$(NO)](PF_6)_3$, 61303-15-9; $Ru(bpy)_2(PPh_3)(NO)^{3+}$, 72378-55-3; $Ru(bpy)_2(pyr)(NO)^{3+}$, 72378-56-4; $Ru(bpy)_2(NH_3)(NO)^{3+}$, 54866-01-2; $Ru(bpy)_2Cl(NO)^{2+}$, 31847-83-3; $Ru(bpy)_2(PPh_3)(NO)^{2+}$, 72378-57-5; $Ru(bpy)_2(CH_3CN)(NO)^{2+}$, 54866-05-6; $Ru(bpy)_2(pyr)(NO)^{2+}$, 72378-58-6; $Ru(bpy)_2(py)(NO)^{2+}$, 72378-59-7; $Ru(bpy)_2(NH_3)(NO)^{2+}$, 72378-60-0; $Ru(bpy)_2Cl(NO)^+$, 54866-04-05; $[Ru(bpy)_2(NO_3)Cl]Cl$, 72402-34-7; $Ru(bpy)_2(PPh_3)(NO_3)^{2+}$, 72378-61-1; $Ru(bpy)_2(CH_3CN)(NO_3)^{2+}$, 72378-62-2; $Ru(bpy)_2$-$(pyr)(NO_3)^{2+}$, 72390-14-8; $Ru(bpy)_2(py)(NO_3)^{2+}$, 72402-35-8; $Ru(bpy)_2(NH_3)(NO_3)^{2+}$, 72378-63-3; $[Ru(bpy)_2(py)(NO_3)]PF_6$, 72378-65-5; $Ru(bpy)_2(PPh_3)(NO_3)^+$, 72378-66-6; $Ru(bpy)_2$-$(CH_3CN)(NO_3)^+$, 72378-67-7; $Ru(bpy)_2(pyr)(NO_3)^+$, 72390-12-6; $Ru(bpy)_2(NH_3)(NO_3)^+$, 72378-68-8; $Ru(bpy)_2Cl(NO_3)$, 72390-13-7; $[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$, 58575-13-6; $Ru(bpy)_2(NO_2)_2$, 29241-01-8; $Ru(bpy)_2(NO_2)Cl$, 34398-51-1; $[Fe(bpy)_3](PF_6)_2$, 70811-29-9; $[Fe(bpy)_3](PF_6)_3$, 28190-88-7; $Ru(bpy)_3^{3+}$, 18955-01-6.

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Effect of Lattice Anions on the Racemization of Optically Active Metal Chelate Salts in the Solid State. 1.[1] [Fe(phen)₃]X₂, [Fe(bpy)₃]X₂, [Ni(phen)₃]X₂, and [Ni(bpy)₃]X₂, Where X⁻ = Cl⁻, Br⁻, I⁻, or ClO₄⁻

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The kinetics of racemization of the anhydrous complexes $(+)$-$[Fe(phen)_3]X_2$, $(+)$-$[Fe(bpy)_3]X_2$, $(-)$-$[Ni(phen)_3]X_2$, and $(-)$-$[Ni(bpy)_3]X_2$, where phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, and $X^- = Cl^-$, Br^-, I^-, or ClO_4^-, have been studied in the solid state. The halide salts of the complexes were found to undergo a very rapid initial loss of optical activity and subsequently to racemize at a lower rate. The former process has been assigned to a process enhanced by lattice defects and the latter to a first-order process with respect to the complex. Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined for the first-order racemization. A similarity between the racemization mechanisms of the phenanthroline and bipyridine complexes of nickel was noted in terms of an isokinetic relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. $\Delta H^{\ddagger}$ values for all the iron complexes were found to be identical, whereas those for the nickel complexes decrease with the lattice anion in the order $X^- = ClO_4^- > I^- > Br^- > Cl^-$. Temperatures at which thermal decomposition of the complexes takes place were determined by both thermogravimetric and differential thermal analysis methods. The results for the nickel complexes showed the temperatures to be linearly related to the $\Delta H^{\ddagger}$ values and the thermal decomposition and racemization processes to be related by the donicity of lattice anions. Different racemization mechanisms involving a 7-coordinate and a trigonal-prismatic intermediate are proposed for the nickel and iron complexes, respectively, and are consistent with the different effects of lattice anions in the kinetic data between them. A retarding effect of lattice water on the rate of racemization was observed.

Introduction

From the results of kinetics studies it was concluded that the major path for racemization of the $[Fe(phen)_3]^{2+}$ ion in aqueous media[2] and various solvent systems[3] is an intramolecular process. The intramolecular mechanism has been thought to proceed by a twisting process.[2,4] It was suggested originally that racemization of $[Ni(phen)_3]^{2+}$ and $[Ni(bpy)_3]^{2+}$ occurred by an intramolecular process.[5] However, later measurements of racemization and dissociation rates showed that both the rates were experimentally the same in aqueous solution, indicating racemization by dissociation.[6,7] In nonaqueous solvents, exchange rates were also shown to be the same as the rates of racemization in the same solvent system;[7] a dissociative intermolecular mechanism is believed to be operative in the various solvents used.[8,9]

Solvent effects on the racemization of the nickel complexes could not be related to the solvent viscosity or to the dielectric constant of the solvent.[5,8,10] We reported that the rates of racemization of $[Ni(phen)_3]^{2+}$ in various solvents are related to Gutmann's donor number of the solvents and that this can be accounted for by a process involving encounter between the complex ion and a solvent molecule and the subsequent formation of a 7-coordinate intermediate with the solvent molecule followed by a rapid dissociation process.[11] Moreover, we showed that the racemization of the complex ion is accelerated by the pairing of the complex ion with a counteranion in water–*t*-BuOH mixtures (the mole fraction of *t*-BuOH > 0.5) and the rates increase with the anion in the order $ClO_4^- < I^- < Br^- < Cl^-$.[12] The dependence of the rates on the anions might arise from the donicity of anions, although the anions are solvated by water and *t*-BuOH. In order to explore this possibility, we have investigated the effect of lattice anions of the solid-state racemization of a series of anhydrous halide

Table I. Elemental Analysis

compd	% calcd			% found		
	C	H	N	C	H	N
$(+)$-$[Fe(phen)_3]Br_2 \cdot 6H_2O$	50.02	4.20	9.72	49.99	4.41	9.52
$(+)$-$[Fe(phen)_3]I_2 \cdot 3H_2O$	47.81	3.34	9.29	48.07	3.29	9.20
$(+)$-$[Fe(bpy)_3]Br_2 \cdot 6H_2O$	45.48	4.58	10.61	44.69	4.81	10.42
$(+)$-$[Fe(bpy)_3]I_2 \cdot 5H_2O$	41.50	3.95	9.68	41.35	4.16	9.97
$(-)$-$[Ni(phen)_3]I_2 \cdot 4H_2O$	46.74	3.49	9.08	46.17	3.54	8.99
$(-)$-$[Ni(bpy)_3]Cl_2 \cdot 6H_2O$	51.02	5.14	11.90	47.49	5.18	11.36
$(-)$-$[Ni(bpy)_3]Br_2 \cdot 6H_2O$	45.31	4.56	10.57	44.93	4.57	10.07
$(-)$-$[Ni(bpy)_3]I_2 \cdot 6H_2O$	40.52	4.08	9.45	40.70	4.04	9.60

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Table II. Rate Constants of the Solid-State Racemization

	T, °C	$10^5 k$, s^{-1}		T, °C	$10^5 k$, s^{-1}
(+)-[Fe(phen)$_3$]I$_2$	131	0.175 ± 0.003	(−)-[Ni(phen)$_3$]I$_2$	185	0.88 ± 0.05
	140	0.540 ± 0.007		189	1.29 ± 0.02
	150	1.89 ± 0.03		190	1.76 ± 0.04
(+)-[Fe(phen)$_3$]Br$_2$	79	0.17 ± 0.01		194	2.66 ± 0.12
	83	0.33 ± 0.02		198	3.83 ± 0.06
	86	0.51 ± 0.06	(−)-[Ni(bpy)$_3$]I$_2$	156	1.52 ± 0.03
	89	0.87 ± 0.03		160	2.51 ± 0.11
(+)-[Fe(bpy)$_3$]I$_2$	115	0.14 ± 0.01		165	3.93 ± 0.23
	120	0.41 ± 0.03	(−)-[Ni(bpy)$_3$]Br$_2$	124	0.027 ± 0.004
	125	0.69 ± 0.10		134	0.056 ± 0.004
(+)-[Fe(bpy)$_3$]Br$_2$	100	0.261 ± 0.006		138	0.113 ± 0.016
	105	0.556 ± 0.016	(−)-[Ni(bpy)$_3$]Cl$_2$	88	0.030 ± 0.006
	110	1.12 ± 0.04		95	0.039 ± 0.005
	115	2.47 ± 0.12		104	0.056 ± 0.010
				108	0.061 ± 0.015

salts of [Ni(phen)$_3$]$^{2+}$ and [Ni(bpy)$_3$]$^{2+}$. Since lattice anions are in contact with the complex cations, they are expected to affect activation parameters for the racemization of the complexes in the solid state as observed for ion pairs in the above lower dielectric constant media. The kinetics of racemization of anhydrous halide salts of the corresponding iron complexes in the solid state have also been studied here for comparison.

Our previous study[13] found that the perchlorates of the iron and nickel complexes in the solid state racemize in a short period after dehydration by heating, although at room temperature the solids do not lose their optical activity for several months.[14] In this paper, we report that change in the donicity of lattice anions changes systematically the values of $\Delta H^{\ddagger}$ for the solid-state racemization of the nickel complex salts whereas no change in $\Delta H^{\ddagger}$ for that of the iron complex salts is observed. The results indicate that the donicity of the anions is an important factor in lowering $\Delta H^{\ddagger}$ for the nickel complex salts.

Experimental Section

Materials. The optically active complex salts (+)-[Fe(phen)$_3$]I$_2$·3H$_2$O, (+)-[Fe(phen)$_3$]Br$_2$·6H$_2$O, (+)-[Fe(bpy)$_3$]I$_2$·5H$_2$O, (+)-[Fe(bpy)$_3$]Br$_2$·6H$_2$O, (−)-[Ni(bpy)$_3$]I$_2$·6H$_2$O, (−)-[Ni(bpy)$_3$]-Br$_2$·6H$_2$O, and (−)-[Ni(bpy)$_3$]Cl$_2$·6H$_2$O were prepared and resolved following the procedures of Dwyer and Gyarfas.[14,15] The preparation and resolution of (−)-[Ni(phen)$_3$]I$_2$·4H$_2$O were carried out according to the method of Kauffman and Takahashi.[16] Potassium antimonyl-(+)-tartrate was used as the resolving agent for these complexes. The magnitude of the heat effects on changes in optical activity made it unnecessary to resort to materials of highest optical purity. Elemental analyses of the complexes are shown in Table I. All the complexes were powdered by grinding with a mortar and pestle to pass a 200-mesh sieve. The anhydrous complexes were prepared by drying the hydrates in a vacuum desiccator over phosphorus pentoxide at room temperature for a few days.

Measurements. The optical rotations of the iron and nickel complexes were measured at 520 and 365 nm by using a Perkin-Elmer Model 141 polarimeter with W and Hg lamps and 2-cm and 1-dm cells, respectively. These cells were water jacketed with a water-circulating thermostat which holds the cell temperature constant within ±0.2 °C. The concentration of the complexes was determined spectrophotometrically by using a Hitachi Perkin-Elmer Model 139 UV–vis spectrophotometer. The wavelengths and molar extinction of absorption maximums employed are as follows: 510 nm and 1.11 × 10^4 mol^{-1} dm^3 cm^{-1} for [Fe(phen)$_3$]$^{2+}$; 522 nm and 8.65 × 10^3 mol^{-1} dm^3 cm^{-1} for [Fe(bpy)$_3$]$^{2+}$; 267.5 nm and 8.47 × 10^4 mol^{-1} dm^3 cm^{-1} for [Ni(phen)$_3$]$^{2+}$; 295 nm and 4.10 × 10^4 mol^{-1} dm^3 cm^{-1} for [Ni(bpy)$_3$]$^{2+}$. Within experimental uncertainties, the specific rotations of aqueous solutions of the complexes were independent of concentration. The concentration of complexes was 10^{-4}–10^{-5} mol dm^{-3}, as this concentration range afforded the most convenient readings of the
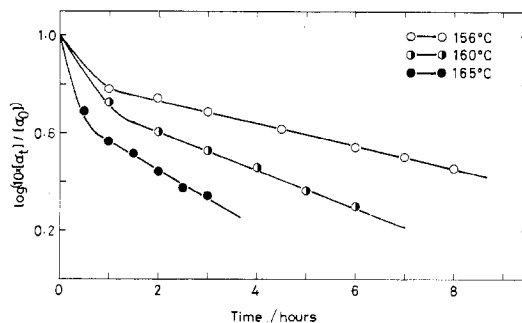
(13) A. Tatehata, T. Kumamaru, and Y. Yamamoto, *J. Inorg. Nucl. Chem.*, **33**, 3427 (1971).
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Figure 1. Racemization of (−)-[Ni(bpy)$_3$]I$_2$.

optical rotations. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out with a Rigaku thermal analyzer, Model 8001. Samples (0.01–0.02 g) of the hydrates were used. A heating rate of 5°/min and a static air atmosphere were employed in each run.

Procedure. Solid samples (0.005–0.007 g) of the anhydrous complexes were placed in NMR tubes (5 mm in diameter, 5 cm in length) and preserved in a desiccator over P$_2$O$_5$. The furnace was a block of metal, containing 10 small vertically drilled wells into which the sample tubes could be placed upright. The temperature-regulation device used here ensured constancy to within ±0.5 °C for the furnace. At timed intervals the samples were taken out of the heating apparatus and cooled rapidly. The optical rotation of each sample was then measured in triplicate on aqueous solutions in the conventional manner. These results have a precision of better than 5%. Due to the rapid rate of racemization of [Fe(phen)$_3$]$^{2+}$, [Fe(bpy)$_3$]$^{2+}$, and [Ni(bpy)$_3$]$^{2+}$ in water, normal polarimetry techniques could not be used. It was necessary to take readings of the optical rotation at timed intervals. A least-squares line through a plot of ln α_{obsd} vs. time data was extrapolated to zero time to obtain the correct value for α_{obsd}.

Results

Racemization Studies. The typical results of the loss of optical activity for (−)-[Ni(bpy)$_3$]I$_2$ at various temperatures in the solid state are illustrated in Figure 1; the data are plotted as log (10[α_t]/[α_0]) vs. time, where [α_t] is the specific rotation at time t and [α_0] is the specific rotation at time zero. A very rapid initial loss of optical activity occurs; heating the complex increases the extent of the initial racemization roughly in proportion to the temperature. Subsequently, the complex racemizes more slowly according to a first-order process with respect to the complex cation. Similar characteristics are exhibited by all the solid samples used here, except for the samples of (−)-[Ni(phen)$_3$]I$_2$ which show an induction period between the former initial racemization process and the latter first-order process as shown in Figure 2. The relationship log [α_t] = log [α_0^f] − (2k/2.303)t was applied to the latter racemization process which exhibits first-order kinetics, where k is the rate constant in s^{-1} for the conversion of one antipodal form to the other and [α_0^f] is the value which was obtained from the first-order kinetic run by extrapolating a least-squares
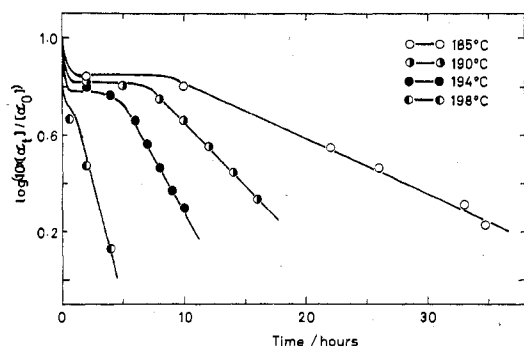
Figure 2. Racemization of (-)-[Ni(phen)$_3$]I$_2$.

Table III. Kinetic Parameters for the Solid-State Racemization of Iron and Nickel Complexes with Thermal Stability

compd	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	T_d,[a] °C
(+)-[Fe(phen)$_3$]Br$_2$	178 ± 10	148 ± 29	195[c]
(+)-[Fe(phen)$_3$]I$_2$	174 ± 3	73 ± 8	240[c]
(+)-[Fe(phen)$_3$](ClO$_4$)$_2$[b]	176 ± 16	71 ± 8	
(+)-[Fe(bpy)$_3$]Br$_2$	173 ± 4	110 ± 9	170
(+)-[Fe(bpy)$_3$]I$_2$	187 ± 14	125 ± 35	180
(+)-[Fe(bpy)$_3$](ClO$_4$)$_2$[b]	184 ± 16	109 ± 12	
(-)-[Ni(phen)$_3$]I$_2$	203 ± 4	99 ± 8	270[c]
(+)-[Ni(phen)$_3$](ClO$_4$)$_2$[b]	268 ± 36	243 ± 20	
(-)-[Ni(bpy)$_3$]Cl$_2$	49 ± 18	-239 ± 47	125
(-)-[Ni(bpy)$_3$]Br$_2$	120 ± 11	-71 ± 28	200
(-)-[Ni(bpy)$_3$]I$_2$	153 ± 4	18 ± 10	225
(+)-[Ni(bpy)$_3$](ClO$_4$)$_2$[b]	205 ± 12	109 ± 8	

[a] T_d = the temperature at which the sample begins to dissociate or decompose in a static atmosphere. [b] Data from ref 6. [c] Data from ref 13.

line through a plot of log [α_t] vs. time back to zero time. The rate constants are presented in Table II. The errors are the standard derivations estimated from the residuals of the least-squares line for each run. Table II shows that there is a wider variation in the rate constants for the nickel complexes than for the iron complexes in changing of lattice anions.

Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, calculated on the assumption that the Eyring equation

$$k = (RT/Nh)[\exp(\Delta S^{\ddagger}/R)][\exp(-\Delta H^{\ddagger}/RT)]$$

is valid, are given in Table III. Estimates of error for the activation parameters are one standard deviation. It was found that $\Delta H^{\ddagger}$ values for all the iron complexes are identical (to within experimental error), whereas those for the nickel complexes decrease in the order X$^-$ = ClO$_4^-$ > I$^-$ > Br$^-$ > Cl$^-$. Plots of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for the nickel complexes show a good linear relationship, as shown in Figure 3, together with data for the perchlorates;[13] the slope is known as the isokinetic temperature,[17] ca. 190 °C.

Dehydration and Decomposition Studies. A TGA run on all the hydrated complexes in static air reveals that dehydration occurs in a single step commencing at 30–40 °C and is almost complete at 90–100 °C. The lattice water is also removed completely in a few days at room temperature by vacuum desiccation over P$_2$O$_5$. The dehydration was accompanied by slight color changes. After dehydration, no further changes are evident. When those anhydrous crystals are allowed to stand in contact with air, they return to their original hydrate color, without any appreciable racemization. These observations reveal that the loss of lattice water is accompanied by the physical modification of the crystal lattice.[18,19] In addition,
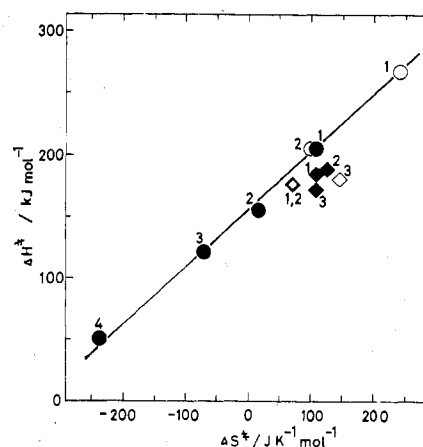

Figure 3. Isokinetic plots for racemization of [Fe(phen)$_3$]X$_2$ (◊), [Fe(bpy)$_3$]X$_2$ (♦), [Ni(phen)$_3$]X$_2$ (○), and [Ni(bpy)$_3$]X$_2$ (●), where X$^-$ = ClO$_4^-$ (1), I$^-$ (2), Br$^-$ (3), and Cl$^-$ (4).
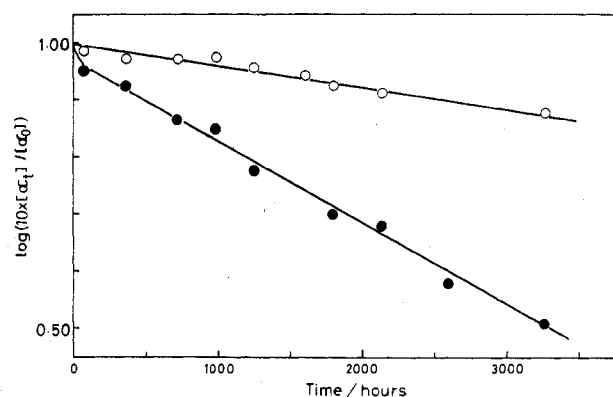

Figure 4. Racemization of hydrated and anhydrous samples at room temperature: (+)-[Fe(phen)$_3$]Br$_2$·6H$_2$O in a static air (○) and (+)-[Fe(phen)$_3$]Br$_2$ in a desiccator over P$_2$O$_5$ (●).

the anhydrous salt of [Fe(phen)$_3$]Br$_2$ preserved in a desiccator over P$_2$O$_5$ at room temperature undergoes rapid racemization compared with the corresponding hydrate allowed to stand under the circumstances of the same temperature and a constant humidity, as shown in Figure 4.

Temperatures (T_d) at which the following thermal decomposition of complexes occurs, resulting in weight loss, are given in Table III, together with the results of our previous study:[20]

$$[ML_3]X_2(s) \rightarrow ML_2X_2(s) + L(g)$$
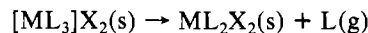
where M is iron or nickel, L is the phenanthroline or bipyridine ligand, and s and g indicate the solid and gaseous states, respectively. Over the temperature ranges where the most convenient rates of racemization were afforded for the kinetic studies, TGA and DTA confirmed the absence of thermal decomposition, and no color changes offered evidence for no change in chemical combination.

Discussion

All runs with anhydrous halide salts of the complexes have the common characteristic of an initial period during which optical activity loss is very rapid, followed by a first-order racemization process (Figure 1). Similar behavior has also been reported for the solid-state racemization of [Co-

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(18) It proved impossible to obtain X-ray powder photographs of the anhydrous complexes, due to extensive cracking upon dehydration, although X-ray analysis is needed for each of the hydrated and anhydrous complexes to understand fully this physical modification of the crystal lattices.

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(en)$_3$]X$_3$·nH$_2$O by Kutal and Bailar.[21] Moreover, they showed that the loss of lattice water is accompanied by extensive cracking. This indicates the introduction of a large number of defects into the solid.[21] In the present case, the color changes resulting from the loss of lattice water suggest the production of defects during the preparation of anhydrous complexes. Since the complex ions near a defect are known to experience enhanced reactivity,[22] their inversion is expected to be rapid. The disrupted lattice formed upon dehydration becomes more ordered in annealing. This process would decrease the number of lattice defects with a consequent reduction in the rate of racemization. Therefore the accelerating effect continues until defects are completely annealed. We found further racemization to be effected at a lower rate by the remaining optically active ions (Figure 1), obeying a first-order rate expression as predicted in another paper.[21] Such behavior has been also reported for the racemization of K$_3$[(+)-Cr(C$_2$O$_4$)$_3$].[23]

The induction period observed for (−)-[Ni(phen)$_3$]I$_2$ evidently divides the former initial racemization process from the latter first-order process (Figure 2). This period seems to be ascribed to the crystal lattice rearrangement process which provides nuclei for further racemization, as pointed out by Chowdhury and Harris.[23] Once nucleation is complete, a constant rate of further reaction is achieved. For other complexes used here, such a period may be too short to be appreciable. Although this period should be related to the unique specificity of the crystal lattice of the complex salt, it was not investigated further in this study, and so our attention is focused on the first-order racemization process as follows.

A linear dependence of $\Delta S^\ddagger$ on $\Delta H^\ddagger$ is observed with the same slope for all the bipyridine complexes of nickel (Figure 3; the isokinetic temperature is ca. 190 °C[24]). The linearity can be taken to imply a qualitative similarity of mechanism along the series. Data for the phenanthroline complexes of nickel lie at the upper end of the isokinetic plot for the bipyridine complexes; this fit, although it might be quite coincidental, could be taken as evidence for the operation of a similar mechanism in both sets of nickel complexes. On the other hand data for all the iron complexes fall below the isokinetic line in Figure 3. Therefore, the racemization mechanism of the nickel complexes should be different from that of the iron complexes.

A dissociation mechanism proposed already for solutions cannot operate in the solid state due to the absence of solvents required for dissolution of a released ligand, and thus an intramolecular mechanism is assumed to be available. The simplest intramolecular mechanism assumes a twisting process.[25] The pressure dependence of the rate of racemization of [Fe(phen)$_3$](ClO$_4$)$_2$ and [Ni(phen)$_3$](ClO$_4$)$_2$ in the solid state suggested that the trigonal prismatic structure is most likely for the activated complex of both the complexes.[26] If such a trigonal-twist mechanism is operative in the solid state, racemization should be independent of the donicity of lattice anions. This is corroborated by the present data on $\Delta H^\ddagger$ for

the iron complexes. Table III shows that for the iron complex alterations of the lattice anion leave $\Delta H^\ddagger$ unaltered within experimental error. The $\Delta H^\ddagger$ values are larger than those for racemization in solutions. This result is reasonable since an increase in $\Delta H^\ddagger$ is probably large due to the absence of solvation of the aromatic ligands as suggested by Van Meter and Neumann.[3] In addition, large positive $\Delta S^\ddagger$ values, inconsistent with the expected negative $\Delta S^\ddagger$ value for a twist mechanism, were found for the iron complexes in the solid state (Table III) as in aqueous solution[2] (+88 J K^{-1} mol^{-1}). Such a large positive entropy of activation can be accommodated in a twist mechanism since an Fe–N bond expansion,[27] spin excitation to a high-spin state, and twisting motion[28] could all occur simultaneously. A recent paper[29] has some evidence about the proposed spin change.

It was pointed out that known trigonal-prismatic complexes have a side to height ratio (s:h) of 1.00[30] as observed with the trigonal-prismatic tris(dithiolene) complexes of Re, Mo, and V.[31] In addition, valence-bond theory led to the conclusion[32] that bonding in a trigonal prism (TP) should be strongest when the TP has square sides. The ratios for TP intermediates derived from tris(phenanthroline) complexes of iron and nickel are calculated to be 0.98 and 1.04, respectively, from the structural data reported for them,[33] on the assumption that the bite distances and angles are the same in the TP as in the ground-state trigonal-antiprismatic configuration. Both the values are quite close to the ratio cited for the above stable trigonal-prismatic complexes. Moreover, the bipyridine complexes of these metals may possess a geometry similar to that of the corresponding phenanthroline complexes. Thereby, such a trigonal-twist mechanism is assumed to be more available for the complexes used here. By a ^{1}H NMR method, a trigonal-twist mechanism has been recently determined for tris-(α-(R)-tropolonato)metal(III, IV) complexes[34] which have the same ratios as cited for the TP. However, the mechanism has also been shown to occur in tris(dithiocarbamato)metal complexes which do not possess a geometry similar to that of the phenanthroline or α-(R)-tropolonato complexes.[35]

On the other hand, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the nickel complexes were found to be altered by alteration of lattice anions (Table III), which indicated the interaction of the complex cations with the anions in the transition state. The results are considered in terms of a mechanism involving expansion of a complex cation to a 7-coordinate intermediate with one lattice anion, for example a capped trigonal prism as presented by Kepert.[36] The intermediate must be the same as proposed in our previous paper for lower dielectric constant media,[12] and in that case the mechanism should be controlled by the

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(25) Three twisting mechanisms have been suggested for the intramolecular racemization of octahedral complexes. These mechanisms and their relation to one another have recently been reviewed: N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
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(27) Ligand–ligand repulsion energies for complexes of the type [M(bidentate)$_3$]$^{x+}$ have been calculated to show that a significant expansion of the complex (lengthening of the Fe–N bonds) is necessary to lower the barrier to racemization by a twisting process: D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).
(28) The $\Delta S^\ddagger$ values are slightly different on changing the lattice anion, which may be related to small differences in an effective space required for twisting motions of the three chelate rings of, especially, the phenanthroline complexes owing to the rigid nature of the ligand.
(29) G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, **17**, 1804 (1978).
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donicity of the anion in the same manner. Table III shows that the $\Delta H^{\ddagger}$ values decrease with the anion in the order ClO_4^- > I^- > Br^- > Cl^-. The trend in $\Delta H^{\ddagger}$ may be attributed to the donicity of the anions[37] to stabilize the intermediate. In such a mechanism, a metal–anion distance will shorten with lengthening of metal–nitrogen bonds. The interaction of the anion with the metal leads to the stability of the intermediate and thus to a lower energy of activation for racemization. Moreover, this leads to a decrease in the degree of freedom of the lattice anion "frozen" in the intermediate, although in any case the degree of freedom of a ligand molecule should be increased somewhat by an expansion of the complex (lengthening of the Ni–N bonds) which is necessary to satisfy the steric requirements.[29,36] Thus, the stronger binding of the anion to the metal leads to a smaller entropy of activation, which is consistent with the decrease in $\Delta S^{\ddagger}$ found as $\Delta H^{\ddagger}$ decreases (Table III).

Additional support for the suggestion described above is furnished by thermal decomposition studies of the complexes used here. T_d may be taken as a measure of the strength of metal–anion bonds in thermal decomposition products. The nucleophilicities of lattice anions toward the complex cations are, in fact, related to the T_d of complexes; an increase in the donicity of the anion lowers T_d (Table III). The nature of the metal–anion interaction in the transition state for the racemization process is assumed to be similar to that for the decomposition process. Since a comparison of the racemization and decomposition reactions of the nickel complexes shows those processes to be related by the donicity of the anions, it is reasonable that the trend is a decrease in T_d as $\Delta H^{\ddagger}$ decreases (Table III). On the other hand, it is noted that for the iron complexes T_d is altered in the same way by the alteration of the donicity of anions whereas $\Delta H^{\ddagger}$ for the racemization is not altered; $\Delta H^{\ddagger}$ is independent of T_d (Table III). This indicates that the transition state for the racemization process should be different from that for the decomposition process and is consistent with the operation of a twist mechanism for the racemization of the iron complexes.

Table III also shows that $\Delta H^{\ddagger}$ for the bipyridine complexes of nickel is lower than that for the corresponding phenanthroline complexes (for example, the iodides or perchlorates). This can be accounted for on the basis of two aspects as follows, providing strong support for the model proposed above. First, the phenanthroline complexes have a larger ligand field stabilization energy than the bipyridine complexes.[38] Thus, the enthalpy required to expand the phenanthroline complexes compared with the bipyridine complexes is larger. Second, the more flexible bipyridine group could remove any steric hindrance to attack of a lattice anion of the metal in forming the transition state. Thus the 7-coordinate intermediate using bipyridine ligands is anticipated to be less unstable than that using phenanthroline ligands, leading to a decrease in $\Delta H^{\ddagger}$. On the other hand, this process puts restrictions on the bipyridine ligands, which are reflected in lower $\Delta S^{\ddagger}$ (Table III).

For the bipyridine complexes, it may be conceivable that the bipyridine ligand can permit one end to detach fully and move away from the positive field of the metal, readily half-bonding, and then the vacant site may be occupied by a lattice anion. However, the mechanism is regarded as quite im-

probable as follows. For the phenanthroline complexes, it is not possible to make a half-bonded intermediate using the phenanthroline ligand, since large rigid flat phenanthroline ligands impose considerable steric constraints on one-ended phenanthroline dissociation. If the mechanism for the bipyridine complexes in the solid state involves such partial dissociation, it is reasonable to expect an increase in the freedom of movement of the ligands in a half-bonded intermediate and thus larger $\Delta S^{\ddagger}$ values for the bipyridine complexes compared with the phenanthroline complexes. Contrary to this view, we found $\Delta S^{\ddagger}$ values for the bipyridine complexes of nickel to be smaller than those for the corresponding phenanthroline complexes (for example, the iodides or perchlorates given in Table III). Moreover, the mechanism involving a fully one-ended detachment of the bipyridine ligands is less likely in the solid state relative to the solution,[39] since the absence of solvation in the transition state should inhibit the breaking of the metal–donor atom bond.

The effect of water on the rates of racemization was studied for the complexes $[Co(C_2O_4)_3]^{3-}$,[40] $[Ni(phen)_3]^{2+}$,[41] and $[Fe(phen)_3]^{2+}$[42] in order to reach some conclusions concerning water-dependent paths. Furthermore, a mechanism involving the formation of covalent hydrates and related pseudobases has been proposed recently for the racemization and dissociation of tris complexes of phenanthroline and bipyridine with iron and nickel ions by Gillard et al.[43] However, we found that the presence of lattice water hinders the solid-state racemization of the bromide salt of $[Fe(phen)_3]^{2+}$ (Figure 4). A similar retarding effect of lattice water on the rates of solid-state racemization under pressure is observed for $K_3[Co(C_2O_4)_3]$[40] and $[Ni(phen)_3](ClO_4)_2$.[41] The results suggest that the covalent hydrate pseudobase mechanism is unlikely in the solid state. Furthermore, it has been pointed out that the order of nucleophile strength in attack on aromatic carbon is I^- > Br^-;[44] the carbon prefers soft bases.[45] If nucleophilic attack of halide anions on the aromatic ligand is important for the racemization, more polarizable nucleophiles such as iodide ion are expected to be more reactive to the ligand than more basic nucleophiles such as chloride ion. However, the kinetic behavior observed for the nickel complexes in the present study is contrary to this view, as shown above. From this investigation, such a mechanism involving a 7-coordinate intermediate as proposed above by us is concluded to be the most probable mechanism for the racemization of both sets of nickel complexes in the solid state. This mechanism is also available to interpret medium effects on the racemization of the nickel complexes, as pointed out by us.[11,12] Further research on other complexes is required in order to understand fully the features of the racemization mechanism which might be favored in the solid state.

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