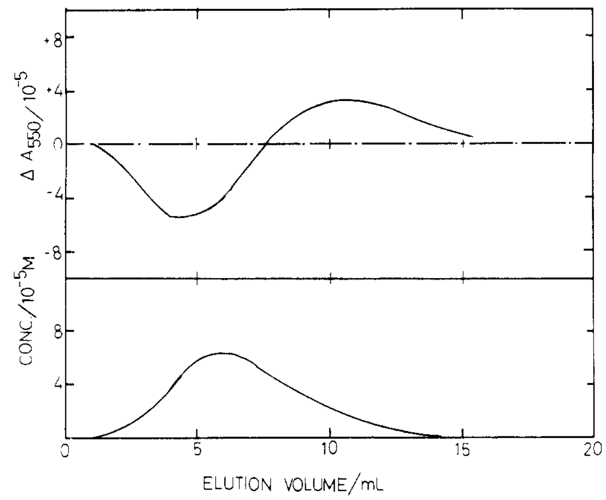

Figure 2. Chromatogram when $Fe(BPS)_3^{4-}$ was eluted on a column of Λ-$Ru(phen)_3^{2+}$–montmorillonite. The upper curve is the amplitude of circular dichroism at 550 nm. The lower curve is the concentration of the complex.

adsorption of a molecule with an optically active metal complex that has been primarily adsorbed by a clay. According to the method, tris(bathophenanthroline)iron(II) ($Fe(BP)_3^{2+}$) and tris(bathophenanthrolinedisulfonato)iron(II) ($Fe(BPS)_3^{4-}$) were resolved partially. These complexes possess bulky functional groups attached to phenanthroline ligands (Figure 1). The presence of such substituents on the ligands was expected to affect greatly the mode of interaction of the complex with the solvent, especially in the activation states of reactions 1 and 2. To our knowledge, there has been no work concerning the racemization kinetics of a complex having substituted phenanthroline ligands.[7] We, therefore, studied the reactions of dissociation and racemization of $Fe(BP)_3^{2+}$ and $Fe(BPS)_3^{4-}$ in water and water–methanol mixtures. As a result, $Fe(BPS)_3^{4-}$ was found to racemize exclusively by a dissociation path in water.

Experimental Section

The racemic complexes $Fe(phen)_3^{2+}$, $Fe(BP)_3^{2+}$ and $Fe(BPS)_3^{4-}$ were prepared by mixing $Fe(SO_4)_2 \cdot 7H_2O$ and the ligands in either a water or a methanol–water mixture. $Fe(phen)_3^{2+}$ was resolved by use of antimony *d*-tartrate.[8] $Fe(BP)_3^{2+}$ and $Fe(BPS)_3^{4-}$ were partially resolved by using an adduct of sodium-montmorillonite clay (Kunimine Ind. Co. Ltd., Japan) with either Λ-$Ru(phen)_3^{2+}$ or Δ-$Ni(phen)_3^{2+}$. Details of the resolution procedures will be described in the succeeding section.

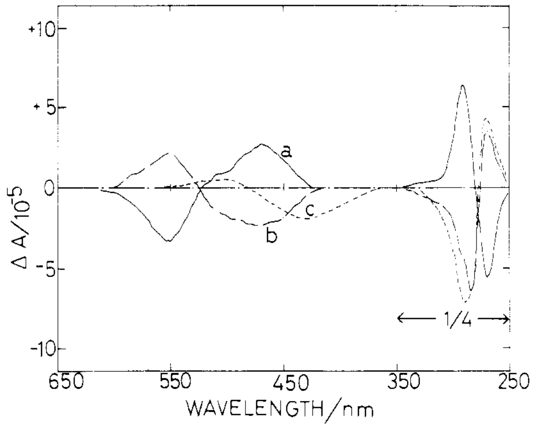

Figure 3. Circular dichroism spectra of a solution of the less retained enantiomer of $Fe(BPS)_3^{4-}$ (curve a), a solution of the more retained enantiomer of $Fe(BPS)_3^{4-}$ (curve b), and a solution of partially resolved $Fe(BP)_3^{2+}$ (curve c).

Table I. Rates of Racemization (k_R) and Dissociation (k_D) of $Fe(BSP)_3^{4-}$ in Water at Various Temperatures[a]

temp/°C	$k_R/10^{-5}$ s^{-1}	$k_D/10^{-5}$ s^{-1}
15.0	0.50	0.50
21.0	1.0	1.0
25.0	2.7	2.8
30.0	7.6	7.7
35.0	13.4	14.0

[a] Average standard error for three runs was ±0.1.

The absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The circular dichroism (CD) spectra were recorded on a JASCO J-500 spectropolarimeter. In the measurement of the absorption or CD spectra, a solution of the sample was placed in a cell thermostated at a constant temperature within an error of 0.2 °C.

Results

Resolution of Complexes. An aqueous solution of 4×10^{-7} mol $Fe(BPS)_3^{4-}$ was placed on a 4 × 0.8 cm (i.d.) column of Λ-$Ru(phen)_3^{2+}$–montmorillonite. When the complex was eluted with water, the chromatogram was obtained as shown in Figure 2. Curves a and b in Figure 3 exhibit the CD spectra of the less strongly and more strongly retained enantiomers, respectively. On the basis of the signs of the two peaks in the local excitation region of ligands (300–250 nm), the less strongly and more strongly retained enantiomers were assigned to Λ-$Fe(BPS)_3^{4-}$ and Δ-$Fe(BPS)_3^{4-}$, respectively.[9] Thus it was concluded that a diastereomeric pair of Δ-$Fe(BPS)_3^{4-}\cdot\Lambda$-$Ru(phen)_3^{2+}$ was more stable than a pair of Λ-$Fe(BPS)_3^{4+}\cdot\Lambda$-$Ru(phen)_3^{2+}$ on a clay surface. The results are analogous to the stacking between a pair of optical isomers of $M(phen)_3^{2+}$.[4]

When a 1:1 (v/v) methanol–water solution of $Fe(BP)_3^{2+}$ was placed on the same column, the complex was adsorbed so tightly that no complex was eluted with either 1:1 (v/v) methanol–water or pure methanol. Thus the resolution of $Fe(BP)_3^{2+}$ was attempted by use of colloidally dispersed clay–metal chelate adduct. A solution containing 5×10^{-7} mol of $Fe(BP)_3^{2+}$ was mixed with 1×10^{-5} mol of Δ-$Ni(phen)_3^{2+}$–montmorillonite in 10 mL of 1:1 (v/v) methanol–water. The mixture was centrifuged at 400 rps for 10 min, and the supernatant was decanted. The supernatant contained 1×10^{-7} mol of $Fe(BP)_3^{2+}$. Curve c is the CD spectrum of the solution, indicating that the solution contained Δ-$Fe(BP)_3^{2+}$ as an excess enantiomer. Thus $Fe(BP)_3^{2+}$ exhibited an adsorptive trend similar to that of optically active $M(phen)_3^{2+}$ as $Fe(BPS)_3^{4-}$ and $Fe(phen)_3^{2+}$ on a clay surface.

Kinetic Results. Racemization rates of partially resolved $Fe(BP)_3^{2+}$ and $Fe(BPS)_3^{4-}$ were measured by following the decrease of the CD amplitudes (θ) at 550 nm with time. Unimolecular

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Table II. Rates of Racemization (k_R) and Dissociation (k_D) of $Fe(BPS)_3^{4-}$ in Various Methanol-Water Solvents at 21.0 °C[a]

mol % of methanol	$k_R/10^{-5}$ s^{-1}	$k_D/10^{-5}$ s^{-1}
0	1.0	1.0
21	1.2	0.84
35	1.7	0.56
55	3.0	0.56

[a] Average standard error for three runs was ±0.1.

Table III. Comparison of Racemization (k_R) and Dissociation (k_D) Rates of $Fe(phen)_3^{2+}$, $Fe(BP)_3^{2+}$, and $Fe(BPS)_3^{4-}$ in 35 mol % of Methanol Solvent at 21 °C[a]

complex	$k_R/10^{-5}$ s^{-1}	$k_D/10^{-5}$ s^{-1}	k_R/k_D
$Fe(phen)_3^{2+}$	51.0	420	8.2
$Fe(BP)_3^{2+}$	14.0	3.4	4.1
$Fe(BPS)_3^{4-}$	1.7	0.56	3.0

[a] Average standard error for three runs was ±0.1.

rate constants (k_R) were obtained from the slopes (m) of straight lines when log θ was plotted against time according to the relation, $k_R = -2.30m$.

Ligand dissociation rates (k_D) were measured by following the decrease of the absorbance (A) of the electronic spectra at 500 nm. In these cases, the sample solutions contained 2.0×10^{-4} M of $Ni(ClO_4)_2$. Unimolecular rate constants (k_D) were obtained in a manner similar to that used for k_R. No other salts were added to the sample solution.

Table I lists the results of k_R and k_D for $Fe(BPS)_3^{4-}$ in water at various temperatures. Each value was the average of three runs. It is seen that k_R is identical with k_D within experimental error. From the temperature dependences of k_R and k_D, the activation parameters were obtained as $\Delta H^\ddagger = 130$ (±20) kJ mol^{-1} and $\Delta S^\ddagger = 90$ (±15) J K^{-1} mol^{-1}.

Table II gives the results of k_R and k_D for $Fe(BPS)_3^{4-}$ in various mixtures of methanol and water at 21 °C. It is deduced that k_R increases with the increase of the mole fraction of methanol, while k_D exhibits the reverse tendency. As a result, the ratio of k_R to k_D increases from unity in water to 5.3 at 55 mol % of methanol.

Table III compares k_R and k_D among three complexes, $Fe(phen)_3^{2+}$, $Fe(BP)_3^{2+}$, and $Fe(BPS)_3^{4-}$ in a solvent containing 35 mol % of methanol at 21 °C. It is notable that the ratio of k_R to k_D is the highest for $Fe(phen)_3^{2+}$ among the investigated complexes.

Discussion

A most important observation in this study is that k_R and k_D are identical for $Fe(BPS)_3^{4-}$ in water at 15–35 °C, leading to the same activation parameters: $\Delta H^\ddagger = 130$ KJ mol^{-1}; $\Delta S^\ddagger = 90$ J K^{-1} mol^{-1}. The results imply that $Fe(BPS)_3^{4-}$ racemizes exclusively by way of a dissociation path (1). The situation is in contrast with what has been observed for the racemization of $Fe(phen)_3^{2+}$. $Fe(phen)_3^{2+}$ racemizes by an intramolecular path (2) nearly 90% of the time in the same temperature range.[2]

It is also notable that k_R and k_D are affected by the methanol content of methanol–water solvent in quite different ways. k_R increases with the increase of methanol fraction, while k_D exhibits the reverse tendency (Table II). The results mean that the intramolecular path becomes predominant in a methanol-rich solvent.

For $Fe(phen)_3^{2+}$ in methanol–water mixtures, both k_R and k_D increase sharply with the increase of methanol fraction until the mole fraction of methanol attains 0.8.[2] The effect of methanol on $Fe(phen)_3^{2+}$ has been previously interpreted in terms of the van der Waals type of solvation around the phenanthroline ligands of the complex cation in the activated state.[2] In an intramolecular racemization (2), an activated intermediate, $M(phen)_3^{2+*}$, lengthens the metal–ligand bonds and so results in more exposure of the ligands to the solvent. On the basis of solubility experiments, phenanthroline is more soluble in methanol than in water, indicating that the molecule is specifically solvated by methanol in methanol–water mixtures.[10] Solvation by methanol may be due to the van der Waals interaction between methanol molecules and the aromatic planes of phenanthroline molecules. Such solvation by methanol molecules takes place to a higher degree in the activated state than in the ground state, leading to the lowering of the free energy of activation of intramolecular racemization. In the dissocation (1), a similar type of solvation by methanol will occur around the phenanthroline ligand that is released from $Fe(phen)_3^{2+}$ to lower the free energy of activation for the dissociation of the ligand. Accordingly, both k_R and k_D are predicted to increase with the increase of methanol content, as observed experimentally.

If the methanol effects between k_R and k_D of $Fe(BPS)_3^{4-}$ are compared, it is apparent that the solvent molecules affect the solvation structures of $Fe(BPS)_3^{4-}$ differently as shown by the racemization and dissociation reactions. In the dissociation of a ligand, negatively charged BPS^{2-} is released from $Fe(BPS)_3^{4-}$. In the activated state, BPS^{2-} is apart from $Fe(BPS)_2^{2-}$ on the assumption of a dissociative mechanism.[3] In the solvation of such an activated state, the van der Waals type of solvation is not considered to be dominant, but the electrostatic solvation due to ion–dipole interaction around released BPS^{2-} will be a main factor in stabilizing the transition state. On this basis, water molecules will be more effective than methanol molecules in solvating dissociated BPS^{2-} with their large dipole moments. Accordingly, the increase of methanol content in methanol–water solvents may result in an increase of activation free energy of dissociation, which is consistent with the observed trend for k_D in Table II.

In the intramolecular racemization process, no free BPS^{2-} ligand is produced, but the complex, $Fe(BPS)_3^{4-}$, is expanded uniformly in the activated state. Within the framework of electrostatics, such expansion of a charged molecule would not affect the external electric field outside the molecule. Accordingly dielectric solvation by water molecules is not considered to be a main factor in determining the magnitude of the activation free energy of intramolecular racemization. Instead, the solvation of the aromatic planes of the BPS^{2-} ligands will be more important since the ligands become more exposed to solvent in the expanded state of $Fe(BPS)_3^{4-}$. Under the expansion of the complex in the activated state, the pocket surrounded by the ligands is wider, allowing the solvent molecules to solvate the aromatic planes of the ligands. Since the methanol molecules are more effective in such kinds of solvation, the transition state of intramolecular racemization will be more stabilized with the increase of methanol content. This expectation agrees with the observed effect of methanol on k_R (Table II).

Among the three kinds of complexes, $Fe(phen)_3^{2+}$, $Fe(BP)_3^{2+}$ and $Fe(BPS)_3^{4-}$, $Fe(phen)_3^{2+}$ has the highest value of the ratio of k_R/k_D at 21.0 °C in a solvent of 35 mol % of methanol. In other words, the ratio of the contribution of the intramolecular process to racemization is the highest for this complex. Most probably, when the rate of intramolecular configurational change is compared among these molecules, the rate is the highest for the complex that possesses the least bulky ligands.

Registry No. $Fe(BPS)_3^{4-}$, 68516-45-0; Δ-$Fe(BPS)_3^{4-}$, 99437-00-0; Λ-$Fe(BPS)_3^{4-}$, 99436-39-2; $Fe(phen)_3^{2+}$, 14708-99-7; $Fe(BP)_3^{2+}$, 21412-03-3.

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