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(31) Ligand abbreviations: en = 1,2-diaminoethane, tn = 1,3-diaminopropane, pn = 1,2-diaminopropane, bn = 1,4-diaminobutane, dien = diethylenetriamine, trien = triethylenediamine, tetren = tetraethylenepentamine, Me_2[14]diene = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me_6[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, salen = bis(salicylaldehyde)ethylenediimine, his = histidine, hm = histamine.
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Volumes of Activation for Racemization of Mixed 1,10-Phenanthroline and 2,2′-Bipyridyl Complexes of Nickel(II) from High-Pressure Solution Kinetics

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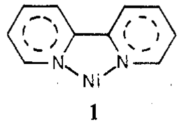
The effect of pressure on the rates of racemization of $Ni(phen)_2(bpy)^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ in solution has been evaluated. Reactions of $Ni(phen)_2(bpy)^{2+}$ exhibit only a minor pressure dependence of the rate, with a volume of activation (ΔV^{*}) of +0.6 $cm^3\ mol^{-1}$ and −0.1 $cm^3\ mol^{-1}$ for racemization in 0.01 and 1.0 M aqueous HCl, respectively. Aquation of $Ni(phen)_2(bpy)^{2+}$ in 1.0 M aqueous HCl exhibits no measurable pressure dependence, with $\Delta V^{*} = 0.0\ cm^3\ mol^{-1}$. Racemization of $Ni(phen)(bpy)_2^{2+}$ proceeds with a minor acceleration upon the application of pressure, with $\Delta V^{*} = -1.9\ cm^3\ mol^{-1}$ and $\Delta V^{*} = -5.2\ cm^3\ mol^{-1}$ in 0.01 and 1.0 M aqueous HCl, respectively. Variation of ΔV^{*} with acidity observed suggests an acid-dependent pathway is the dominant mechanism at high acidity but is not important at low acidity. A common mechanistic pathway for racemization and aquation of these complexes is favored since reported rates, enthalpies, entropies, and volumes of activation are very similar. A one-ended dissociative mechanism via a half-bonded bpy ligand is consistent with experimental ΔV^{*} data.

Introduction

Kinetic studies of racemization and aquation reactions of nickel(II) complexes have attracted continuing interest.[2] Extensive kinetic studies of 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy) complexes of nickel(II) and other metal ions have been reported.[2,3] The rates of dissociation, racemization, and labeled ligand exchange in $Ni(phen)_3^{2+}$ have been shown to be very similar,[4,5] providing consistent evidence for an intermolecular mechanism with rate-determining release of a chelated phen ligand. In nonaqueous solvents, exchange rates are also the same as the rates of racemization in the same solvents for $Ni(phen)_3^{2+}$,[5] although rates of racemization and associated activation parameters show a solvent dependence,[6,7] indicating that solvent–complex interactions may be significant.

While racemization of $Ni(bpy)_3^{2+}$ also appears to proceed via an intermolecular mechanism, the rate of racemization and also aquation is much faster than that observed for $Ni(phen)_3^{2+}$ and further exhibits acid-dependence and specific-ion effects.[6-8] The mixed complexes $Ni(phen)_2(bpy)^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ have also been subject to kinetic investigation,[9] and racemization and aquation appear to proceed by a mechanism analogous to that proposed for $Ni(bpy)_3^{2+}$, involving a half-bonded bpy molecule in the transition state. Chelated bpy (**1**) is capable of rotation about the internal C(2)–C(2′) bond joining the pyridine residues, a process which is forbidden by the fused ring system in chelated phen (**2**).



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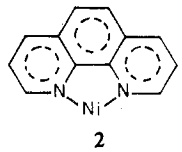

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One-ended dissociation in complexes with chelated bpy can readily proceed via rotation of one pyridine residue about the C(2)–C(2′) bond while the second ring remains fixed. A one-ended dissociative process may occur for chelated phen,

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or alternatively for chelated bpy, by pivoting of the ligand about one coordination site with concomitant stretching of the adjacent metal–nitrogen bond. In tris-chelate complexes, however, this process is restricted by severe steric interactions, since ring protons in the 2 and 9 positions of phen are virtually in van der Waals contact with adjacent phen rings. Subsequently, a dissociative mechanism involving simultaneous stretching of both metal–nitrogen bonds in the transition state has been proposed for $M(phen)_3^{n+}$ complexes.[10,11]

Volumes of activation ($\Delta V^{\ddagger}$) determined from the effect of high pressure on reaction rates in solution have been applied to the elucidation of mechanistic problems in a range of inorganic reactions, and this application has been reviewed.[12] Recently, the determination of $\Delta V^{\ddagger}$ for racemization reactions of Cr(III) and Fe(II) complexes with phen or bpy chelates has proved important in the elucidation of mechanisms of racemization.[11,13] Racemization reactions of Cr(III) complexes at low acidity proceed with essentially identical $\Delta V^{\ddagger}$ values for analogous phen or bpy complexes,[13] indicating that the mechanism is not dependent on the diimine ligand. While $\Delta V^{\ddagger}$ for aquation and racemization of $Ni(phen)_3^{2+}$ have been measured and shown to be identical within experimental error,[11] consistent with a dissociative mechanism for racemization, the essentially zero value of $\Delta V^{\ddagger}$ is not readily interpreted in terms of a dissociative mechanism. The racemization rate of $Ni(phen)_3^{2+}$ is acid independent, and this is reflected in a $\Delta V^{\ddagger}$ which is effectively independent of acidity.

The acid dependence of aquation and racemization of complexes with chelated bpy is well documented and has been interpreted in terms of protonation of the half-bonded bpy in the transition state.[4,14,15] The possibly different mechanistic pathways available to phen and bpy complexes of nickel(II) suggest that an investigation of $\Delta V^{\ddagger}$ for racemization at different acidities of complexes with bpy chelates to supplement a prior study[11] of $Ni(phen)_3^{2+}$ is warranted. We report here results of a study of the rate of reaction at various high pressures and subsequently determined $\Delta V^{\ddagger}$ values for racemization of $Ni(phen)_2(bpy)^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ in both 0.01 and 1.0 M aqueous hydrochloric acid and also for the aquation of $Ni(phen)_2(bpy)^{2+}$ in 1.0 M aqueous HCl.

Experimental Section

The complexes $Ni(phen)_2(bpy)^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ were prepared and resolved by previously reported methods.[16] The perchlorate salts were used in racemization studies and the more soluble chloride salts in aquation studies.

Rates of racemization in both 0.01 and 1.0 M aqueous HCl solution were measured at various high pressures using a stainless steel high-pressure sampling vessel in which the reaction solution, contained in a plastic inner vessel, was pressurised 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 path length microcell. The high-pressure sampling vessel was thermostated (±0.1 °C) at the required temperature by immersion in an oil bath fitted with a heating element and a refrigerated cooling coil. Racemization rate constants were evaluated from ln (rotation) vs. time graphs.

Rates of aquation of $Ni(phen)_2(bpy)^{2+}$ in 1.0 M aqueous HCl at various high pressures were determined by monitoring absorbance change at 400 nm using a Varian 635D spectrophotometer incorporating a high-pressure cell with sapphire windows in which the reaction solution was pressurized up to 1380 bar. Temperature within the cell block was maintained to within ±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 are important at acidities below 3.0 M.[9] Aquation reaction 1 is only a pseudoequilibrium, since the $Ni(phen)_2^{2+}$ product

$$Ni(phen)_2(bpy)^{2+} \rightleftharpoons Ni(phen)_2^{2+} + bpy \qquad (1)$$

itself is subject to further dissociation.[9] Subsequently, errors in determined rate constants for aquation are large compared to those found for racemization rate constants. The rapid aquation rate and limited dissociation of $Ni(phen)(bpy)_2^{2+}$ in 1.0 M acid did not permit sufficiently accurate rate constants at various pressures to be determined in the available high-pressure cell to allow estimation of $\Delta V^{\ddagger}$ in this latter case.

Table I. Rates of Racemization and Aquation of $Ni(phen)_2(bpy)^{2+}$ at Various High Pressures

	$10^4 k_P$,[b] s^{-1}	
P, bar	aquation	racemization
	0.01 M HCl[a]	
1		4.45 ± 0.03 (4)
690		4.36 ± 0.03 (2)
1380		4.33 ± 0.04 (3)
2070		4.26 ± 0.05 (4)
2760		4.11 ± 0.04 (3)
	1.0 M HCl[a]	
1	7.2 ± 0.4 (5)	7.08 ± 0.03 (5)
345	6.9 ± 0.2 (5)	
690	7.0 ± 0.3 (5)	
1034	6.7 ± 0.2 (3)	
1380	6.9 ± 0.4 (5)	7.11 ± 0.03 (5)
2760		7.13 ± 0.04 (3)

[a] t = 20 °C. [b] The average standard error and the number of independent runs (in parentheses) are included.

Table II. Rates of Racemization of $Ni(phen)(bpy)_2^{2+}$ at Various High Pressures

	$10^3 k_P$,[c] s^{-1}	
P, bar	0.01 M HCl[a]	1.0 M HCl[b]
1	1.15 ± 0.02 (4)	1.49 ± 0.04 (4)
690	1.22 ± 0.03 (3)	1.69 ± 0.06 (3)
1380	1.29 ± 0.02 (3)	2.11 ± 0.04 (4)
2070	1.36 ± 0.03 (4)	2.39 ± 0.06 (3)
2760	1.46 ± 0.05 (3)	

[a] t = 20 °C. [b] t = 10 °C. [c] The average standard error and the number of independent runs (in parentheses) are included.

Volumes of activation ($\Delta V^{\ddagger}$) were determined from expression 2[12]

$$(\partial \ln k_P/\partial P)_T = -\Delta V^{\ddagger}/RT \qquad (2)$$

since graphs of ln k_P vs. pressure (P) are essentially linear with slopes of $-\Delta V^{\ddagger}/RT$, showing no pressure dependence of $\Delta V^{\ddagger}$ itself over the pressure range used in this study.

Results

Rates of both racemization in 0.01 and 1.0 M aqueous HCl and of aquation in 1.0 M aqueous HCl for $Ni(phen)_2(bpy)^{2+}$ exhibit little or no pressure dependence, with volumes of activation close to zero in each case. The pressure dependence of the racemization and aquation rates are shown in Table I, while volumes of activation calculated from this data using eq 2 are included in Table III.

Rates of racemization of $Ni(phen)(bpy)_2^{2+}$ in 0.01 and 1.0 M aqueous HCl show an acceleration upon the application of pressure. While the acceleration is minor at low acid strength, it is more marked in 1.0 M acid solution. The pressure dependence of the racemization rates are shown in Table II, while calculated volumes of activation are included in Table III. Enthalpies and entropies of activation previously determined for these reactions[9] are included in Table III for comparative purposes, together with activation parameters[11] for reactions of $Ni(phen)_3^{2+}$.

Discussion

The high-spin d^8 nickel(II) complexes $Ni(phen)_2(bpy)^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ exhibit very similar rates of aquation and racemization, with similar activation parameters for each process.[9] Similar rates of aquation, racemization and labeled ligand exchange have been reported for $Ni(phen)_3^{2+}$ and

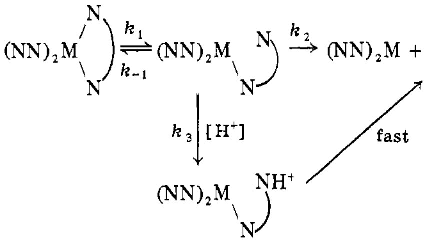
Table III. Activation Parameters for Racemization and Aquation Reactions

	[HCl], M	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$,^{a} cm^3 mol^{-1}	ref
		$Ni(phen)_3^{2+}$			
racemization	0.01	104	+3	−0.4 (±0.2)	11
	1.0	105	+12	−1.5 (±0.3)	11
aquation	1.0	102	+3	−1.2 (±0.2)	11
	4.0	103	+1		11
		$Ni(phen)_2(bpy)^{2+}$			
racemization	0.01	96^b	$+16^b$	+0.6 (±0.2)	*c*, 9
	1.0	90	+7	−0.1 (±0.05)	*c*, 9
aquation	1.0	92	+12	0.0 (±0.5)	*c*, 9
	5.0	85	−4		9
		$Ni(phen)(bpy)_2^{2+}$			
racemization	0.01	93^b	$+18^b$	−1.9 (±0.2)	*c*, 9
	1.0	88	+16	−5.2 (±0.5)	*c*, 9
aquation	5.0	82	−7		9

[a] The standard error is in parentheses. [b] Determined in water only. [c] This work.

$Ni(bpy)_3^{2+}$.[3,4] An intermolecular dissociative mechanism for racemization of nickel(II) diimine complexes is consistent with these observations.

The favored mechanism[4,14,15] for dissociative release of chelated bpy in metal complexes can be represented as



for which a steady-state treatment produces an expression for k_{obsd} of

$$k_{obsd} = \left\{ \frac{k_2 + k_3[H^+]}{k_{-1} + k_2 + k_3[H^+]} \right\} k_1 \tag{3}$$

At low acid strength $k_3[H^+] << k_{-1} + k_2$, and hence eq 3 approximates to

$$k'_{obsd} = k_1 k_2/(k_{-1} + k_2) \tag{4}$$

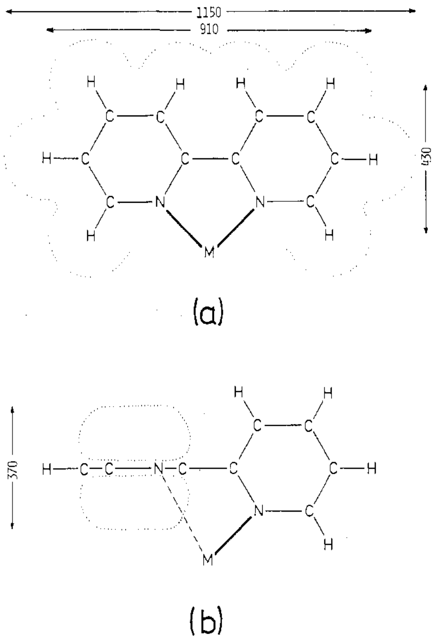
while at high acid strength $k_3[H^+] >> k_{-1} + k_2$, and consequently eq 3 approaches

$$k''_{obsd} = k_1 \tag{5}$$

Combination of eq 4 and 5 produces a further relationship:

$$k''_{obsd}/k'_{obsd} - 1 = k_{-1}/k_2 \tag{6}$$

The half-bonded bpy intermediate represents a situation in which one-ended dissociation via rotation about the C(2)–C(2′) bond has occurred. The proposed mechanism is consistent with the acid dependence of aquation and racemization, since protonation of the nonbonded part of the bpy can be considered. This dissociative mechanism is distinctly different from the one considered most appropriate for acid-independent $M(phen)_3^{n+}$ reactions,[10,11] where simultaneous stretching of both metal–nitrogen bonds of the leaving phen indicates a transition state which may approach four-coordination. The one-ended dissociative mechanism proposed for complexes with at least one chelated bpy ligand leads to generation of a five-coordinate transition state, assuming no associative character in either system.



(a)

(b)

Figure 1. Schematic diagram of (a) chelated bpy and (b) half-bonded bpy after rotation of one ring through 90°.

The bpy chelate may best be visualized as a flat bulky ligand with dimensions calculated using normal bond lengths, angles, and van der Waals radii as illustrated in Figure 1(a). Each pyridine ring has a thickness estimated as 370 pm, as shown in Figure 1(b). The chelated ligand presents to the solvent a face of maximum width 1150 pm and of averge thickness 370 pm. It is reasonable to expect that protons at least in the 3 and 4 (or 3′ and 4′) positions of the ring are in intimate contact with the secondary solvation layer. Substitution in the 3 or 4 position of pyridine (py) does not affect the experimental $\Delta V^{\ddagger}$ in dissociative substitution reactions of $Fe(CN)_5(py)^{3-}$ or $Fe(CN)_5(CN\text{-}py)^{3-}$ complexes,[17] indicating that the extremities of the imine ligand are fully solvated and substitution at these positions does not contribute to $\Delta V^{\ddagger}$. The solvent presumably adjusts to motion of the leaving ligand in that region. Proton magnetic resonance studies of solvation of $Cr(phen)_3^{2+}$ indicate[18] that solvent can penetrate partially some 200 pm into the V-shaped pockets between the diimine ligands, consistent with solvation of the outer regions of the chelated diimine ligands.

Rotation of one pyridine ring about the C(2)–C(2′) bond by 90° leads to stretching of the Ni–N bond in the model from 205 to 320 pm, a substantial bond extension of over 50%. The thickness of the py ring (370 pm) is similar to the width of the ring, excluding solvated protons in the 3 and 4 positions, of approximately 430 pm. Thus it appears that the volume occupied by the half-bonded form of the molecule approximates that of the chelated precursor, since the thickness and effective unsolvated width of the rotating ring are similar. For a one-ended dissociative mechanism of this type, therefore, a zero $\Delta V^{\ddagger}$ is predicted to a first approximation. The observation of zero or near-zero experimental $\Delta V^{\ddagger}$ values for the complexes under study (Table III) is reasonably consistent with such a mechanism.

The transition state with a substantially stretched Ni–N bond may allow a change in solvation with closer approach of solvent molecules to the dissociated site. Although it is unlikely that solvent can approach to within bonding distances due to steric restrictions from the three bulky diimine ligands, the negative $\Delta V^{\ddagger}$ for $Ni(phen)(bpy)_2^{2+}$ is consistent with some change in solvation between initial and transition states. The more negative $\Delta V^{\ddagger}$ for $Ni(phen)(bpy)_2^{2+}$ compared with $Ni(phen)_2(bpy)^{2+}$ racemization may reflect greater solvation of the transition state. This could arise as the number of more flexible bpy ligands about the metal ion increases.

While little effect of acidity on $\Delta V^{\ddagger}$ is observed for Ni(phen)$_2$(bpy)$^{2+}$, a clear change from $\Delta V^{\ddagger} = -5.2$ cm^3 mol^{-1} in 1.0 M acid to $\Delta V^{\ddagger} = -1.9$ cm^3 mol^{-1} in 0.01 M acid is observed for Ni(phen)(bpy)$_2$$^{2+}$. Assuming the expression for k_{obsd} in eq 3 represents the acting mechanism, it is apparent that while the determined $\Delta V^{\ddagger}_{\mathrm{exptl}}$ in 1.0 M acid represents the volume of activation for one-ended dissociation (eq 5), $\Delta V^{\ddagger}_{\mathrm{exptl}}$ in 0.01 M acid is a composite value (eq 4). From a treatment indicated in eq 6 of observed rates, adjusted to the same temperature using known activation energies, a graph of ln $(k''_{\mathrm{obsd}}/k'_{\mathrm{obsd}} - 1)$ vs. pressure produces a volume of activation from the slope of the linear graph of +3.1 ± 1.0 cm^3 mol^{-1}, which is equal to $\Delta V^{\ddagger}_2 - \Delta V^{\ddagger}_{-1}$ for the reaction steps k_2 and k_{-1}. Errors in this calculation are compounded, but nevertheless a reasonably linear graph can be obtained.

The value of +3.1 ± 1.0 cm^3 mol^{-1} is the same within experimental error as a value of +2.5 ± 1.1 cm^3 mol^{-1} obtained from an equivalent analysis of $\Delta V^{\ddagger}$ for aquation of Fe(bpy)$_3$$^{2+}$ in 0.01 and 1.0 M aqueous HCl.[19] Since bond lengths for the octahedral Ni–N and Fe–N complexes are similar and the complexes are of the same formal charge, the $\Delta V^{\ddagger}_2 - \Delta V^{\ddagger}_{-1}$ term should be essentially independent of metal ion if the same mechanism is operating, and this behavior is observed experimentally. Of the two components, $\Delta V^{\ddagger}_{-1}$ should be near zero if the sixth coordination site has remained vacant or positive if solvent partially occupying the site must be released prior to chelation. Subsequently, such an analysis requires $\Delta V^{\ddagger}_2$ to be positive, consistent with an overall dissociative mechanism for complete release of the half-bonded bpy ligand.

Although $\Delta V^{\ddagger}$'s for racemization of Ni(phen)$_2$(bpy)$^{2+}$ and Ni(phen)(bpy)$_2$$^{2+}$ are similar to those previously reported for Ni(phen)$_3$$^{2+}$,[11] distinctly different dissociative mechanisms most likely operate. The very similar behavior of the rate of racemization of Ni(phen)(bpy)$_2$$^{2+}$, Ni(phen)$_2(bpy)^{2+}$, and Ni(bpy)$_3$$^{2+}$ in mixed aqueous–ethanol solvent[9] is consistent with a common mechanism when at least one bpy ligand is present, most likely via a half-bonded bpy in the transition state. The inability of phen in Ni(phen)$_3$$^{2+}$ to distort from planarity, together with steric interactions between adjacent chelates, requires an energetically less favored mechanism involving simultaneous stretching of both Ni–N bonds of the leaving chelate in the transition state.[11] The higher enthalpy of activation for racemization of Ni(phen)$_3$$^{2+}$ compared with that of analogues containing bpy (Table III) is consistent with this mechanistic differentiation.

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Registry No. Ni(phen)$_2$(bpy)$^{2+}$, 25504-10-3; Ni(phen)(bpy)$_2$$^{2+}$, 25504-11-4.

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