In summary, two independent methods have been used to measure the self-exchange rate of several ligand derivatives of the active-site heme peptide from cytochrome *c*. These methods give a consistent estimate of $k_{11}^{OP} = (3 \pm 1) \times 10^6$ $M^{-1}\ s^{-1}$, which significantly exceeds the rate constant for native cytochrome *c*: $k_{11}^{cyt\ c} \simeq 10^3\text{–}10^4\ M^{-1}\ s^{-1}$. This rate difference between the protein and isolated active site is consistent with the accessibility model proposed by Gray,[13] but alternative explanations cannot be excluded. Finally, excited-state electron transfer appears to offer a powerful probe of the electron-transfer reactions of metalloproteins and peptides which are difficult to study by conventional means. Further studies in this vein are in progress.[7,8]

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Registry No. Cytochrome *c*, 15710-60-8; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$, 47860-47-9; $Ru(bpm)_3^{2+}$, 80263-32-7; pyridine, 110-86-1; imidazole, 288-32-4; methionine, 63-68-3.

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Kinetics and Mechanism of the Equilibration Reactions of Diaquochromium(III)–Schiff Base Derivatives, $Cr(Schiff\ base)(H_2O)_2^+$, and Their Conjugate Bases with Thiocyanate, Azide, Imidazole, Pyridine, and Nicotinic Acid as Ligands

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The kinetic studies of the reactions of the complexes $Cr(Schiff\ base)(H_2O)_2^+$ where Schiff base is either *N,N'*-ethylenebis(salicylidenimine), viz., salen, or *N,N'*-ethylenebis(acetylacetonimine), viz., acacen, reveal high aquo ligand substitution rates. The Schiff base complexes $Cr(Schiff\ base)(H_2O)_2^+$ and their conjugate bases equilibrate with a variety of nucleophiles, X^{n-}, viz., thiocyanate ion, azide ion, pyridine, imidazole, and nicotinic acid. The forward rates for the equilibration reactions of X^{n-} with either $Cr(salen)(H_2O)_2^+$ or $Cr(acacen)(H_2O)_2^+$ are independent of the nature of X^{n-}. The invariance of the forward rate constants and a linear free energy relation between log (aquation rate constants) and log (equilibration constant) with a slope of 0.94 ± 0.05 for the reactions of $Cr(salen)(H_2O)_2^+$ support a dissociative interchange (I_d) mechanism for the aquo cation. On the other hand, the forward rate constants for the conjugate base of $Cr(salen)(H_2O)_2^+$ exhibit a marked dependence on the nature of the incoming nucleophiles, X^{n-}. On the basis that the conjugate base exhibits a probable five-coordinate structure in solution, a bimolecular addition mechanism has been proposed for the reactions with X^{n-}. The study reports one of the few examples in the aqueous chemistry of Cr(III) wherein a high kinetic lability resulting from ground-state distortion has been demonstrated.

Introduction

Whereas a vast majority of aquo ligand substitution reactions of chromium(III) complexes has established the kinetic inertness of the metal ion,[1-4] ground-state distortion has recently been shown to give rise to kinetic lability in Cr(III)–Schiff base complexes.[5] The X-ray structure of the diaquochromium(III) complex, $Cr(salen)(H_2O)_2^+$ as a chloride salt reveals a distortion in the $H_2O\text{–}Cr\text{–}OH_2$ axis,[6-8] and such a distortion has led to the substitution of an aquo ligand by NCS^- or N_3^- in the stopped-flow time scale.[5] We have recently reported the synthesis and characterization of the perchlorate salt of $Cr(salen)(H_2O)_2^+$ as well as of the new complexes $Cr(acacen)(H_2O)_2^+$ and $Cr(salophen)(H_2O)_2^+$.[9] Although the Schiff base ligands salen, acacen, and salophen have strong structural resemblances, with cobalt(III), they have been known to form either five- or six-coordinate complexes depending on the nature of the tetradentate[10] ligand. The kinetic studies of the aquo ligand substitution reactions of chromium(III)–Schiff base complexes where Schiff base is either salen or acacen or salophen are of interest. Further with the salen derivative of chromium(III), under alkaline conditions, a complex of the formulation of Cr(salen)OH has already been isolated and characterized.[6] There have been recent reports on the interesting features of the mechanisms of the reactions of five-coordinate complexes.[11] The kinetics and mechanism of the reactions of $Cr(Schiff\ base)(H_2O)_2^+$ complexes (where Schiff base = salen or acacen or salophen) and of their conjugate bases with a variety of nucleophiles $X^{n-} = NCS^-$, N_3^-, pyridine (py), imidazole ($C_3H_4N_2$) and nicotinate ion (3-py-COO^-) have, therefore, now been reported.

Experimental Section

Materials. The complexes $Cr(Schiff\ base)(H_2O)_2ClO_4$, where Schiff base is salen, salophen, or acacen, were prepared by the adaptation of the procedures already described for the chloride salt of the salen derivative and characterised as already described.[6,9] Lithium thiocyanate and lithium azide were prepared from KNCS and KN_3 and $LiClO_4$. The other reagents pyridine, imidazole, and sodium nicotinate used were of reagent grade and were used without further purification. The concentrations of the solutions of the ligands investigated were analysed by standard methods.[12]

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(1) Garner, C. S.; House, D. A. *Transition Met. Chem.* **1970**, *6*, 59.
(2) Dasgupta, T. P. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974**, *9*, 63.
(3) Langford, C. H.; Sastri, V. S. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *9*, 203.
(4) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.
(5) Rajendra Prasad, D.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Inorg. Chem.* **1980**, *19*, 3181.
(6) Coggon, P.; McPhail, A. T.; Mabbs, F. E.; Richards, A.; Thronley, A. S. *J. Chem. Soc., Dalton Trans.* **1970**, 3296.
(7) Yamada, S.; Iwasaki, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1463 and references therein.
(8) Yamada, S.; Iwasaki, K. *Inorg. Chim. Acta* **1971**, *5*, 3.
(9) Rajendra Prasad, D.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 431.
(10) Bigotto, A.; Costa, G.; Mestroni, G.; Pellizer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, E.; Tauzher, G. *Inorg. Chim. Acta Rev.* **1970**, *4*, 41.
(11) Ramasami, T.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 1523.
(12) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis"; E.L.B.S. Pub.: London, 1978; p 263. Fritz, F. S. *Anal. Chem.* **1950**, *22*, 1028. Cowgill, R. W. *Ibid.* **1955**, *27*, 1521.

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Equilibrium Measurements. The dissociation constant for the aquo ligand hydrolysis in the complex *trans*-Cr(salen)$(H_2O)_2^+$ was measured spectrophotometrically in $[H^+]$ region of 10^{-4}–10^{-11} M at 25 °C. The spectra of the complex Cr(salen)$(H_2O)_2^+$ and that of its conjugate base varied markedly, lending a convenient means of measuring the equilibrium constant for the acid dissociation as in eq 1. The

$$MOH_2^+ \overset{K_a}{\rightleftharpoons} MOH + H^+ \tag{1}$$

equilibrium constant, K_a, was related to molar absorptivities according to eq 2 where M = Cr(Schiff base) adduct and ϵ_{OH_2}, ϵ_{OH}, and ϵ_{obsd}

$$\epsilon_{obsd} - \epsilon_{OH_2} = \frac{K_a(\epsilon_{OH} - \epsilon_{OH_2})}{[H^+] + K_a} \tag{2}$$

correspond to molar absorptivities of the diaquo, hydroxo, and the mixture of the two derivatives, respectively.

A similar analysis of the UV–visible spectra of the reaction mixtures of the complex *trans*-Cr(salen)$(H_2O)_2^+$, at various concentrations of the ligands when X^{n-} = NCS^-, N_3^-, py, imidazole, and 3-pyCOO$^-$, indicated that in all the cases an equilibrium of the type in (3) was established.

$$Cr(salen)(H_2O)_2^+ + X^{n-} \overset{K_{app}}{\rightleftharpoons} Cr(salen)(H_2O)X^{(1-n)+} + H_2O \tag{3}$$

However, in the $[H^+]$ region investigated, viz., 10^{-4}–10^{-11} M, equilibrium 1 was also involved in the reaction 3. At any particular $[H^+]$, the equilibrium constant, K_{app}, could be obtained by a modified Benesi–Hilderbrand-type equation as in (2). The equilibrium constants, K_{app}, could be expressed as a function of $[H^+]$ according to (4) where K_1 and K_2 are the equilibrium constants for the reactions of X^{n-} with Cr(salen)$(H_2O)_2^+$ and its conjugate base, respectively.

$$K_{app} = (K_1[H^+] + K_2K_a)/([H^+] + K_a) \tag{4}$$

Kinetic Studies. The kinetics of the equilibration of the type in (3) with the Schiff base being either salen or acacen were monitored with an Aminco stopped-flow spectrophotometer. In the case of salen derivatives, a single-stage kinetics was observed under pseudo-first-order excess of $[X^{n-}]$ where [Cr(III)] = 5×10^{-4}–10^{-3} M, [thiocyanate] = 0.013–0.25 M, [azide] = 0.013–0.25 M, [pyridine] = 0.05–0.25 M, [imidazole] = 0.05–0.25 M, and [nicotonic acid] = 0.025–0.125 M in the $[H^+]$ range of $(0.069–10) \times 10^{-6}$ M at 30 °C and I = 1.0 W ($LiClO_4$). With the diaquo derivative of acacen, however, a slow second stage associated with a poorly soluble secondary product was observed. Since infinity time measurements in these cases could not be measured accurately, the Guggeinheim method was employed. The concentration ranges employed for studies on acacen complexes were [thiocyanate] = 0.01–0.5 M, [azide] = 0.04–0.26 M, [pyridine] = 0.02–0.25 M, and $[H^+]$ = $(0.316–3.16) \times 10^{-5}$ M at 30 °C. The acid concentrations for the kinetic studies were estimated with a pH meter radiometer 4d fitted with a glass and a calomel electrode and precalibrated with standard $[H^+]$ at 1 M $LiClO_4$. When equal volumes of Cr(III) and X^{n-}, solutions at a chosen $[H^+]$ were mixed and the pH measured; the $[H^+]$ before and after the reaction was the same within experimental error. The pseudo-first-order plots were linear to 4–5 half-lives in the case of both Schiff base derivatives. In the case of weak acids as ligands, from their analytical concentrations, $[X^{n-}]$ was calculated from their ionization constants already reported.[13]

Product Analyses. The products of the equilibrium reactions of NCS^-, N_3^-, and pyridine with Cr(Schiff base)$(H_2O)_2^+$, where Schiff base is either salophen or acacen, were isolated and characterized. In the case of salen derivatives, complexes of the formulation Cr(salen)$(H_2O)X^{(1-n)+}$, where X^{n-} = NCS^-, N_3^-, pyridine, imidazole, or 3-pyCOO$^-$, were obtained and characterized by means of elemental analyses, UV–visible and infrared spectra and conductometric studies as described elsewhere.[9]

Instrumentation. An Aminco stopped-flow spectrophotometer and a Beckman-D 25 UV–visible spectrophotometer were used for the kinetic and equilibrium studies. Radiometer pH meter 4d in conjunction with a glass electrode was used for pH measurements. The optical density changes as a function of time were analysed with a HP 2200 Hindustan microcomputer. The dependence of pseudo-first-order rate constants on concentration variables were analyzed with an IBM 370 computer and a nonlinear least-squares Los Almos program written by Newton and Moore[14] and implemented by Espenson et al.[15]

Table I. Spectrophotometric Equilibrium Constants for the Reactions of Various X^{n-} with Cr(salen)$(H_2O)_2^+$ at 30 °C and I = 1.0 M ($LiClO_4$)

$10^6[H^+]$/ M	const/M^{-1}			
	N_3^-	C_5H_5N	$C_3H_4N_2$	3-pyCOO$^-$
0.063	4.9		1.3	2.2
0.125	6.7		3.1	2.1
0.25	9.4	8.7	1.5	2.4
0.50		13.8	32.0	2.4
1.00	16.0	14.1	31.1	1.6
2.00	30.0	15.6	46.0	

Results

Equilibrium Studies on Metal Ion Hydrolysis. The UV-visible spectra of Cr(salen)$(H_2O)_2^+$ exhibit a systematic dependence on $[H^+]$. The analyses of optical density changes as a function of $[H^+]$ according to (2) with a nonlinear least-squares program gave a value of $(9.5 \pm 0.9) \times 10^{-9}$ M as K_a. A Benesi–Hilderbrand-type plot of the inverse of optical density differences between [Cr(salen)$(H_2O)_2^+$] and a mixture of the diaquo and conjugate base derivatives against $[H^+]$ was linear. The linearity establishes that in the pH region 5–11 only one aquo ligand underwent hydrolysis reaction.

Formation Constant Measurements on Cr(salen)H_2O) $X^{(1-n)+}$ Complexes. The formation constants of equilibrium 3 were measured spectrophotometrically with (5) at various $[H^+]$

$$\epsilon_{obsd} - \epsilon_0 = \frac{(\epsilon_{CrL} - \epsilon_0)[X^{n-}]K_{app}}{1 + K_{app}[X^{n-}]} \tag{5}$$

where X^{n-} = N_3^-, NCS^-, pyridine, imidazole, and 3-pyCOO$^-$. In the case of weak ligands, equilibria of the type in (6) were

$$HL \overset{K_6}{\rightleftharpoons} H^+ + L^- \tag{6}$$

also taken into account, and the values of K_6 used for HN_3, $C_5H_5NH^+$, imidazole–H^+, as 3-pyCOOH were 2.4×10^{-5}, 6.2×10^{-6}, 9.8×10^{-8}, and 1.5×10^{-5} M, respectively.[13] The analysis of the dependence of K_{app} on $[H^+]$ as in Table I for the salen derivative indicated the overall equilibration process (7).

$$\begin{tikzcd}
Cr(salen)(H_2O)_2^+ + X^{n-} \arrow[r, shift left, "K_1"] \arrow[d, shift left, "K_a"] & Cr(salen)X(H_2O)^{(1-n)+} + H_2O \arrow[l, shift left] \arrow[d, shift left, "K_a'"] \\
Cr(salen)OH(H_2O) + X^{n-} \arrow[r, shift left, "K_2"] \arrow[u, shift left, "{[H^+]}"] & Cr(salen)OH\ X^{n-} + H_2O \arrow[l, shift left] \arrow[u, shift left, "{[H^+]}"]
\end{tikzcd} \tag{7}$$

Although K_{app} exhibited a qualitative dependence on $[H^+]$ in all the cases, with N_3^- and pyridine as X^{n-} quantitative estimates of K_1 and K_2 were obtained. However, it is known that this spectrophotometric technique gives a measure of the composite quantity of outer-sphere and inner-sphere equilibrium constants of the type in (8) and (9). The measured

$$Cr(salen)(H_2O)_2^+ + X^{n-} \overset{K_{OS}}{\rightleftharpoons} Cr(salen)(H_2O)_2^+, X^{n-} \tag{8}$$

$$Cr(salen)(H_2O)_2, X^{n-} \overset{K_{IS}}{\rightleftharpoons} Cr(salen)(H_2O)X^{(1-n)+} + H_2O \tag{9}$$

equilibrium constants in such cases correspond to K_{OS} + $K_{IS}K_{OS}$. Nevertheless, because of the low cationic charge on

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(13) McDonald, J. R.; Rabelais, J. W.; McGlynn, S. P. *J. Chem. Phys.* **1970**, *52*, 1332. Albert, A.; Goldacre, R.; Phillips, J. *J. Chem. Soc.* **1948**, 2240. Kirby, A. H. M.; Neuberger, A. *Biochem. J.* **1938**, *32*, 1146. Hughes, E. B.; Jellinck, H. H. G.; Ambrose, B. A. *J. Phys. Chem.* **1949**, *53*, 414.

(14) Moore, R. H.; Ziegler, R. K. Report LA 2367 and Addenda; Los Almos Scientific Laboratory: Los Alamos, NM, 1959. Revised by J. P. Birk and D. A. Williams.

(15) Espenson, J. H., personal communication.

Table II. Rate Parameters and the Equilibrium Constant K_1 for the Reactions of X^{n-} with $Cr(salen)(H_2O)_2^+$ and Its Conjugate Base at 30 °C and I = 1.0 M ($LiClO_4$)

ligand	10^2k_{-1}, s^{-1}	$10^8k_{-2}K_a'$, M s^{-1}	k_1, M^{-1} s^{-1}	$10^7k_2K_a$, s^{-1}	K_1, M^{-1}
NCS^-	1.0 ± 0.4	5.1 ± 0.9	0.15 ± 0.04	5.1 ± 0.7	14.6
N_3^-	0.82 ± 0.2	1.2 ± 0.07	0.21 ± 0.02	0.23 ± 0.12	25.6
C_5H_5N	0.21 ± 0.4	1.4 ± 0.4	0.21 ± 0.10	0.21 ± 0.12	100.0
$C_3H_4N_2$	0.75	1.6 ± 0.2	0.53 ± 0.3	55.0 ± 27	70.7
3-pyCOO$^-$	8.3 ± 3.7	3.2 ± 0.4	0.16 ± 0.03	0.85 ± 0.09	1.9

the Schiff base complex, at an ionic strength of 1.0 M ($LiClO_4$), K_{OS} is not expected to make significant contribution. At the high [H^+] conditions employed for the investigation of K_{app} values, the conjugate base is a minor component and $K_{app} = K_1$. The values of K_1 obtained for N_3^- and C_5H_5N are 35 and 70 M^{-1}, respectively. With nicotonic acid the apparent equilibrium constant was 1.6 ± 0.2 M^{-1} at any [H^+] studied.

Kinetic Studies. Although there are two replaceable aquo ligands in the complex $Cr(salen)(H_2O)_2^+$, both spectrophotometric equilibrium and stopped-flow kinetic studies revealed that only monosubstitution occurred preferentially. The observed rate constants for the equilibration k_{obsd} for the reactions of N_3^-, NCS^-, C_5H_5N, imidazole, and 3-pyCOO$^-$ with *trans*-$Cr(salen)(H_2O)_2^+$ have been analyzed as a function of [H^+] and [ligand] at 30 °C and I = 1.0 M ($LiClO_4$). At any given [H^+], k_{obsd}, varied linearly with ligand concentration for all the five ligands as shown in Figure 1. Similarly the second-order rate constants for anation reactions (obtained from the slopes of the linear plots) exhibited an inverse first-order dependence on [H^+] in the region investigated as shown in the example for X^{n-} = NCS^- as in Figure 2. On the basis of the evidence obtained for the hydrolysis behavior of the metal ion (with a K_a of 9.1 × 10^{-9} M), eq 10 can be

$$\begin{tikzcd}
\mathrm{Cr(salen)(H_2O)_2^+} + X^{n-} \arrow[r, shift left, "k_1"] \arrow[d, shift left, "K_a"] & \mathrm{Cr(salen)(H_2O)X^{(1-n)+}} + \mathrm{H_2O} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "K_a'"] \\
\mathrm{Cr(salen)OH(H_2O)} + X^{n-} \arrow[r, shift left, "k_2"] \arrow[u, shift left, "{[H^+]}"] & \mathrm{Cr(salen)(OH)X^{n-}} + \mathrm{H_2O} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left, "{[H^+]}"]
\end{tikzcd} \qquad (10)$$

proposed. Since [H^+] ≫ K_a (9.1 × 10^{-9} M), the rate law for (10) can be derived and k_{obsd} may be expressed as in (11). The

$$k_{obsd} = k_{-1} + \frac{k_{-2}K_a'}{[H^+]} + \left(k_1 + \frac{k_2K_a}{[H^+]}\right)[X^{n-}] \qquad (11)$$

rearrangement of eq 11 using the apparent equilibrium constants, K_{app}, gives (12) and (13), and K_{app} is obtained from

$$k_1 + k_2K_a[H^+]^{-1} = (K_{app} + 1)^{-1}K_{app}k_{obsd}[X^{n-}]^{-1} \qquad (12)$$

$$k_{-1} + k_{-2}K_a'[H^+]^{-1} = k_{obsd}(K_{app} + 1)^{-1}[X^{n-}]^{-1} \qquad (13)$$

(14) by kinetic methods. By means of a nonlinear least-squares

$$K_{app} = (k_1 + k_2K_a/[H^+])[X^{n-}](k_{-1} + k_{-2}K_a'/[H^+])^{-1} \qquad (14)$$

fit of k_{obsd} according to (11), with use of Los Alamos computer program and suitable subroutines, the values of k_1, k_{-1}, k_2K_a, $k_{-2}K_a'$, and K_{app} as a function of [H^+] were obtained. The equilibrium constants obtained by the kinetic and spectrophotometric methods were in satisfactory agreement (within a factor of 2) considering the differences in the two methods giving rise to $K_{OS}K_{IS}$ and $K_{OS} + K_{OS}K_{IS}$, respectively. The values obtained for k_1, k_{-1}, k_2K_a, and $k_{-2}K_a'$ obtained for the reactions of the various X^{n-} with the diaquo salen complex are listed in Table II along with the equilibrium constant K_1 obtained from kinetic methods at 30 °C, and I = 1.0 M ($LiClO_4$). The fit of the experimental data according to (11) was generally within ±15% of the error. For the computation of the rate parameters for the reactions with weak acids as ligands, an allowance for their degree of dissociation according to (6) was made. The analysis of the kinetic data with the assumption that the protonated ($C_5H_5NH^+$ and imidazole H^+) and neutral (HN_3 and 3-pyCOOH) species were reactive gave a poor statistical fit. This is not surprising in view of the unfavorable electrostatic interaction expected between monopositive and neutral or positively charged species.

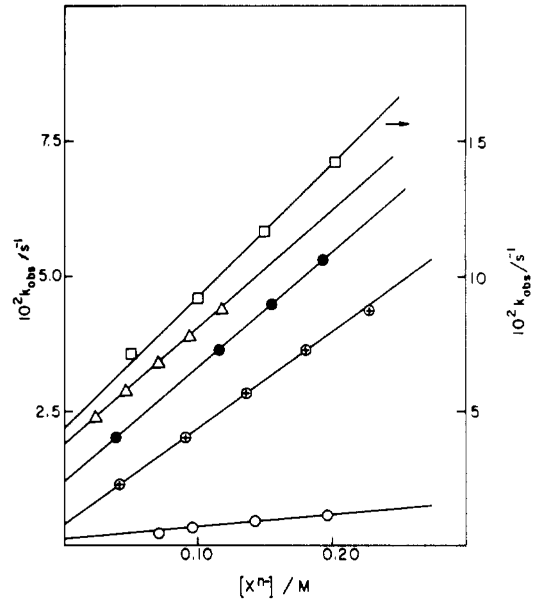

Figure 1. Ligand dependence of the rate of equilibration, k_{obsd} at [H^+] = 2 × 10^{-6} M and X^{n-} = N_3^- (⊕), NCS^- (□), C_5H_5N (●), $C_3H_4N_2$ (△) and 3-pyCOO$^-$ (○), T = 30 °C, I = 1.0 M ($LiClO_4$), for $Cr(salen)(H_2O)_2^+$.

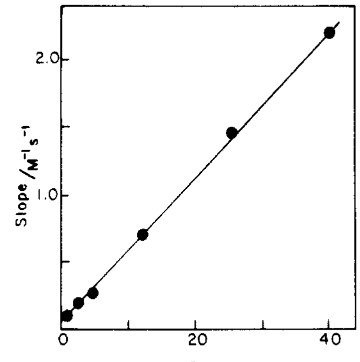

Figure 2. $[H^+]^{-1}$ dependence of the forward rates in NCS^- anation of $Cr(salen)(H_2O)_2^+$ at 30 °C, I = 1.0 M ($LiClO_4$).

The data in Table II show clearly the invariance of k_1 for the range of ligands investigated. Further a linear relation between log k_{-1} and −log K_1 has been observed as shown in Figure 3, with a slope of 0.94 ± 0.05 when the case with imidazole has not been included in the computation. Such a linear free energy relation along with the trends in the k_1 values were used as diagnostic parameters in the assignment of the mechanism for the diaquo derivative of the Cr(III)–salen complex.

A similar analyses of the rate data on the reactions of the complex $Cr(acacen)(H_2O)_2^+$ with NCS^-, N_3^-, and pyridine established the applicability of rate law in (11) under the [H^+]

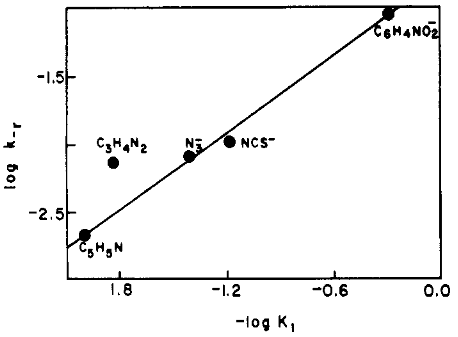

Figure 3. Linear free energy relationship between the log (aquation rate) and –log (equilibrium constant) for the substitution reactions of Cr(salen)$(H_2O)_2^+$, at $T = 30$ °C, $I = 1.00$ M ($LiClO_4$) (error bars not shown).

Table III. Rate Parameters and the Ratio $k_1/k_{-1} = K_1$ (Equilibrium Constant) for the Reactions of X^{n-} with Cr(acacen)$(H_2O)_2^+$ and Its Conjugate Base at 30 °C and $I = 1.0$ M ($LiClO_4$)

	10^2k_{-1}, s^{-1}	$10^8k_{-2}K_a'$, M s^{-1}	k_1, M^{-1} s^{-1}	$10^7k_2K_a$, s^{-1}	K_1, M^{-1}
NCS⁻	6.5 ± 4.5	4.3 ± 2.3	0.18 ± 0.005	14.6 ± 2.7	2.8
N_3^-	1.2 ± 0.4	98 ± 34	0.11 ± 0.006	1.2 ± 0.3	0.9
C_5H_5N	7.9 ± 0.5	10.5 ± 2.6	0.24 ± 0.08	4.4[a]	3.0

[a] This parameter was used as a fixed quantity in computation.

region investigated (3.16×10^{-6}–3.16×10^{-5} M). The anation rates with NCS⁻ showed a $[H^+]^{-1}$ dependence. On the basis of the results on the salen diaquo derivative, the $[H^+]^{-1}$ dependence of k_{obsd} was attributed to a conjugate-base pathway with a $K_a \ll 3.16 \times 10^{-6}$ M. The first-order dependence of k_{obsd} on [free ligand] without any rate saturation but with a positive intercept supports that, in the case of acacen complex, the first step is an equilibration. The analysis of k_{obsd} as a function of [free ligand] and $[H^+]^{-1}$ as in Figures 4 and 5 supported (11). The nonlinear least-squares fit of k_{obsd} gave the values of the corresponding k_1, k_{-1}, k_2K_a, $k_{-2}K_a'$, and K for all the three ligands as in Table III. The values obtained and the trends observed are comparable to those evaluated for the salen derivatives.

Discussion

The dissociation constant for *trans*-Cr(salen)$(H_2O)_2^+$ has been determined to be 9.1×10^{-9} M, which is 1 order of magnitude smaller than that for the corresponding Co(III) derivative.[16] With undistorted octahedral complexes of Cr(III) and Co(III), generally the aquo ligands coordinated to Cr(III) are found to be more acidic. The inverse trends in the values of K_a of the salen complexes of Co(III) and Cr(III) are perhaps the result of varying degrees of distortion in the ground-state geometries of Co(III) and Cr(III) complexes. With the Cr(III) center being about 5% larger in size than Co(III),[4] the distortion will be more manifest in the former case. Even with the Co(III) derivative (which is more acidic) only one pK_a could be measured. It is not surprising, therefore, that in the case of Cr(III)–salen complex, there was only one dissociation constant in that $[H^+]$ region for the Cr(III) complex. Previous studies have shown that the conjugate base isolated from a solution of Cr(salen)$(H_2O)_2^+$ at $[H^+] = 10^{-11}$ M analyzed for Cr(salen)(OH).

The $[H^+]^{-1}$ dependence of k_{obsd} for the reaction of Cr(salen)$(H_2O)_2^+$ with the conjugate bases of strong acids like thiocyanate indicates the participation of a conjugated base pathway.[17] It is generally observed in the substitution chemistry of Co(III) and Cr(III) complexes that the conjugate bases of the metal complexes undergo more facile substitution than the corresponding aquo complexes with coordinated hydroxide or amide labilizing other ligands in the coordination sphere due to their π-donating ability. The special features of the substitution reaction of Cr(salen)$(H_2O)_2^+$ at various pH values lie, however, in the relative magnitudes of the rate constants. Whereas Cr(III) is known to be an inert metal ion in aquo ligand environments, the rate constants for the equilibration in this study in the region of 0.01–3 s^{-1} show the effects of distortion in a ground-state geometry on the substitution behavior of the metal ion.

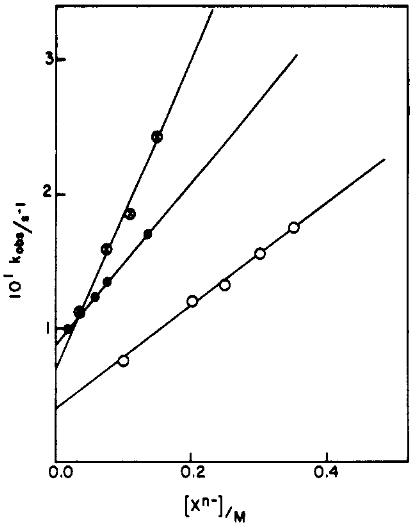

Figure 4. [Ligand] dependence of the rate of equilibration k_{obsd} at $[H^+] = 10^{-5}$ M and $X^{n-} = N_3^-$ (⊗), NCS⁻ (○) and C_5H_5N (●), $T = 30$ °C, $I = 1.0$ M ($LiClO_4$) for Cr(acacen)$(H_2O)_2^+$.

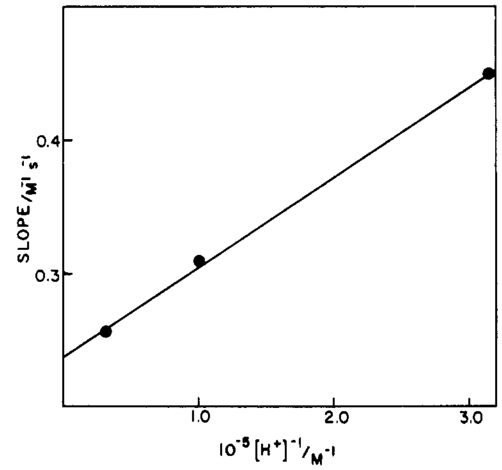

Figure 5. $[H^+]^{-1}$ dependence of the forward rates in NCS⁻ anation of Cr(acacen)$(H_2O)_2^+$, 30 °C, $I = 1.0$ M ($LiClO_4$).

There was no rate saturation with increasing concentration of the free ligand for any of the ligands investigated. Therefore, the bimolecular rate coefficient k_1 does not provide a compelling evidence for a dissociative mechanism for the reactions of Cr(salen)$(H_2O)_2^+$. However, when the dissociative interchange mechanism with a low ion-pairing constant is involved, the bimolecular rate law is often encountered. In the present study an outer-sphere complexation between 1+,1– and 1+,0 charged electrolytes at an ionic strength of 1.0 M has to be invoked. Since ion-pairing constants in such cases are not expected to be large, the bimolecular rate law for the k_1 path is not entirely inconsistent with an I_d mechanism.

On the other hand, the small variation in the values of k_1 for a series of ligands with widely differing nucleophilicities is suggestive of a dissociative interchange process I_d for the

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[16] Costa, G.; Mestroni, G.; Tauzher, G. *J. Chem. Soc., Dalton Trans.* **1972**, 450.

[17] Wells, P. R. *Chem. Rev.* **1963**, *63*, 172.

mechanism of the aquo ligands substitution in the Cr(salen)$(H_2O)_2^+$ complex also. The X-ray structure of this complex also reveals that one of the water molecules is more weakly bound to Cr(III) compared to the other. This is expected to lead not only to a single-stage kinetic behavior but also to dissociative mechanism for the substitution of water. The linearity of the plot of $-\log K_1$ against $\log k_{-1}$ (Figure 3) with a slope of 0.94 ± 0.05 and invariant k_1 provides compelling evidence for an I_d mechanism expected on the basis of X-ray structure of Cr(salen)$(H_2O)_2^+$. The deviation of the imidazole system from the linear plot of $\log k_{-1}$ against $-\log K_1$ may be due to more than one reason. The charge characteristics of imidazole as compared to nicotinic acid, azide, and thiocyanate may well be one of the contributing factors for the deviation. Imidazole is also known to exhibit complex behavior due to the formation and isomerization of a carbon-bonded isomer when bonded to Ru(II).[18] Pyridine correlates with the linear free energy relationship plot for mononegatively charged ligands as in Figure 3. This is perhaps a consequence of the low charges on the reactants.

It can be seen from Table II that, unlike k_1, the k_2K_a values vary markedly for the salen complexes. If the conjugate base of Cr(salen)$(H_2O)_2^+$ were to be six-coordinate Cr(salen)OH(H_2O) in solution, the wide variation in k_2K_a values cannot be reconciled with any dissociative mechanism for the reactions of X^{n-}. Since an I_d mechanism is assigned to the substitution of Cr(salen)$(H_2O)_2^+$, the coordination of hydroxide in place of water may give rise to increasing degree of dissociative character of the $Cr-OH_2$ bond. If on the other hand such a labilization by hydroxide were to give rise to a five-coordinate Cr(salen)(OH) in solution also, the reaction with X^{n-} may well be one of a bimolecular addition to yield a six-coordinate product. The open square-pyramidal geometry enforced by the salen ligand on the conjugate base Cr(salen)OH would facilitate a biomolecular addition mechanism. Since all the five ligands studied are more nucleophilic than water, six-coordinate products are likely to be stable.

The assignment of bimolecular addition process would necessitate marked variations of k_2K_a in the order thiocyanate (5.16×10^{-7} s^{-1}), N_3^- (0.23×10^{-7} s^{-1}), and py (0.21×10^{-7} s^{-1}). This is the same as the order of their nucleophilicities 4.4 (NCS^-), 4.0 (N_3^-), and 3.6 (C_5H_5N) and the parameters E_n/H (1.83 (NCS^-), 0.25 (N_3^-), and 0.17 (C_5H_5N)) formulated by Edwards.[17] On similar arguments, the large k_2K_a value in the case of imidazole (5.5×10^{-6} s^{-1}) may be explained as due to the high nucleophilicity of the ligand.

Thus, a variation of k_2K_a over 275 times for the range of ligands studied is more in keeping with a bimolecular addition process than a nucleophilic substitution mechanism for the reactions of the conjugate base of Cr(salen)$(H_2O)_2^+$. A higher nucleophilicity and π-donating characteristics of hydroxide over water will tend to disfavor any I_a mechanism if the conjugate base were to be six-coordinate in solution. On the arguments that a complex of the formulation Cr(salen)(OH) has already been isolated in the solid state, from the kinetic data five-coordination for the conjugate base of Cr(salen)$(H_2O)_2^+$ in solution and a bimolecular addition mechanism may be inferred. Although rates of diffusion-controlled limit may be expected for the bimolecular addition reactions of transient intermediates, the formation of five-coordinate species with definite life time (rather than a transient), which may form outer-sphere complexes with X^{n-}, will explain the relative magnitude of second-order rate coefficient k_2 (2.3–600 M^{-1} s^{-1}) and its dependence on the nature of X^{n-}.

The behavior of the acacen complex Cr(acacen)$(H_2O)_2^+$ is very similar to that of a Cr(III)–salen derivative with respect to the substitution characteristics. It has been established that with Co(III)–Schiff base complexes the acacen ligand stabilizes five-coordination to a greater extent than salen does. However, high-frequency conductometric titrations[9] establish that, unlike in the case of Co(III) derivative, acacen does indeed form the six-coordinate diaquo derivative with Cr(III). The similarities in the rate law and the magnitude of the rate constants, k_{obsd}, also indicate that the Cr(III)–acacen derivative has a strong structural resemblance to the Cr(III)–salen derivative. The bimolecular rate constant k_1 for the diaquo–acacen complex is similar to that for Cr^{III}(salen)$(H_2O)_2^+$. All three ligands, viz., thiocynate, azide, and pyridine, have k_1 terms within a factor of 2. With k_2K_a term also, thiocyanate and azide show marked variations (12 times). The aquation rate constants k_{-1} and $k_{-2}K_a'$ are larger in magnitude in the case of acacen derivative as compared to the salen case. This may be the result of an increased degree of π delocalization when acacen is the equatorial ligand. The influence of ligand environment on the substitution rate of Cr(III) has already been shown by the marked variation in the water exchange rates of $Cr(H_2O)_6^{3+}$ (4.16×10^{-7} s^{-1}) and of $Cr(NH_3)_5H_2O^{3+}$ (9.60×10^{-5} s^{-1})[19] at 25 °C. However, ligand field strength effects may offer only partial contribution to the substitution lability of Cr(salen)$(H_2O)_2^+$ and Cr(acacen)$(H_2O)_2^+$ since comparable systems like cyclam and tetracyano derivatives do not give rise to high aquo ligand substitution rates.[20,21] The anchimeric assistance prevalent in the other kinetically labile Cr(III) system reported, viz., Cr(EDTA)H_2O^-,[22–24] is also not applicable for the Cr(III)–Schiff base complexes investigated. Therefore, the kinetic lability observed in the system may be attributed largely to the ground-state distortion effects.

Thus summarizing our observations, the present study presents one of the few examples in the aqueous chemistry of chromium(III) wherein a high kinetic lability resulting from ground-state distortion has been demonstrated.

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Registry No. Cr(salen)$(H_2O)_2^+$, 47248-17-9; Cr(acacen)$(H_2O)_2^+$, 73347-24-7; NCS^-, 302-04-5; N_3^-, 14343-69-2; C_5H_5N, 110-86-1; $C_3H_4N_2$, 288-32-4; 3-pyCOOH, 59-67-6.

Supplementary Material Available: Tables of the pseudo-first-order rate constants, k_{obsd}, under various conditions (9 pages). Ordering information is given on any current masthead page.

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(18) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F., Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.

(19) Duffy, N. V.; Earley, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 272. Stranks, D. R.; Swaddle, T. W. *Ibid.* **1972**, *94*, 8357.

(20) Campi, E.; Ferguson, J.; Tobe, M. L. *Inorg. Chem.* **1970**, *9*, 1781.

(21) Schaap, W. B.; Krishnamurthy, R.; Wakefield, D. K.; Coleman, W. F. "Coordination Chemistry"; Kirschner, S.; Ed.; Plenum Press: New York, 1969; p 177.

(22) Ogino, H.; Watanabe, T.; Tanaka, N. *Chem. Lett.* **1974**, 91.

(23) Sulfab, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2388.

(24) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1979**, *18*, 2497 and references therein.