Figure 1. Plot of $\bar{n}$ vs. χ_{DMF} at 25 °C and $[H^+] \approx 10^{-3}$ M. The solid line is the least-squares fit of the data.

0.069, respectively. The value of Q_1 for NCS^- is 4.50 ± 0.06.[3]

Unfortunately, no other values of Q have been measured for cis-$Cr(C_2O_4)_2(OH_2)_2^-$. Hence, comparisons and trends cannot be discussed yet.

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Mechanistic Information from the Effect of Pressure on the Kinetics of Some Anation Reactions of Aquopentaamminecobalt(III), -rhodium(III), and -chromium(III) Ions in Acidic Aqueous Solution[1]
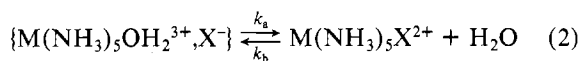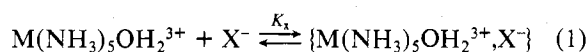
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The anations of $Co(NH_3)_5OH_2^{3+}$ by Cl^- and SO_4^{2-}, $Rh(NH_3)_5OH_2^{3+}$ by Cl^-, and $Cr(NH_3)_5OH_2^{3+}$ by NCS^- were studied in acidic aqueous solution as a function of nucleophile concentration and pressure up to 1.5 kbar. No kinetic evidence for the participation of ion pairs could be found. The volumes of activation for the anation reactions are +1.4 ± 0.8 (μ = 2 M, 60 °C), +2.3 ± 1.8 (μ = 2 M, 60 °C), +3.0 ± 0.7 (μ = 2 M, 60 °C), and −4.9 ± 0.6 cm^3 mol^{-1} (μ = 1 M, 50 °C), respectively. These values were used in conjunction with the volumes of activation for the corresponding aquation reactions to estimate the overall volume changes incurred in the reactions. The latter could then be compared with independently obtained values of $\Delta\bar{V}$. The results are discussed in terms of an interchange mechanism and compared with data reported in the literature.

Introduction

The anation reactions of Co(III), Rh(III), and Cr(III) pentaammine complexes have been extensively studied for a wide range of organic and inorganic entering ligands in aqueous medium.[4-21] During the anation process, the ammonia ligands are tightly bound to the metal ion[22] and, in most cases,[20] are substitution inert. These reactions are generally accepted[5] to proceed according to an interchange mechanism:[7,23]

$$M(NH_3)_5OH_2^{3+} + X^- \underset{}{\overset{K_x}{\rightleftharpoons}} \{M(NH_3)_5OH_2^{3+},X^-\} \quad (1)$$

$$\{M(NH_3)_5OH_2^{3+},X^-\} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} M(NH_3)_5X^{2+} + H_2O \quad (2)$$

where M = Co(III), Rh(III), or Cr(III) and X = Cl, Br, NCS, CH_3COO, etc. Burnett[18] suggested that ion triplets also participate in the above mechanism at high concentrations of X^-, although this suggestion was criticized in later work.[24]

In many of these studies, K_x, k_a, and k_b were estimated from the dependence of k_{obsd} (observed first-order rate constant) on $[X^-]$. Various independent methods have been used[19,25-27] to estimate values for K_x. These measurements were usually restricted to low ionic strengths, whereas the kinetic studies

Table I. Kinetic Data for Anation Reactions of M(NH$_3$)$_5$OH$_2$$^{3+}$ Ion in Aqueous Acidic Solution

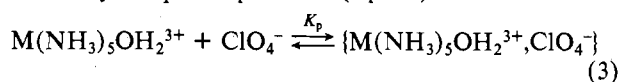| M	entering ligand	temp, °C	μ, M	k_a, s^{-1}	K_x, M^{-1}	k_aK_x,^{a} M^{-1} s^{-1}	ref
Co(III)	NCS$^-$	25	0.5	2.9 × 10^{-7}	4.5	1.3 × 10^{-6}	4
		45	0.5	1.6 × 10^{-5}	0.43	6.8 × 10^{-6}	7
	Cl$^-$	45	0.5	2.1 × 10^{-5}	3.1	6.5 × 10^{-5}	7
		45	1.0	3.5 × 10^{-5}	1.21	4.2 × 10^{-5}	24
	CH$_3$COO$^-$	70	1.0	1.6 × 10^{-4}	5.2	8.7 × 10^{-4}	12, 37
	C$_2$O$_4$$^{2-}$	70	1.0	4.0 × 10^{-4}	9.2	3.7 × 10^{-3}	11
Rh(III)	Cl$^-$	65	1.5	3.4 × 10^{-3}	0.18	6.2 × 10^{-4}	17
		65	4.0	3.6 × 10^{-3}	0.25	9.0 × 10^{-4}	15
	CH$_3$COO$^-$	65	1.0	1.5 × 10^{-3}	0.35	5.2 × 10^{-4}	38
		70	1.0	1.5 × 10^{-4}	6.4	9.5 × 10^{-4}	39
	C$_2$O$_4$$^{2-}$	69	1.0	2.6 × 10^{-4}	6.5	1.7 × 10^{-3}	34
Cr(III)	NCS$^-$	45	0.1	3.1 × 10^{-5}	10.1	3.1 × 10^{-4}	36
		50	1.0	6.1 × 10^{-4}	0.68	4.2 × 10^{-4}	21
	Cl$^-$	45	0.1	2.2 × 10^{-5}	2.8	6.3 × 10^{-5}	36
		50	1.0			7.0 × 10^{-5}	21
	HC$_2$O$_4$$^-$	50	1.0	6.2 × 10^{-4}	1.2	7.2 × 10^{-4}	20
	C$_2$O$_4$$^{2-}$	50	1.0	6.2 × 10^{-4}	4.5	2.8 × 10^{-3}	20

^{a} Calculated second-order rate constant, valid at low values of [entering ligand] only when significant ion pairing occurs.

were generally conducted at higher, constant ionic strengths due to the necessity of providing a sufficiently high [X$^-$]. As both K_x and the rate constants are particularly sensitive to ionic strength, equating these values can lead to substantial errors.

The trends in k_a and its activation parameters for various X$^-$ have frequently been used to distinguish between I$_a$ and I$_d$ mechanisms.[5,28,29] On the basis of this and other arguments, an I$_d$ mechanism was assigned to anation reactions of Co-(NH$_3$)$_5$OH$_2$$^{3+}$,[7-11,13,24,30-32] an I$_a$ mechanism to most of the anation reactions of Rh(NH$_3$)$_5$OH$_2$$^{3+}$,[10,14-17,19,33,34] and both I$_a$ and I$_d$ mechanisms to anation reactions of Cr-(NH$_3$)$_5$OH$_2$$^{3+}$.[5,21,35,36]

A weakness of this discrimination procedure is that the calculation of k_a depends on knowing the value of K_x, which varies substantially for similarly charged species, as illustrated by the examples quoted in Table I. For example, the values of K_x for ion pairing with chloride ion vary from 0.18 to 3.1 M^{-1}. Although differences in experimental conditions may partially account for these fluctuations, they do lead to large variations in the values of k_a and subsequently make the differentiation between I$_a$ and I$_d$ mechanisms extremely difficult. Swaddle et al.[28] recently proposed that the enthalpies of activation for k_a provide better criteria to distinguish between the associative and dissociative characters of interchange reactions. Unfortunately, large fluctuations in the reported values of k_a are naturally reflected in the values of the activation parameters[40,41] and make quantitative comparisons almost impossible. Although it should be mentioned that in many nonaqueous solvents where ion pairing is readily observable, this method of distinguishing between mechanisms is very effective.

Pavelich and co-workers[19] recently pointed out the serious shortcomings of using kinetic data for anation reactions of octahedral transition-metal complexes, obtained at high constant ionic strength, to elucidate mechanistic information.[17,42] Evidence exists[18,25] that a component of the inert salt (generally perchlorate ion), used to maintain the high constant ionic strength, is capable of forming ion pairs with the complex ion to such an extent that the observed values of k_a and K_x are actually composite quantities (eq 3-5). Pavelich et al.[19] developed a low, variable ionic strength approach, involving

$$M(NH_3)_5OH_2{}^{3+} + ClO_4{}^- \overset{K_p}{\rightleftharpoons} \{M(NH_3)_5OH_2{}^{3+},ClO_4{}^-\} \tag{3}$$

$$(k_a)_{obsd} = k_aK_x/(K_x - K_p) \tag{4}$$

$$(K_x)_{obsd} = (K_x - K_p)/(1 + K_p\mu) \tag{5}$$

considerable computer-assisted data fitting, to determine the values of the activity coefficients and ion-pairing constants for the anation of Rh(NH$_3$)$_5$OH$_2$$^{3+}$ by chloride ion.

We have adopted a different approach to the problem. A recent investigation in this laboratory[43] illustrated how the use of a volume profile diagram can lead to a better understanding of the intimate mechanism for the aquation reactions of Co(III) and Cr(III) pentaammine complexes. The results of such an investigation for a series of anation reactions at high, constant ionic strength are now reported.

Experimental Section

Material. The following complexes were prepared, recrystallized, and converted to perchlorate salts according to standard procedures: [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$,[44] [Co(NH$_3$)$_5$SO$_4$]ClO$_4$,[45] [Rh(NH$_3$)$_5$O-H$_2$](ClO$_4$)$_3$,[46,47] [Rh(NH$_3$)$_5$Cl](ClO$_4$)$_2$,[46] [Cr(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$,[48,49] [Cr(NH$_3$)$_5$NCS](ClO$_4$)$_2$.[50] [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ was prepared by treating [Co(NH$_3$)$_5$CO$_3$]NO$_3$[51] with concentrated HClO$_4$ and recrystallizing from 0.1 M HClO$_4$. Chemical analyses (Hoechst AG, Analytical Laboratory, Frankfurt) and visibile–UV spectra were in agreement with the theoretical values and with those reported in literature, respectively. Chemicals were of reagent grade, and doubly distilled water was used throughout the investigation.

Kinetic Measurements. The reactions were followed "in situ" in two different Zeiss PMQ II spectrophotometers equipped with a thermostated (±0.1 °C) high-pressure cell[52] and a thermostated (±0.05 °C) normal, commercial cell holder, respectively. The kinetics were studied at wavelengths corresponding to the maximum absorbance changes and were monitored for at least 10 half-lives. The observed first-order rate constants, k_{obsd}, were calculated from plots of ln ($A_t - A_\infty$) vs. t, where A_t and A_∞ are the absorbances at time t and infinity, respectively. These plots proved to be linear for at least 2 or 3 half-lives.

Results and Discussion

The rates of equilibration of Co(NH$_3$)$_5$OH$_2$$^{3+}$ with chloride ion are summarized in Table II as a function of [Cl$^-$] and pressure. Significantly, plots of k_{obsd} vs. [Cl$^-$] are linear within experimental error limits. In other words, these results, especially the more accurate data at atmospheric pressure, enable us to establish a maximum value for $(K_x)_{obsd}$ of less than 0.1 M^{-1}, otherwise meaningful curvature would have been observed in the plots. This is in contrast to the results reported in earlier studies[7,24] (see Table I) but is in agreement with other data reported recently for a similar system.[10] The values of k_1 and k_2 included in Table II were estimated by using a linear least-squares treatment according to the equation $k_{obsd} = k_1 + k_2$[Cl$^-$] and represent the (reverse) aquation and (forward) anation reactions, respectively. The values of k_1 at 60 and 70 °C (P = 1 bar), calculated in this manner, are in good agreement with the rate constants for aquation determined

Table II. Rate Data for the Reaction

$$Co(NH_3)_5OH_2{}^{3+} + Cl^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Co(NH_3)_5Cl^{2+} + H_2O^e$$

temp, °C	pressure, bar	$10^4 k_{obsd}$, s^{-1} [Cl$^-$], M								$10^4 k_1$, s^{-1}	$10^4 k_2$, M^{-1} s^{-1}	$10^4 k_1$,^{c} s^{-1}
		0.0^a	0.25^b	0.5^b	0.75^b	1.0^b	1.25^b	1.5^b	1.75^b			
70	1	1.83 1.91^d	3.37	5.25	5.63	7.96	8.37	10.6	11.5	1.97 ± 0.21	5.52 ± 0.22	1.87 ± 0.04
60	1	0.66 0.63	0.98	1.58	1.90	2.38	2.83	3.13	3.55	0.65 ± 0.03	1.70 ± 0.03	0.65 ± 0.02
	500	0.72 0.71	0.67 0.68	1.50	1.76	2.63 2.42	2.84	3.04 3.24	3.87 3.40	0.60 ± 0.10	1.80 ± 0.08	0.72 ± 0.01
	1000	0.96 0.92	0.85	1.12	1.53	2.06	2.71	3.35	3.70	0.62 ± 0.16	1.68 ± 0.14	0.94 ± 0.02
	1500	0.90 1.05	1.07	1.28	2.26 1.82	2.42	2.91	3.14 3.16	3.69 3.47	0.83 ± 0.09	1.61 ± 0.08	0.98 ± 0.08

^{a} Data obtained by using [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$ as starting material. ^{b} Data obtained by using [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ as starting material. ^{c} Calculated from k_{obsd} at [Cl$^-$] = 0.0 M (i.e., aquation rate data). ^{d} [H$^+$] = 0.01 M. ^{e} [Co(III)] = 7.5 × 10^{-3} M, [H$^+$] = 0.1 M, ionic strength = 2.0 M (LiClO$_4$), wavelength = 555 nm; chloride added as LiCl.

Table III. Rate Data for the Reaction

$$Co(NH_3)_5OH_2{}^{3+} + SO_4{}^{2-} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Co(NH_3)_5SO_4{}^+ + H_2O^{a,b,f}$$

[SO$_4{}^{2-}$], M	$10^4 k_{obsd}$, s^{-1} (60 °C)				$10^6 k_{obsd}$, s^{-1} (25 °C, 0.1 M H$^+$)
	0.1 M H$^+$ ^{c}	0.1 M H$^+$ ^{c}	0.01 M H$^+$	0.001 M H$^+$	
0.0	0.62^d				
0.05	0.91				
0.10	1.08	1.08^e	0.86	0.91	2.43
0.15	1.46				
0.20	1.66	1.58^e	1.44	1.39	2.89
0.25	1.94				
0.30	2.26	2.12^e	1.79	1.98	2.99
0.35	2.42				
0.40	2.71	2.66^e	2.30	2.53	3.62
0.45	2.84				
0.50	3.13	3.13^e	2.95	2.96	4.30
0.55	3.46				
0.60	3.62	3.67^e		3.44	4.73
$10^4 k_1$, s^{-1}	0.64 ± 0.03		0.36 ± 0.09	0.41 ± 0.05	0.018 ± 0.001
$10^4 k_2$, M^{-1} s^{-1}	5.04 ± 0.07		5.04 ± 0.27	5.11 ± 0.12	0.046 ± 0.004

^{a} A sampling technique was used for these reactions, and each aliquot analyzed spectrophotometrically. ^{b} Data obtained by using [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ as starting material. ^{c} Data presented in Figure 1. ^{d} Data obtained by using [Co(NH$_3$)$_5$SO$_4$]ClO$_4$ as starting material. ^{e} See ref 82. ^{f} At atmospheric pressure, [Co(III)] = 1 × 10^{-2} M, ionic strength = 2.0 M (NaClO$_4$), wavelength = 540 nm; sulfate added as Na$_2$SO$_4$.

directly in the absence of added chloride ion and also with the corresponding rate data reported elsewhere.[53] At higher pressures, the larger experimental errors in k_{obsd} are magnified in the k_1 values. Thus, only the directly determined, more accurate aquation rate data will be considered later in the discussion.

As a result of our inability to find any kinetic evidence for ion-pair formation in the chloride anation of Co(NH$_3$)$_5$OH$_2{}^{3+}$, we investigated the corresponding reaction with sulfate ion for which ion-pair formation constants of 10.6 M^{-1} (31.1 °C)[54] and 11.2 M^{-1} (24.5 °C),[55] at 1 M ionic strength, were reported. The rate data are summarized as a function of [SO$_4{}^{2-}$], [H$^+$], and temperature at atmospheric pressure in Figure 1 and Table III and as a function of [SO$_4{}^{2-}$] at various pressures in Table IV. Within experimental errors, plots of k_{obsd} vs. [SO$_4{}^{2-}$] (viz. Figure 1) are again linear under all conditions. The intercept, calculated from a least-squares fit of the data in Figure 1 over the range 0.05 ≤ [SO$_4{}^{2-}$] ≤ 0.60 M (60 °C and [H$^+$] = 0.1 M), is (0.64 ± 0.03) × 10^{-4} s^{-1} which is in good agreement with the directly determined aquation value at zero [SO$_4{}^{2-}$] of 0.62 × 10^{-4} s^{-1}. For the calculations of k_1 and k_2 at higher pressures (see Table IV), the values of k_{obsd} at [SO$_4{}^{2-}$] = 0.1 M were taken from data in which [Co(NH$_3$)$_5$SO$_4$]ClO$_4$ was used as starting material. Larger absorption changes are involved under such conditions, which makes the determination

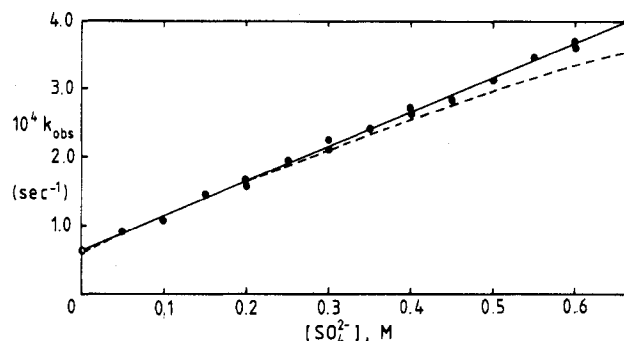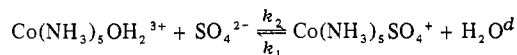**Figure 1.** k_{obsd} vs. [SO$_4{}^{2-}$] for the reaction Co(NH$_3$)$_5$OH$_2{}^{3+}$ + SO$_4{}^{2-}$ ⇌ Co(NH$_3$)$_5$SO$_4{}^+$ + H$_2$O (temperature 60 °C; ionic strength = 2.0 M; wavelength = 540 nm; [Co(III)] = 0.01 M; [H$^+$] = 0.1 M): ●, [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ as starting material; ○, [Co(NH$_3$)$_5$SO$_4$]ClO$_4$ as starting material.

of k_{obsd}, especially at higher pressures, more accurate. As shown in Table IV, the k_1 values so obtained are in reasonable agreement with those measured directly at [SO$_4{}^{2-}$] = 0.0 M.

The absence of any kinetic evidence for the participation of an ion-pair intermediate in the above reaction encourged us to have a closer look at the data in Figure 1. The value of the rate constant for the aquation of Co(NH$_3$)$_5$SO$_4{}^+$ was

Table IV. Rate Data for the Reaction

$$Co(NH_3)_5OH_2{}^{3+} + SO_4{}^{2-} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Co(NH_3)_5SO_4{}^+ + H_2O^d$$

temp, °C	pressure, bar	$10^4 k_{obsd}$, s⁻¹ [SO₄²⁻], M 0.0^a	0.1^a	0.2^b	0.3^b	0.4^b	0.5^b	0.6^b	$10^4 k_1$, s⁻¹	$10^4 k_2$, M⁻¹ s⁻¹	$10^4 k_1$,^{c} s⁻¹
30									0.104		
								0.100			
								0.090^a			
								0.091^a			
	1500							0.101			
								0.103^a			
60	10	0.81	1.38	1.90	2.70	3.62	3.69	4.13	0.88 ± 0.10	5.66 ± 0.32	0.88 ± 0.06
		0.90				2.88					
		0.92									
	500	1.13	1.54	2.06	2.72	3.53	3.76	4.87	0.94 ± 0.10	6.07 ± 0.27	1.04 ± 0.12
		1.10		1.79^a			4.17	4.40			
		0.90									
	1000	1.16	1.73	2.27	2.87	3.68	4.16	4.49	1.19 ± 0.06	5.76 ± 0.18	1.19 ± 0.04
		1.21		2.42							
	1500	1.31	1.89	2.16	2.63	3.54	3.89	4.68	1.34 ± 0.10	5.01 ± 0.29	1.36 ± 0.04
		1.39		2.35			3.99	3.85			
		1.38									

^{a} Data obtained by using [Co(NH₃)₅SO₄]ClO₄ as starting material. ^{b} Data obtained by using [Co(NH₃)₅OH₂](ClO₄)₃ as starting material. ^{c} Calculated from k_{obsd} at [SO₄²⁻] = 0.0 M (i.e., aquation rate data). ^{d} At elevated pressures; [Co(III)] = 1 × 10² M, [H⁺] = 0.1 M, ionic strength = 2.0 M (NaClO₄), wavelength = 540 nm; sulfate added as Na₂SO₄.

subtracted from all the other k_{obsd} values to obtain the "forward" anation rate constant. The resulting values were submitted to the usual inverse plot of k^{-1} vs. [SO₄²⁻]⁻¹ and yielded an ion-pair formation constant of 0.33 M⁻¹ and an interchange rate constant of 16.6 × 10⁻⁴ s⁻¹. With these values, a theoretical curve for k_{obsd} vs. [SO₄²⁻] could be calculated and is represented by the dashed line in Figure 1. At low [SO₄²⁻] the plot is almost linear in good agreement with the experimental data. However, at higher [SO₄²⁻] the curve deviates significantly from the data points so that it must be concluded that if ion pairing does occur, then the formation constant must be substantially smaller than 0.33 M⁻¹. Despite an unusual [SO₄²⁻] dependence of the rate of aquation of Rh(NH₃)₅SO₄⁺, Monacelli[57] used part of his kinetic data to derive an ion-pair formation constant for {Rh(NH₃)₅OH₂³⁺, SO₄²⁻} of 0.65 M⁻¹ at 65 °C and 4 M ionic strength. This value helps to confirm that the formation constant for 3+/2− ion pairs at high ionic strength could indeed be small.

Nevertheless, this surprisingly low $(k_x)_{obsd}$ value could result from the partial protonation of SO₄²⁻ in 0.1 M acid (pK of HSO₄⁻ is 1.57 (μ = 1.0) and 1.30 (μ = 4.0) at 65 °C).[57] However, as shown in Table III, k_{obsd} remains a strictly linear function of [SO₄²⁻] at 0.01 and 0.001 M acid concentrations, such that the k_2 values are independent of [H⁺]. The decrease in k_1 with decreasing acidity is consistent with the known enhancement of the aquation process at lower pH.[57] Temperature is a further variable which may affect the value of $(K_x)_{obsd}$, but once again our data at 25 °C in Table III confirm the linearity of the k_{obsd} vs. [SO₄²⁻] plot. A change in reaction medium from perchlorate to nitrate ions, in which significant ion-pair formation has been reported for a similar system,[56] did not have any measurable influence on the k_{obsd} values and the [SO₄²⁻] dependence of k_{obsd} at 60 °C and 0.1 M acid. All these results underline our inability to detect any kinetic evidence for the formation of ion pairs during the anation of Co(NH₃)₅OH₂³⁺ by sulfate ion.

Another representative system involves the chloride anation of Rh(NH₃)₅OH₂³⁺, for which the data at 50 °C and normal pressure are presented in Figure 2. This figure is included to illustrate the type of experimental scatter obtained in such measurements. The reaction is extremely slow, especially at 50 °C, and absorbance changes were monitored for periods of 13–90 h by using an "in situ" spectrophotometric procedure.
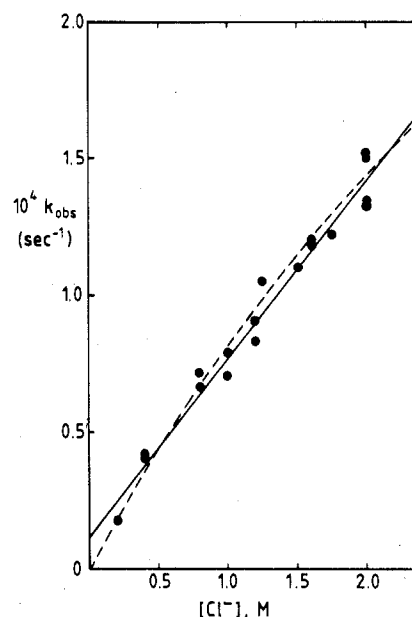

Figure 2. k_{obsd} vs. [Cl⁻] for the reaction Rh(NH₃)₅OH₂³⁺ + Cl⁻ → Rh(NH₃)₅Cl²⁺ + H₂O (temperature 50 °C; ionic strength = 2.0 M; wavelength = 360 nm; [H⁺] = 0.1 M; [Rh(III)] = 5 × 10⁻³ M).

A least-squares analysis of these data resulted in an intercept of (1.2 ± 0.4) × 10⁻⁵ s⁻¹ and a slope of (6.5 ± 0.3) × 10⁻⁵ M⁻¹ s⁻¹ at 50 °C. The former can only be ascribed to the aquation of Rh(NH₃)₅Cl²⁺, but it is larger than the extrapolated value obtained under other experimental conditions from direct studies of this reaction.[14,58-60] The difference may be largely due to experimental errors in k_{obsd} and possibly to a nonlinear relation between k_{obsd} and [Cl⁻]. For examination of the latter, an inverse plot of $k_{obsd}{}^{-1}$ vs. [Cl⁻]⁻¹ was constructed from which an ion-pair formation constant of 0.15 ± 0.5 M⁻¹ and an interchange rate constant of (6.3 ± 2.1) × 10⁻⁴ s⁻¹ were estimated; see the calculated (dashed) curve in Figure 2. These values are in close agreement with previously reported data,[15,17] and the error limits are symptomatic of such studies (viz., Poë and co-workers[17] report an ion-pair formation constant of 0.09 ± 0.04 M⁻¹ and an interchange rate constant of (7.0 ± 3.0) × 10⁻³ s⁻¹ for this reaction at 35 °C and an ionic strength of

Table V. Rate Data for the Anation of $Rh(NH_3)_5OH_2^{3+}$ by Chloride Ion[a]

pressure, bar	$10^4 k_{obsd}$, s⁻¹ [Cl⁻], M								$10^4 k_1$, s⁻¹	$10^4 k_2$, M⁻¹ s⁻¹
	0.1	0.25	0.5	0.75	1.0	1.25	1.5	1.75		
1	0.29	0.63	1.26 1.35	1.96	2.45	2.96	3.48	4.21	0.11 ± 0.05	2.31 ± 0.05
500	0.23	0.70 0.91	1.08	1.42	2.40	2.67 2.59	3.33	3.91 3.63	0.13 ± 0.09	2.07 ± 0.09
1000	0.26 0.32	0.59	1.16 1.21	1.69	2.27	2.94	3.28	3.85 3.29	0.14 ± 0.09	2.04 ± 0.09
1500	0.46	0.68	1.16	1.87	2.04 2.13	2.91	3.00 3.33	3.50	0.26 ± 0.10	1.93 ± 0.09

[a] Data obtained by using $[Rh(NH_3)_5OH_2](ClO_4)_3$ as starting material: $[Rh(III)] = 5 \times 10^{-3}$ M, $[H^+] = 0.1$ M, ionic strength = 2.0 M $(LiClO_4)$, wavelength = 360 nm; chloride added as LiCl; 60 °C.

Table VI. Rate Data for the Anation of $Cr(NH_3)_5OH_2^{3+}$ by Thiocyanate Ion[a]

pressure, bar	$10^4 k_{obsd}$, s⁻¹ [NCS⁻], M									$10^4 k_2$, M⁻¹ s⁻¹
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
10	0.36 0.47	0.58 0.47	0.96	1.11 0.96	1.48 2.03	1.92 2.06	2.18 2.51	2.31 2.36	2.68 3.12	3.18 ± 0.19
500	0.28	0.72	0.69	1.13 1.23	1.28	2.14	2.35	2.57	2.78	3.31 ± 0.22
1000	0.41	0.85	0.78	1.75 1.34	1.50	2.04	2.66	2.92	3.50	3.78 ± 0.28
1500	0.28	0.85 0.77	1.01 1.09	1.60	1.83	2.62	2.82	3.50	3.30 3.66	4.13 ± 0.18

[a] Data obtained by using $[Cr(NH_3)_5OH_2](ClO_4)_3$ as starting material. Acid was added at zero time to minimize the decomposition of thiocyanate.[45] $[Cr(III)] = 5 \times 10^{-3}$ M, $[H^+] = 0.1$ M, ionic strength = 1.0 M $(NaClO_4)$, wavelength = 485 nm; thiocyanate added as NaSCN; 50 °C.

1.5 M). Both lines in Figure 2 describe the data satisfactorily so that it is difficult to decide which treatment is preferable. As the application of pressure invariably reduces the value of the association constants[61–65] and because there are larger experimental errors involved in the measurements of k_{obsd} at elevated pressures, the results at 60 °C (Table V) are more conveniently described by the linear function $k_{obsd} = k_1 + k_2[Cl^-]$. It is important to mention that regardless of which treatment is used in such cases, the same volume of activation will emerge.

The anation of $Cr(NH_3)_5OH_2^{3+}$ by thiocyanate ion was chosen as it is one of the few known examples of such reactions for which a kinetically determined ion-pair formation constant has been reported.[21,36] The kinetic data are summarized in Table VI as a function of $[NCS^-]$ and pressure. However, plots of k_{obsd} vs. $[NCS^-]$ were again linear within experimental error, and no meaningful intercept was obtained. The value of k_2 at ca. 1 bar is close to that found in the literature[21,36] (see Table I). Experiments conducted at a lower ionic strength (see Table VII) indicated that a linear $[NCS^-]$ dependence of k_{obsd} still exists under these conditions and that k_2 decreases with decreasing ionic strength.

At this stage in the discussion it is clear that in none of the systems investigated were we able to detect ion-pair formation in the anation rate data at high ionic strength. The overall rate expression for reactions 1 and 2 is given by eq 6. If K_x

$$k_{obsd} = k_b + k_a K_x [X^-]/(1 + K_x [X^-]) \qquad (6)$$

is sufficiently small (<0.1 M), then $1 + K_x[X^-] \approx 1$, so that eq 6 takes the form of the linear empirical equation used to fit all the data in this investigation (i.e., $k_{obsd} = k_1 + k_2[X^-]$) and $k_1 = k_b$, while $k_2 = k_a K_x$. However, if reaction 3 is included in the reaction scheme, the overall rate expression is given by eq 7. A combination of eq 6 and 7 leads to the

$$k_{obsd} = k_b + \frac{k_a K_x [X^-]}{1 + K_x [X^-] + K_p [ClO_4^-]} \qquad (7)$$

Table VII. Rate Data for the Anation of $Cr(NH_3)_5OH_2^{3+}$ by Thiocyanate Ion at Low Ionic Strength[a]

pressure, bar	$10^5 k_{obsd}$, s⁻¹	$10^4 k_2$, M⁻¹ s⁻¹
10	5.59 6.26	2.96 ± 0.23
500	6.56 6.28	3.21 ± 0.09
1000	6.79 7.34	3.53 ± 0.19
1500	6.44 6.87	3.32 ± 0.15

[a] Data obtained by using $[Cr(NH_3)_5OH_2](ClO_4)_3$ as starting material. Acid was added at zero time to minimize the decomposition of thiocyanate.[45] $[Cr(III)] = 5 \times 10^{-3}$ M, $[H^+] = 0.1$ M, ionic strength = 0.3 M $(NaClO_4)$, wavelength = 485 nm, $[NaSCN] = 0.2$ M; 50 °C.

expressions given for $(k_a)_{obsd}$ and $(K_x)_{obsd}$ in eq 4 and 5, respectively. Since the observed values for K_x in this investigation are approximately zero, it follows from eq 5 that $K_p \simeq K_x$. This is in agreement with the results reported by Pavelich et al.[19] ($K_{ClO_4^-} \simeq K_{Cl^-} = 26.5$ M⁻¹) for the anation of Rh-$(NH_3)_5OH_2^{3+}$ by chloride ion at low ionic strength (<0.3 M). Ion association constants at zero ionic strength for ion pairs of the type $\{Rh(en)_2LX^{3+}, Y^{n-}\}$ have been calculated by using the Fuoss equation[66] to be $K_{ClO_4^-} = K_{Cl^-} = 17$ M⁻¹, which is comparable to the experimental values quoted above.[19] However, the Fuoss treatment predicts a value of 340 M⁻¹ for ion-pair formation with sulfate ion. This then rules out the possibility that $K_p \approx k_x$ for the anation by sulfate ion, and, according to eq 5, K_x must be very small but considerably larger than K_p. By analogy, we would have to conclude that if the same ratio exists between the K_x values at $\mu = 2$ M, then with $(K_x)_{obsd}$ for the $\{Co(NH_3)_5OH_2^{3+}, SO_4^{2-}\}$ ion pair estimated at <0.33 M⁻¹, $K_{Cl^-} \approx K_{SCN^-} \approx K_{ClO_4^-} < 0.02$ M⁻¹. It is perhaps worth commenting that formation constants of this order of magnitude are more in line with encounter complex formation

Table VIII. Activation Volumes for the Anation and Aquation Reactions of Co(III), Rh(III), and Cr(III) Pentaammine Complexes

reaction	temp, °C	[H⁺], M	ionic strength, M	$\Delta V^{\ddagger}_{exptl}$, cm³ mol⁻¹	remark
$Co(NH_3)_5OH_2^{3+} + Cl^-$	60	0.1	2.0	+1.4 ± 0.8	calcd from k_2 in Table II
$Co(NH_3)_5Cl^{2+} + H_2O$	60	0.1	2.0	−8.2 ± 1.6	calcd from k_1 ^{c} for k_{obsd} at [Cl⁻] = 0.0 M in Table II
	25	5 × 10⁻⁵	0.1	−10.6 ± 0.4	from ref 45
	60	0.1	0.1	−7.5 ± 1.0	from ref 53
$Co(NH_3)_5OH_2^{3+} + SO_4^{2-}$	60	0.1	2.0	+2.3 ± 1.8	calcd from k_2 in Table IV
$Co(NH_3)_5SO_4^+ + H_2O$	60	0.1	2.0	−8.2 ± 1.2	calcd from k_1 in Table IV
	60	0.1	2.0	−7.9 ± 0.3	calcd from k_1 ^{c} for k_{obsd} at [SO₄²⁻] = 0.0 M in Table IV
	25	5 × 10⁻⁵	0.1	−18.5 ± 0.7	from ref 45
$Rh(NH_3)_5OH_2^{3+} + Cl^-$	60	0.1	2.0	+3.0 ± 0.7	calcd from k_2 in Table V
$Rh(NH_3)_5Cl^{2+} + H_2O$	60	0.1	2.0	−14.5 ± 4.6	calcd from k_1 in Table V
$Cr(NH_3)_5OH_2^{3+} + NCS^-$	50	0.1	1.0	−4.9 ± 0.6	calcd from k_2 in Table VI
	50	0.1	0.3	−2.4 ± 1.3	calcd from k_2 in Table VII
$Cr(NH_3)_5NCS^{2+} + H_2O$	80	0.1	0.1	−8.6 ± 1.0	from ref 53

than ion-pair formation. We thus tend to favor a scheme in which ion-pair formation with ClO_4^- has no kinetic consequences at high ionic strength. This is in agreement with the insensitivity of the water-exchange rate constant[33] of Rh-$(NH_3)_5OH_2^{3+}$ for an increase in $[ClO_4^-]$ from 0.12 to 0.52 M and with arguments reported elsewhere.[57]

Since K_x is not known for the investigated systems, a direct comparison of the interchange rate constants (k_a) with the water exchange rate data[30,35] for $M(NH_3)_5OH_2^{3+}$ complexes (M = Co(III), Rh(III), Cr(III)) is not possible. To illustrate this important point, the anation of $Co(NH_3)_5OH_2^{3+}$ by sulfate ion should be considered. If the curve in Figure 1 is a true description of the experimental data, then the interchange rate constant (16.6 × 10⁻⁴ s⁻¹ at 60 °C) would be *larger* than the water-exchange rate constant (7.02 × 10⁻⁴ s⁻¹ at 60 °C). Thus on the basis of the arguments outlined before,[5] it must be concluded that the mechanism is of the I_a type in contrast to the generally accepted[7,9] notion of an I_d mechanism for such reactions. It follows that this comparison cannot reliably distinguish between an I_a and an I_d mechanism under such circumstances. Nevertheless, a comparison of the k_2 values for the anation of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ by chloride ion (Tables II and V) indicates that they are very similar but considerably smaller than those reported for the anation of $Co(NH_3)_5OH_2^{3+}$ by sulfate ion in Table IV. This tendency does emphasize the role played by ion-pair, or encounter-type, intermediates and the importance of the interchange mechanism. It should be kept in mind that even for very small ion-pair formation constants (i.e., <0.1 M⁻¹), ion pairs can still be present in sufficient quantities to provide the principal reaction route.

We now turn to the pressure dependence of the various rate constants in Tables II and IV–VII. Considering the experimental uncertainties in the values of k_1 and k_2, the plots of ln k vs. pressure are all linear, and the values of $\Delta V^{\ddagger}_{exptl}$, summarized in Table VIII, are independent of pressure. The values of k_1 and k_2 were not corrected for the compressibility of the solvent, since such corrections can only be made when the exact nature of the intimate mechanism is known. Our $\Delta V^{\ddagger}_{exptl}$ value for the aquation of $Co(NH_3)_5Cl^{2+}$ is in close agreement with those reported elsewhere.[45,53] The discrepancy between our value for the aquation of $Co(NH_3)_5SO_4^+$ and that reported by Swaddle and co-workers[45] is ascribed to differences in experimental conditions. Kinetic measurements were also performed under pressure at a lower ionic strength and at a lower acidity. $\Delta V^{\ddagger}_{exptl}$ at 60 °C was found to be −8.1 ± 0.6 (0.1 M acid and ionic strength 0.1 M) and −8.0 ± 0.4 cm³ mol⁻¹ (pH 4.5 and ionic strength 0.1 M), respectively (cf. corresponding values in Table VIII), implying that the remaining variable, temperature, is responsible for these deviations.

In general, $\Delta V^{\ddagger}_{exptl}$ consists of two components:[5,67,68] an intrinisic part, $\Delta V^{\ddagger}_{intr}$, due to alterations in bond lengths and angles during the formation of the transition state, and a solvation part, $\Delta V^{\ddagger}_{solv}$, resulting from variations in solvation, mainly due to electrostriction. For the anation ("an") reactions, a further complication arises in that $\Delta V^{\ddagger}_{exptl}$ is generally a composite quantity consisting of a volume change, $\Delta \bar{V}_{IP}$, incurred upon ion-pair formation and $\Delta V^{\ddagger}_{IC}$, the volume of activation for the rate-determining interchange step. Thus

$$(\Delta V^{\ddagger}_{exptl})_{an} = \Delta \bar{V}_{IP} + \Delta V^{\ddagger}_{IC}$$
$$= \Delta \bar{V}_{IP} + (\Delta V^{\ddagger}_{intr})_{IC} + (\Delta V^{\ddagger}_{solv})_{IC}$$

It follows that a detailed discussion of these terms is necessary in order to deduce the sign and magnitude of the mechanistically indicative term $(\Delta V^{\ddagger}_{intr})_{IC}$.

Since under our experimental conditions we were unable to determine $\Delta \bar{V}_{IP}$ from the pressure dependence of K_{IP}, assumptions must be made as to the significance of this value. Numerous examples in the literature[61-65] illustrate that $\Delta \bar{V}_{IP}$ is positive and decreases with increasing temperature. For instance, in the formation of the ion pair $\{Co(NH_3)_6^{3+}, SO_4^{2-}\}$, $\Delta \bar{V}_{IP}$ decreases from +10.8 to +4.5 cm³ mol⁻¹ on increasing the temperature from 15 to 40 °C.[69] The positive sign of $\Delta \bar{V}_{IP}$ is generally attributed to a reduction in the extent of electrostriction resulting from a partial neutralization of charges. An increase in ionic strength also decreases[70] the value of $\Delta \bar{V}_{IP}$. The anation of $Co(NH_3)_5OH_2^{3+}$ by SO_4^{2-} was investigated at 60 °C and 2 M ionic strength so that $\Delta \bar{V}_{IP}$ is expected to be virtually zero or, at most, a very small positive quantity. In the other three systems studied, the anating nucleophile was a singly charged anion, viz., Cl⁻ and NCS⁻, and the values of $\Delta \bar{V}_{IP}$ are expected to be even smaller[70] than for the anation by sulfate ion under the prevailing experimental conditions. Analogously, $\Delta \bar{V}_{IP}$ for ion-pair formation with perchlorate ion must also be equally small. Therefore it may be concluded that the contribution of $\Delta \bar{V}_{IP}$ toward $(\Delta V^{\ddagger}_{exptl})_{an}$ (an = anation) is very small and probably negligible.

For the interchange step, $(\Delta V^{\ddagger}_{solv})_{IC}$ is expected to be small since no significant changes in the overall charge are involved after ion pairing. $(\Delta V^{\ddagger}_{solv})_{IC}$ will become even smaller at higher temperatures and ionic strengths for the same reasons outlined above, such that this term should also be of little significance here. It follows that $(\Delta V^{\ddagger}_{intr})_{IC}$ is the dominant term in the expression for $(\Delta V^{\ddagger}_{exptl})_{an}$. Furthermore, it is known to be virtually insensitive to temperature and ionic strength.

The values of $(\Delta V^{\ddagger}_{exptl})_{an}$, summarized in Table IX, seem to be in accord with the above mentioned arguments. Their absolute values are small, consistent with the generally accepted interchange mechanism.[5,67] For this type of mechanism, it is inappropriate to make allowances for the compressibility

Table IX. Summary of Volume Data for the Systems $M(NH_3)_5OH_2^{3+} + X^{n-} \rightleftharpoons M(NH_3)_5X^{(3-n)+} + H_2O^a$

M	X^{n-}	$(\Delta V^{\ddagger}_{exptl})_{an}$	$(\Delta V^{\ddagger}_{exptl})_{aq}$	$\Delta \bar{V}^b$	$\Delta \bar{V}^c$
Co	Cl^-	$+1.4 \pm 0.8$	-8.2 ± 1.6	$+9.6 \pm 2.4$	$+11.6$ (45)
Co	SO_4^{2-}	$+2.3 \pm 1.8$	-7.9 ± 0.3	$+10.2 \pm 2.1$	$+19.2$ (45)
Rh	Cl^-	$+3.0 \pm 0.7$	-14.5 ± 4.6	$+17.5 \pm 5.3$	$+18.3$ (71)
Cr	NCS^-	-4.9 ± 0.6^d			
Cr	NCS^-	-2.4 ± 1.3^e	-8.6 ± 1.0^f	$+6.2 \pm 2.3$	$+9.8$ (43)

^{a} Data taken from Table VIII; $[H^+] = 0.1$ M; 60 °C; ionic strength = 2.0 M; volumes quoted in cm^3 mol^{-1}. ^{b} $\Delta \bar{V} = (\Delta V^{\ddagger}_{exptl})_{an} - (\Delta V^{\ddagger}_{exptl})_{aq}$. ^{c} Data reported in literature: references quoted in parentheses. ^{d} 50 °C; ionic strength = 1.0 M. ^{e} 50 °C; ionic strength = 0.3 M. ^{f} 80 °C; ionic strength = 0.1 M.

of the ionic medium. The similarity between the values of $\Delta V^{\ddagger}_{exptl}$ for the anation of $Co(NH_3)_5OH_2^{3+}$ by Cl^- and SO_4^{2-} seems to verify that $\Delta \bar{V}_{IP}$ and $(\Delta V^{\ddagger}_{solv})_{IC}$ are indeed very small. In addition, the increase in $\Delta V^{\ddagger}_{exptl}$ for the anation of $Cr(NH_3)_5OH_2^{3+}$ by NCS^- on decreasing the ionic strength from 1.0 to 0.3 M is also in accord with the outlined arguments. The few high-pressure experiments performed at 30 °C (see Table IV) illustrate the insensitivity of $(\Delta V^{\ddagger}_{exptl})_{an}$ to temperature, in line with the above arguments. The values of $(\Delta V^{\ddagger}_{exptl})_{an}$ at high ionic strength (i.e., first four entries in Table IX) are therefore considered to represent $(\Delta V^{\ddagger}_{intr})_{IC}$. A direct comparison with the values of $\Delta V^{\ddagger}_{exptl}$ for the water-exchange reactions of these complexes is now possible. Stranks et al.[67,72] recently made use of similar comparisons[73] to determine the nature of the interchange process involved in the anation of cis-$Co(en)_2(OH_2)_2^{3+}$ by oxalate.

Hunt and Taube[30] reported a $\Delta V^{\ddagger}_{exptl} = 1.2 \pm 0.2$ cm^3 mol^{-1} at 25 and 35 °C for the water-exchange reaction of $Co(NH_3)_5OH^{3+}$ and interpreted[35] this as evidence for an I_d mechanism. This value is very close to that reported here for the interchange steps in the anation reactions of $Co(NH_3)_5OH_2^{3+}$ with Cl^- and SO_4^{2-} (see Table IX) and emphasizes the I_d character of these reactions. This complies with earlier findings[7,9] and recently reported results.[10,13,72] A similar agreement exists between the $\Delta V^{\ddagger}_{exptl}$ values for the water-exchange reaction of $Cr(NH_3)_5OH_2^{3+}$ (viz., -5.8 ± 0.2 cm^3 mol^{-1} at 25 °C[35]) and the anation by NCS^- (Table IX), such that an I_a mechanism[5,35] can also be assigned to the latter reaction. Sykes and co-workers[21] recently presented arguments in favor of an I_d mechanism for the $Cr(III)$ reactions based on the magnitude of the interchange rate constant which could be successfully determined from the observed curvature in the k_{obsd} vs. $[NCS^-]$ plot. However, as we were unable to observe this phenomenon, our arguments must be based on the value of $\Delta V^{\ddagger}_{exptl}$. $\Delta V^{\ddagger}_{exptl}$ for the interchange step of the anation of $Rh(NH_3)_5OH_2^{3+}$ by Cl^-, quoted in Table IX, is not in agreement with the value reported[35] for the corresponding water-exchange reaction of -4.1 ± 0.4 cm^3 mol^{-1} at 35 °C, which was considered as evidence for an I_a mechanism. Our result is more in line with those for the anation of $Co(NH_3)_5OH_2^{3+}$, indicating that a dissociatively activated transition state is involved. In other words, bond stretching must play a significant role, which is in keeping with the conclusions of other investigations.[34,39,74] Furthermore, the ratio (interchange rate constant/solvent-exchange rate constant) determined at low ionic strength[19] also suggests an I_d mechanism is operative, although this evidence alone was not considered conclusive.

It must be emphasized that the values of $(\Delta V^{\ddagger}_{exptl})_{an}$ in Table IX are rather small and subject to considerable errors, so that the above conclusions should only be regarded as limited evidence for the suggested mechanisms. Some examples[72,75-77] are available in which similar arguments have been used to elucidate intimate reaction mechanisms.

The $\Delta V^{\ddagger}_{exptl}$ values for the aquation reactions are presented merely to underline earlier work on these systems[43,45] and are therefore not discussed in any further detail. By combination of $(\Delta V^{\ddagger}_{exptl})_{an}$ and $(\Delta V^{\ddagger}_{exptl})_{aq}$ (aq = aquation), the overall volume change ($\Delta \bar{V}$) can be calculated. With the exception of the sulfate reaction, these values shown in Table IX correlate well with those measured by dilatometry[45,78] or those calculated from the partial molar volumes[43,71] of the participating species at lower ionic strengths and temperatures.

To conclude, we feel obliged to make some comments concerning the validity of differentiating between I_a and I_d interchange mechanisms for anation reactions on the basis of interchange rate constants. In this respect, our results emphasize the importance of estimating the ion-pair formation constant under the same experimental conditions as were employed in the kinetic study.[79] It is known that ion-pair formation constants decrease substantially on increasing the ionic strength (see eq 5), so that investigations carried out at lower ionic strength would improve the probability of detecting and accurately determining the value of K_x kinetically.[19] However, this places an upper limit on the concentration of the anating nucleophile and subsequently makes it virtually impossible to perform kinetic experiments, especially under high pressure. For systems in which only very small ion-pair formation constants can be derived, it would be safer not to try to distinguish between I_a and I_d mechanisms only on the basis of the interchange rate constant. On the other hand, more meaningful ion-pair formation constants have been reported for other systems[13,72] involving weak acids as ligands where H bonding can account for the strength of these interactions which are, in fact, not so sensitive to the charges involved. In such cases, distinctions could be made between I_a and I_d mechanisms on the basis of a comparison of the interchange rate constant with the solvent-exchange rate constant. The implication that ion-pair formation originates from dominant electrostatic interactions seems to be an oversimplification in these type of systems, and one surely has to think in terms of more specific interactions[80,81] to account for ion-pair formation. Although high ionic strengths (~ 2 M) are unfavorable in the kinetic determination of ion-pair formation constants, it has the advantage of reducing solvation contributions toward $\Delta V^{\ddagger}_{exptl}$ and so simplifies its interpretation. Our results once again emphasize the efficacy of high-pressure kinetics for the elucidation of intimate mechanisms in cases where the results of normal pressure kinetic studies are somewhat ambiguous.

Registry No. $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5SO_4^+$, 18661-07-9; $Rh(NH_3)_5OH_2^{3+}$, 15337-79-8; $Rh(NH_3)_5Cl^{2+}$, 15379-09-6; $Cr(NH_3)_5OH_2^{3+}$, 15975-

47-0; Cl⁻, 16887-00-6; SO₄²⁻, 14808-79-8; NCS⁻, 302-04-5.

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Mixed-Ligand Complexes of Copper(II) with Imidazole and Selected Ligands

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The formation constants have been measured for the mixed-ligand complexes MLA and MLA₂, where M = Cu(II), A = imidazole, and L = bipyridyl, histamine, glycine, aspartic acid, malonic acid, and 5-sulfosalicylic acid. The lower stability of the MLA₂ complexes as compared to that of MLA is attributed to the loss of π bonding resulting from the two cis-coordinated imidazoles being out of plane. Imidazole, unlike bipyridyl, does not enhance the affinity of Cu(II) for the oxygen donor sites of anionic ligands. In the series of mixed complexes studied the order of stability for the ligand L is glycine > aspartic acid > bipyridyl > malonic acid > 5-sulfosalicylic acid > histamine.

Introduction

The imidazole group of histidine is one of the important binding sites for Cu(II) in biological systems. X-ray, spectroscopy, and various other techniques show that the imidazole moiety binds Cu(II) in sperm whale myoglobin,[1a] bovine serum albumin,[1b] human albumin,[1c] hemocyanin,[1d] ceruloplasmin, and ribonuclease as well as in a number of other bimolecules.[1c] The effectiveness of the imidazole group to act as a metal binding site has been attributed to its great flexibility (the metal–N bond can lie up to 30° from the imidazole plane), its availability at physiological pH (pK ca. 7.0), and its capacity to form both σ and π bonds with metal ions.[2]

In recent years considerable research has been carried out on model mixed-ligand complexes in an effort to understand the nature of metal-ion complexation in biological systems. Studies on mixed-ligand complexes containing bipyridyl[3] and