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## Volumes of Activation for Racemization and Aquation of Tris(1,10-phenanthroline) Complexes of Nickel(II) and Iron(II) in Solution

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The effect of high pressure on the rates of racemization and aquation of  $\text{Ni}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{2+}$  (phen = 1,10-phenanthroline) in solution has been evaluated. Reactions of  $\text{Fe}(\text{phen})_3^{2+}$  exhibit a significant retardation upon the application of pressure, with volumes of activation ( $\Delta V^\ddagger$ ) of +14.2 and +15.6  $\text{cm}^3 \text{mol}^{-1}$  for racemization in 0.01 and 1.0 M aqueous HCl, respectively, while aquation in 1.0 M aqueous HCl exhibits a  $\Delta V^\ddagger$  of +15.4  $\text{cm}^3 \text{mol}^{-1}$ . Possible mechanisms are considered, and a positive contribution to  $\Delta V^\ddagger$  from excitation to a high-spin transition state, associated with a general Fe-N bond expansion, is proposed as a component of the mechanism for aquation and racemization. Reactions of  $\text{Ni}(\text{phen})_3^{2+}$  show only a minor acceleration of rates upon the application of pressure with  $\Delta V^\ddagger = -0.4 \text{ cm}^3 \text{mol}^{-1}$  and  $\Delta V^\ddagger = -1.5 \text{ cm}^3 \text{mol}^{-1}$  for racemization in 0.01 and 1.0 M aqueous HCl, respectively, while aquation in 1.0 M aqueous HCl exhibits a  $\Delta V^\ddagger$  of -1.2  $\text{cm}^3 \text{mol}^{-1}$ . A common mechanistic pathway is favored since determined rates and enthalpies and entropies of activation as well as volumes of activation for aquation and racemization are very similar. A dissociative mechanism for release of a phen ligand with possible formation in the transition state of a high-spin four-coordinate species of reduced volume compared with the low-spin octahedral precursor is favored from analysis with  $\Delta V^\ddagger$  data.

### Introduction

The kinetics of racemization and aquation of low-spin iron(II) and of nickel(II) complexes have attracted continuing interest during recent decades.<sup>2</sup> The mechanism for aquation of  $d^6$  low-spin iron(II) complexes, while usually considered to be dissociative in nature, is not yet unequivocally established. Although low-spin  $d^6$  cobalt(III) complexes aquate via a dissociative interchange ( $I_d$ ) or dissociative (D) mechanism, the analogy cannot be readily extended to low-spin  $d^6$  iron(II) complexes. While the acid-dependent aquation of  $\text{Fe}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) is commonly explained in terms of a dissociative mechanism,<sup>3</sup> some evidence for the possible incorporation of incoming water into the transition state has been presented.<sup>4</sup> Reactivity trends for aquation in mixed aqueous solvents of  $\text{Fe}(5\text{-NO}_2\text{phen})_3^{2+}$  and  $\text{Fe}(4,7\text{-Me}_2\text{phen})_3^{2+}$  (phen = 1,10-phenanthroline) can be rationalized in terms of more associative character for the former complex.<sup>5</sup> However, the observed rate trends could equally well be rationalized in terms of variation of the degree of solvation of either the initial or transition states of a dissociative aquation mechanism. Aquation reactions of nickel(II) complexes are usually dissociative in nature, although racemization reactions proceeding by both intermolecular and intramolecular mechanisms have been assigned previously.<sup>6</sup> Racemization reactions of low-spin iron(II) complexes have generally been assigned intramolecular mechanisms.<sup>6</sup>

The determination of volumes of activation ( $\Delta V^\ddagger$ ) for aquation of several substituted phenanthroline complexes of iron(II) from high-pressure solution kinetics has been reported previously, and the large positive volumes of activation in the range +13 to +16  $\text{cm}^3 \text{mol}^{-1}$  interpreted as evidence for a dissociative mechanism.<sup>7</sup> While no volumes of activation for aquation reactions of nickel(II) have been reported, formation reactions of nickel(II) with various amine and imine ligands have been found to exhibit positive  $\Delta V^\ddagger$  values of about 7  $\text{cm}^3 \text{mol}^{-1}$ , again consistent with a dissociative mechanism.<sup>8</sup> No volumes of activation for racemization reactions of nickel(II) or iron(II) complexes have been reported previously, although we have recently reported activation volumes for racemization reactions of a series of chromium(III) complexes.<sup>9</sup>

Extensive kinetic studies of phen and bpy complexes of nickel(II) and low-spin iron(II) have been reported.<sup>2,6</sup> The rates of dissociation, racemization, and labeled phen exchange in  $\text{Ni}(\text{phen})_3^{2+}$  have been shown to be very similar,<sup>10,11</sup> providing consistent evidence for an intermolecular mechanism for racemization involving rate-determining release of a bi-

dentate phenanthroline ligand. Although exchange rates in nonaqueous solvents are the same as the rates of racemization in the same solvents for  $\text{Ni}(\text{phen})_3^{2+}$ ,<sup>11</sup> rates of racemization and associated activation parameters show a solvent dependence,<sup>12,13</sup> indicating that solvent-complex interactions may be significant.

Unlike the corresponding nickel(II) complex, the rate of racemization of  $\text{Fe}(\text{phen})_3^{2+}$  is faster than the rate of aquation and has been interpreted in terms of a predominantly intramolecular racemization mechanism.<sup>3,14-16</sup> Specific solvent effects on the rates of both aquation and racemization have been interpreted differently in terms of a dissociative mechanism for aquation and a trigonal twist mechanism for racemization.<sup>5,13-16</sup> The positive entropy of activation ( $\Delta S^\ddagger$ ) of +89  $\text{J K}^{-1} \text{mol}^{-1}$  for racemization of  $\text{Fe}(\text{phen})_3^{2+}$  is inconsistent with a twist mechanism, however, for which a negative or zero  $\Delta S^\ddagger$  is expected. This observation can be interpreted in terms of an excitation of the complex from a low-spin to a high-spin state prior to the twisting motion, which consequently leads to an expansion of the coordination sphere and hence a greater degree of freedom.<sup>17,18</sup> The volumes of activation for both racemization and aquation of  $\text{Fe}(\text{phen})_3^{2+}$  should involve a positive contribution from such a low-spin  $\rightarrow$  high-spin transition if it is operating, due to expansion of the coordination sphere. An estimation of the expected contribution to  $\Delta V^\ddagger$  from this effect is deferred to the Discussion.

The high-spin  $d^8$  nickel(II) complex cannot participate in a spin change in forming a transition state of the type proposed for low-spin  $d^6$  iron(II). However, complete dissociative release of one bidentate phen ligand during either aquation or racemization could conceivably lead to the formation of a four-coordinate, possibly square-planar, transition state in which the nickel(II) may adopt a low-spin configuration. Analysis of this concept is deferred until the Discussion.

In this paper we report the first volumes of activation measured for the aquation of  $\text{Ni}(\text{phen})_3^{2+}$  and for the racemization of  $\text{Ni}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{2+}$ . The volume of activation for aquation of  $\text{Fe}(\text{phen})_3^{2+}$  measured earlier in these laboratories is reinterpreted. Enthalpies and entropies of activation determined in this study or reported previously are included for comparative purposes.

### Experimental Section

**Preparation of Complexes.** The racemic complexes  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Ni}(\text{phen})_3^{2+}$  were prepared and the resolution of each complex was performed using previously reported techniques,<sup>19,20</sup> with the optical isomers being isolated as the perchlorate salts.

**Table I.** Rates of Racemization and Aquation of  $\text{Fe}(\text{phen})_3^{2+}$  at 25 °C and Various High Pressures

P, bar	Aquation, <sup>a</sup> $10^4 k_P, \text{s}^{-1}$		Racemization, <sup>b</sup> $10^4 k_P, \text{s}^{-1}$	
	0.01 M HCl		1.0 M HCl	
	0.01 M HCl	0.01 M HCl	0.01 M HCl	1.0 M HCl
1	0.73	5.77	6.01 (5.28) <sup>c</sup>	
345		4.68		
690	0.47	3.98	3.90 (3.43)	
1034		3.22		
1380	0.30	2.63	2.52 (2.22)	

<sup>a</sup> Calculated from data in ref 7. <sup>b</sup> Average of three independent runs; average standard error  $\pm 0.06$ . <sup>c</sup> Values in parentheses represent aquation-independent racemization rates from  $(k_{\text{rac}} - k_{\text{aqn}})$  at pressure P.

**Table II.** Rates of Racemization and Aquation of  $\text{Ni}(\text{phen})_3^{2+}$  at 45 °C and Various High Pressures

P, bar	Aquation, <sup>a</sup> $10^4 k_P, \text{s}^{-1}$		Racemization, <sup>a</sup> $10^4 k_P, \text{s}^{-1}$	
	1.0 M HCl		1.0 M HCl	
	1.0 M HCl	0.01 M HCl	0.01 M HCl	1.0 M HCl
1	1.62	1.74	1.74	
345		1.74		
690	1.67	1.75		
1034		1.77		
1380	1.72	1.78	1.89	
1930	1.77			
2070		1.80		
2760		1.82	2.03	

<sup>a</sup> Average of three independent runs; average standard error  $\pm 0.03$ .

**Kinetic Studies.** The rates of aquation of  $\text{Ni}(\text{phen})_3^{2+}$  in 1.0 M HCl at various high pressures were determined by monitoring absorbance changes at 360 nm using a Varian 635D spectrophotometer incorporating a high-pressure cell in which the reaction solution was pressurized up to 1930 bar. Temperatures within the high-pressure cell block were maintained to within  $\pm 0.1$  °C by thermostated water circulation. Rate constants were evaluated via the Guggenheim method from the rate expression for an opposed first- and second-order reaction, since back-reactions may be important at acidities below 3.0 M.<sup>10,21</sup>

Rates of racemization of  $\text{Ni}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{2+}$  in both 0.01 and 1.0 M hydrochloric acid solution were measured at various high pressures using a steel high-pressure sampling vessel in which the reaction solution contained in a plastic inner vessel was pressurized up to 2760 bar. Samples were collected from the vessel via a bleed valve at appropriate time intervals, and the optical rotation of each sample was measured immediately on an adjacent Perkin-Elmer 241D polarimeter in a 1-dm pathlength microcell. The high-pressure sampling vessel was thermostated ( $\pm 0.05$  °C) at the appropriate temperature by immersion in an oil bath. Racemization rate constants were evaluated using least-squares analysis of  $\ln(\text{rotation})$  vs. time data.

Volumes of activation were determined from the expression<sup>22</sup>

$$-RT(\partial \ln k_P / \partial P)_T = \Delta V^\ddagger \quad (1)$$

since plots of  $\ln k_P$  vs. pressure (P) are essentially linear with slopes of  $-\Delta V^\ddagger / RT$ .

Rates of aquation at room pressure and various temperatures were measured using a Cary 17 spectrophotometer fitted with a thermostated cell compartment. Rates of racemization at room pressure and various temperatures were measured using a Perkin-Elmer 241D polarimeter fitted with a thermostated 1-dm pathlength microcell. Rate constants were evaluated as above, and entropies and enthalpies of activation were calculated in the usual manner from graphs of  $\ln k_{\text{obsd}}$  vs.  $1/T$ .

## Results

Rates of both racemization in 0.01 and 1.0 M aqueous HCl and of aquation in 1.0 M aqueous HCl for  $\text{Fe}(\text{phen})_3^{2+}$  exhibit significant retardation upon the application of high pressure. The pressure dependences of the racemization and aquation rates are shown in Table I, while volumes of activation cal-

**Table III.** Rates of Racemization and Aquation of  $\text{Ni}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{2+}$  at Room Pressures and Various Temperatures<sup>a</sup>

Solvent	Temp, °C	Aquation, Racemization, $10^4 k_{\text{obsd}}, \text{s}^{-1}$		
		$10^4 k_{\text{obsd}}, \text{s}^{-1}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$	
0.01 M HCl	$\text{Ni}(\text{phen})_3^{2+}$			
	35.0		0.48	
	40.0		0.89	
	45.0		1.82	
	50.0		3.23	
	55.0		5.93	
1.0 M HCl	35.0	0.43	0.45	
	40.0	0.80	0.85	
	45.0	1.62	1.71	
	50.0	2.87	3.13	
	55.0	5.12	5.75	
	4.0 M HCl	35.0	0.20	
40.0		0.39		
45.0		0.78		
50.0		1.37		
55.0		2.45		
0.01 M HCl		$\text{Fe}(\text{phen})_3^{2+}$		
	15.0		1.12	
	20.0		2.87	
	25.0		5.77	
	30.0		15.2	
	36.0		40.0	
	1.0 M HCl	15.0		1.17
		20.0		3.00
		25.0		6.01
		30.0		14.0
		36.0		38.0

<sup>a</sup> Average of three independent runs; average standard error  $\pm 0.04$ .

**Table IV.** Activation Parameters for Racemization and Aquation Reactions<sup>a</sup>

	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ , J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ , cm <sup>3</sup> mol <sup>-1</sup>
	$\text{Fe}(\text{phen})_3^{2+}$		
Racemizn (0.01 M HCl)	122 ( $\pm 3$ )	+104 ( $\pm 10$ )	+14.2 ( $\pm 0.3$ )
Racemizn (1.0 M HCl)	118 ( $\pm 3$ )	+89 ( $\pm 8$ )	+15.6 ( $\pm 0.3$ )
Aquation (1.0 M HCl)	135 ( $\pm 2$ ) <sup>b</sup>	+117 ( $\pm 8$ ) <sup>b</sup>	+15.4 ( $\pm 0.3$ ) <sup>c</sup>
$\text{Ni}(\text{phen})_3^{2+}$			
Racemizn (0.01 M HCl)	104 ( $\pm 1.5$ )	+8 ( $\pm 5$ )	-0.4 ( $\pm 0.2$ )
Racemizn (1.0 M HCl)	105 ( $\pm 1$ )	+12 ( $\pm 3$ )	-1.5 ( $\pm 0.3$ )
Aquation (1.0 M HCl)	102 ( $\pm 2$ )	+3 ( $\pm 6$ )	-1.2 ( $\pm 0.2$ )
Aquation (4.0 M HCl)	103 ( $\pm 1.5$ )	+1 ( $\pm 4$ )	

<sup>a</sup> Average standard error in parentheses. <sup>b</sup> Data from ref 23.

<sup>c</sup> Data from ref 7.

culated from these data using eq 1 are included in Table IV. By contrast, rates of both racemization in 0.01 and 1.0 M aqueous HCl and aquation in 1.0 M aqueous HCl for  $\text{Ni}(\text{phen})_3^{2+}$  all show a small acceleration upon the application of high pressure. The pressure dependences of these rates are shown in Table II with volumes of activation calculated from these data using eq 1 included in Table IV.

The effect of temperature on the room-pressure rates of racemization of both  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Ni}(\text{phen})_3^{2+}$  in 0.01 and 1.0 M HCl and on the room-pressure rates of aquation of  $\text{Ni}(\text{phen})_3^{2+}$  in 1.0 and 4.0 M HCl are shown in Table III. Enthalpies and entropies of activation calculated from these data are included in Table IV, together with activation parameters previously determined<sup>23</sup> for aquation of  $\text{Fe}(\text{phen})_3^{2+}$  in 1.0 M HCl.

## Discussion

The volumes of activation for aquation of  $\text{Fe}(\text{phen})_3^{2+}$  and the 5-NO<sub>2</sub> and 4,7-Me<sub>2</sub> derivatives have been reported previously.<sup>7</sup> While the high activation enthalpies and positive

activation entropies can be accommodated in a dissociative mechanism, it is the markedly positive activation volumes which give the most direct evidence for a dissociative mechanism for aquation of all three complexes. The rigid structure of the phen chelate does not permit a one-ended dissociative mechanism analogous to the mechanism proposed for chelated bpy via rotation about the internal C(2)–C(2') bond.<sup>3,24</sup> Since the hydrogen atoms in the 2 and 9 positions about the phen ring are virtually in van der Waals contact with the adjacent phen rings, a one-ended dissociative mechanism by pivoting about one nitrogen atom is precluded, and a simultaneous stretching of both Fe–N bonds is thus the most probable dissociative mode.

A convenient, though crude, description of a coordinated phen ligand as a polygonal sandwich of 1150-pm width and 380-pm thickness, based on accepted covalent bond lengths, has been proposed previously.<sup>7</sup> An estimate of the positive volume contribution on Fe–N bond extension arising from this sandwich pushing into the solvent has been made, and an extension of both Fe–N bonds by 61 pm in the transition state can account for a positive volume change of 15.4 cm<sup>3</sup> mol<sup>-1</sup> observed for Fe(phen)<sub>3</sub><sup>2+</sup>. Such a bond extension is not considered sufficient to allow water molecules to approach easily to bonding distances with the iron chromophore, and, thus, the positive  $\Delta V^\ddagger$  presumably reflects primarily dissociative processes.

This analysis does not consider, however, possible contributions from a process of bond expansion postulated to arise from excitation of low-spin d<sup>6</sup> iron(II) to a high-spin transition state. This particular spin excitation has been proposed previously<sup>17,18</sup> for racemization of Fe(phen)<sub>3</sub><sup>2+</sup> and aquation of Fe(bpy)<sub>3</sub><sup>2+</sup>. Excitation to the high-spin <sup>5</sup>T<sub>2</sub> state of iron(II) from a low-spin <sup>1</sup>A<sub>1</sub> state may be visualized in terms of expansion in phen or bpy Fe–N bond lengths. Spin-equilibrium studies in solution have determined  $\Delta H^\circ = 16.1$  kJ mol<sup>-1</sup> and  $\Delta S^\circ = +48$  J K<sup>-1</sup> mol<sup>-1</sup> for bis[hydrotris(1-pyrazolyl)borate]iron(II),<sup>27</sup> which may indicate an expanded high-spin state. An expansion analogous to the average 12-pm difference reported<sup>25</sup> in bond lengths of low-spin and high-spin forms of Fe(bpy)<sub>2</sub>(NCS)<sub>2</sub> would increase the average bond length in low-spin Fe(phen)<sub>3</sub><sup>2+</sup> from the measured<sup>26</sup> 197 pm to an expected 209 pm in a high-spin form.

That a spin excitation of the type proposed for Fe(phen)<sub>3</sub><sup>2+</sup> may be facile has been shown previously, since excitation to high-spin Fe(phen)<sub>3</sub><sup>2+</sup> can even be induced in the solid complex by the application of very high pressures alone, as indicated from Mössbauer studies.<sup>28–30</sup> The spin change in the solid state, however, most likely arises from an electronic transition on the ligand changing the bonding characteristics of the ligand to the metal, and subsequently the field at the metal ion, at very high pressure.<sup>30</sup> It does not necessarily indicate the mechanism for spin change in solution at moderate pressures considered here. Using the schematic volume model<sup>7</sup> of a bidentate phen in Fe(phen)<sub>3</sub><sup>2+</sup>, it is apparent that any estimation of the contribution to  $\Delta V^\ddagger$  from spin excitation in terms of a mechanism of general Fe–N bond extension producing the high-spin state depends critically on the estimated bond length expansion.

Conversion of the low-spin <sup>2</sup>T<sub>2</sub> state of iron(III) *N,N'*-di-alkyldithiocarbamates to the high-spin <sup>6</sup>A state proceeds with a positive partial molar volume change ( $\Delta V^\circ$ ) of the order of 5–6 cm<sup>3</sup> mol<sup>-1</sup>.<sup>31</sup> This  $\Delta V^\circ$  was identified with a general bond expansion of the FeS<sub>6</sub> complex core by up to 10 pm. The volume swept out by a dithiocarbamate ligand can be shown schematically to be smaller than that of a phen ligand, and hence the volume change associated with a general expansion of all six Fe–L bonds in the dithiocarbamate complex would be smaller than that expected with expansion in the phen

complex, even assuming an identical change in bond lengths in each complex. For spin equilibria of bis(2-(2-pyridylamino)-4-(2-pyridyl)thiazole)iron(II) chloride in aqueous solution a  $\Delta V^\circ$  of +11 cm<sup>3</sup> mol<sup>-1</sup> has been observed recently.<sup>32</sup>

The racemization of Fe(phen)<sub>3</sub><sup>2+</sup> is of the order of 9 times more rapid than the aquation process. In a range of solvent systems, the racemization rate remains faster than the aquation rate. This evidence has led to the proposal of an intramolecular mechanism for racemization. Since one-ended dissociation can be discounted on steric grounds, a twist mechanism for racemization<sup>6</sup> has been proposed. The solvent and viscosity dependencies observed have been related to preferential solvation of the ligands and the viscous resistance of the solvent to reorganization in the vicinity of the ion.<sup>15,16</sup> Although a twist mechanism is expected to be associated with negative or zero entropy of activation, a large positive entropy of activation can be accommodated in a twist mechanism if spin excitation prior to twisting motion is invoked. A positive contribution to  $\Delta S^\ddagger$  of the order of 50 J K<sup>-1</sup> mol<sup>-1</sup> can be expected for the spin excitation by analogy to previous experimental data.<sup>27</sup> As for aquation, a positive contribution to the experimental  $\Delta V^\ddagger$  for racemization can be ascribed to bond expansion in forming the high-spin state.

A most important observation in this study is that the activation volumes for aquation<sup>7</sup> (+15.4 cm<sup>3</sup> mol<sup>-1</sup>) and racemization (+15.6 cm<sup>3</sup> mol<sup>-1</sup>) measured in 1.0 M HCl are identical within experimental error. This observation can most readily be interpreted in terms of identical mechanisms for aquation and racemization, that is, dissociative in nature, with positive contributions to  $\Delta V^\ddagger$  from both bond stretching of the leaving group and spin excitation. However, the ninefold difference in rates, together with enthalpy and entropy differences of 17 ± 5 kJ mol<sup>-1</sup> and 28 ± 16 J K<sup>-1</sup> mol<sup>-1</sup>, respectively, for aquation and racemization do not lend support to such a proposition.

If spin excitation to a high-spin state occurs prior to or concomitant with aquation or racemization and involves a predicted general Fe–N bond expansion of 12 pm, this would lead to a positive volume contribution of approximately 9 cm<sup>3</sup> mol<sup>-1</sup>. This estimated volume contribution can be derived using the volume model for a phen ligand described previously<sup>7</sup> and does approximate experimental  $\Delta V^\circ$  for spin equilibria discussed earlier. A more positive experimental  $\Delta V^\ddagger$  for aquation is consistent with an I<sub>d</sub> description of aquation involving further bond stretching of the leaving phen ligand. An additional positive component of the experimental  $\Delta V^\ddagger$  for racemization does not at first appear to favor the previously proposed twist mechanism, for which a negligible volume of activation is predicted.<sup>9</sup> However, racemization reactions of Cr(phen)<sub>3</sub><sup>2+</sup> and Cr(bpy)<sub>3</sub><sup>3+</sup> which proceed via a twist mechanism have small positive volumes of activation of 3 cm<sup>3</sup> mol<sup>-1</sup> in 0.01 M HCl solution,<sup>9</sup> presumably arising from variation in solvation of the precursor and transition states. These small positive volumes do not differ all that much from the estimated "excess" volume of approximately +5 cm<sup>3</sup> mol<sup>-1</sup> for racemization of Fe(phen)<sub>3</sub><sup>2+</sup> in the same solvent and, hence, indicate that an intramolecular racemization mechanism may be acceptable. While trigonal twisting mechanisms are usually associated with high activation energies, a twist performed in an expanded high-spin state may be more facile than would be the case in a more compact ion. The latter analysis above is consistent with previous interpretation of aquation and racemization in terms of two distinctly different mechanisms, although similar  $\Delta V^\ddagger$ 's for each process lend support to related dissociative mechanisms operating.

The high-spin d<sup>8</sup> nickel(II) complex Ni(phen)<sub>3</sub><sup>2+</sup> has been shown previously to exhibit very similar rates of aquation, racemization, and labeled phen exchange, with similar acti-

parameters for each process. This evidence is consistent with an intermolecular dissociative mechanism for racemization involving rate-determining release of a phen chelate. Dissociation of a phen chelate, by invoking similar arguments to those used in discussion of the  $\text{Fe}(\text{phen})_3^{2+}$  case, most likely occurs by simultaneous stretching of both Fe-N bonds of the chelate in order to avoid severe steric interactions.

As distinct from the large positive activation volumes reported for  $\text{Fe}(\text{phen})_3^{2+}$ , the  $\text{Ni}(\text{phen})_3^{2+}$  complex exhibits volumes of activation of  $-1.2 \text{ cm}^3 \text{ mol}^{-1}$  for aquation and  $-1.5 \text{ cm}^3 \text{ mol}^{-1}$  for racemization in 1.0 M aqueous HCl. These activation volumes are identical within experimental error, as is the case for activation enthalpies and entropies (Table IV), consistent with a common mechanism for aquation and racemization. While a trigonal twist mechanism for racemization is consistent with the near-zero  $\Delta V^\ddagger$ , such a twist is not a pathway for aquation. A mechanism involving appreciable associative character arising from approach of a water molecule to a bonding position with the nickel(II) ion would lead to a negative activation volume. While reactions previously assigned  $I_a$  mechanisms usually exhibit appreciable negative activation volumes, some reactions with volumes of activation as small as  $-1 \text{ cm}^3 \text{ mol}^{-1}$  are apparently associative in character.<sup>22</sup>

The earlier observation of a dependence of the rates and activation parameters for aquation and racemization of  $\text{Ni}(\text{phen})_3^{2+}$  on solvent are consistent with an associative mechanism. However, formation reactions of nickel(II) with unidentate amine and imine ligands exhibit positive volumes of activation of approximately  $7 \text{ cm}^3 \text{ mol}^{-1}$  and have been interpreted in terms of an  $I_d$  mechanism.<sup>8</sup> Further, the bulky phen ligands may prevent solvent molecules approaching to within bonding distances of the complex, which would not favor an associative mechanism. An associative mechanism involving a transition state of higher coordination number may not provide a pathway for phen ligand exchange or aquation at a rate similar to that for racemization unless each act of solvent association is followed by a release or substantial bond stretching of a phen ligand.

Although square-planar nickel(II) complexes are commonly low spin, it is usually not necessary to consider a transition state of coordination number as low as 4 for octahedral complexes. However, the proposed mechanism of dissociative release of one phen for both aquation and racemization by simultaneous stretching of both chelate bonds suggests the formation of a transition state which can be visualized in the limit as four-coordinate. Such a mechanism need not be invoked for bpy complexes, where a viable one-ended dissociative mechanism leading to a five-coordinate intermediate is available. While it would be incautious to make firm predictions regarding the geometry of the four-coordinate transition state, it is apparent that a square-planar species, providing a pathway for racemization as well as aquation, is one possibility. Extremely rapid square-planar-octahedral interconversion in nickel(II) amine complexes has been reported.<sup>33</sup> Further, an X-ray structure of nickel(II) bis(stilbenediamine) species in both octahedral and square-planar environments shows a bond contraction from 205 pm in the high-spin octahedral to 189 pm in the low-spin square-planar form.<sup>34</sup>

A similar contraction of the Ni-N bonds occurring in the case of the  $\text{Ni}(\text{phen})_3^{2+}$  transition state would make a significant negative contribution to  $\Delta V^\ddagger$ , even assuming that a four-coordinate intermediate and its six-coordinate precursor sweep out the same volumes in space for identical metal-

nitrogen bond lengths. The open nature of a four-coordinate transition state indicates that solvent interaction by some contraction about the coordination sphere is likely, consistent with the observation of solvent dependence of the rates of racemization and aquation and associated activation parameters.

While there is insufficient experimental data to assess the size of component effects, a negative reaction volume contribution arising from a spin change in the transition state implies that an appreciable positive volume contribution for the release of the phen chelate is necessary in order to produce the near-zero experimental activation volume. A dissociative mechanism for aquation and racemization in terms of phen release is thus implied, consistent with a dissociative mechanism for formation reactions of nickel(II) determined previously from  $\Delta V^\ddagger$  data. The dissociative spin-change mechanism proposed above is consistent with the near-equivalence of rates and activation parameters for aquation, racemization, and labeled phen exchange.

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**Registry No.**  $\text{Ni}(\text{phen})_3^{2+}$ , 17085-38-0;  $\text{Fe}(\text{phen})_3^{2+}$ , 14708-99-7.

## References and Notes

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