TABLE II

COPPER TETRAGLYCINE EQUILIBRIUM CONSTANTS[a]

Log K_1	pk'_a	pk'_b	pk'_c	I, M	Temp, °C	Ref
5.13 ± 0.02	5.41 ± 0.02	6.81 ± 0.02	9.15 ± 0.05	0.10 ($NaClO_4$)	25.0	This work
5.4	5.6	6.77	9.0	0.10 (KNO_3)	24.9	12
4.93	5.45	6.91	9.23	0.16	25	14

[a] For detailed methods of calculation, order Document No. NAPS-00186 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Remit $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

TABLE III

THERMODYNAMIC FUNCTIONS AT 25° AND $I = 0.10\ M$

Reacn no.	Reacn	ΔG, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, cal deg^{-1} mol^{-1}
1	$H_2GGGG^+ \rightleftharpoons HGGGG + H^+$	4.33 ± 0.02	+0.18 ± 0.1	−13.9 ± 0.3
2	$HGGGG \rightleftharpoons GGGG^- + H^+$	10.75 ± 0.02	+10.40 ± 0.02	−1.2 ± 0.1
3	$Cu^{2+} + GGGG^- \rightleftharpoons CuGGGG^+$	−7.00 ± 0.02	−6.0 ± 0.6	+3.3 ± 2.0
4	$CuGGGG^+ \rightleftharpoons CuA + H^+$	7.38 ± 0.02	+7.5 ± 0.8	+0.4 ± 3
5	$CuA \rightleftharpoons CuB^- + H^+$	9.28 ± 0.02	+6.6 ± 0.3	−9.0 ± 1.0
6	$CuB^- \rightleftharpoons CuC^{2-} + H^+$	12.49 ± 0.05	+8.9 ± 0.3	−12.0 ± 1.2

tion and retention of a degree of solvent orientation contrast the much more effective charge neutralization in CuG^+ in which the copper ion is bound to the carboxyl group. In the latter complex the short-bond formation in the *xy* plane of coordination would also be expected to produce a greater degree of tetragonal distortion of the octahedral symmetry and freeing of the axial water molecules.[15] At higher pH, it is seen (Table III) that, as with the di- and triglycines, the labilization of the peptide hydrogen atoms as compared with the ligand molecule (reaction 2) is predominantly an enthalpy effect; the ΔH value for reaction 4 is less endothermic than that for reaction 2.

Thermodynamic functions for successive proton dissociation from H_2GGGG^+ are seen to be closely similar to the corresponding tri- and diglycine reactions.[2] The considerably more negative ΔS for reaction 1 as compared with reaction 2 is a consequence of the appreciable solvent-ordering properties of the zwitterion HGGGG, especially at the $-NH_3^+$, and also the greater internal structure of HGGGG as compared with $GGGG^-$. Removal of a proton from the zwitterion is more difficult than from the positive ion H_2GGGG^+ and this is reflected in the more endothermic enthalpy change for reaction 2 as compared with that for reaction 1. In the former, the fields associated with an anion and a cation have to be created.

In reaction 4, a proton dissociates from $CuGGGG^+$ which, by structure I, retains a degree of solvent-ordering properties. The entropy decrease predicted from changes in solvent structure will thus be moderately small. The positive contribution to ΔS resulting from the increased number of species will be compensated to some extent by the loss in freedom of the tetraglycine molecule as the multichelated CuA is formed from I. In reaction 5 the creation of the fields associated with the oppositely charged ions CuB^- and H^+ is characterized once more by an appreciable negative entropy change. Taking into account the experimental uncertainties, ΔH for reaction 5 is similar to that for reaction 4 in which the proton is removed from a positively charged ion. On the basis purely of electrostatic effects, ΔH_5 might have been expected to be more positive than ΔH_4. However, these reactions reflect not only the proton separation but also the breaking of a Cu–O, the making of Cu–N bonds, and concomitant structural rearrangement. For reaction 6, in which the proton is removed from a uninegative ion in the formation of CuC^{2-} and H^+, the additional work required is reflected in the more endothermic ΔH term.

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Kinetics of Aqueous Scandium(III) Perchlorate Hydrolysis and Dimerization[1]

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Received August 5, 1968

From the number and length of chemical relaxations observed in aqueous solutions of a trivalent metal perchlorate one can deduce the minimum number of hydrolysis and polymerization equilibria present and their respective rates. We report here such a relaxation method investigation of dilute aqueous scandium(III) perchlorate.

Experimental Section

American Potash and Chemical Corp. scandium oxide was dissolved in excess perchloric acid, and crystals of scandium(III) perchlorate appeared on cooling from perchloric acid and water.[2]

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[1] (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grant AF-AFOSR-476-66. (b) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **100**, 85 (1953).

TABLE I

EXPERIMENTAL RELAXATION TIMES, pH, AND CALCULATED CONCENTRATIONS IN AQUEOUS SCANDIUM(III) PERCHLORATE AT 25°

10^5c_0,[a] *M*	pH[b]	τ,[c] μsec	$10^5[H^+]$,[d] *M*	$10^6[Sc^{3+}]$,[d] *M*	$10^6[ScOH^{2+}]$,[d] *M*	$10^6[Sc(OH)_2^+]$,[d] *M*	$10^6[Sc_2(OH)_2^{4+}]$,[d] *M*	$10^6[HIn]$,[d] *M*
			E-Jump Data ($\mu < 5 \times 10^{-4}$ *M*)					
1.05	5.010	2.91	0.99	0.42	3.37	2.71	0.12	
3.16	4.876	2.06	1.35	1.54	9.07	5.34	0.88	
5.26	4.461	1.57	3.53	3.99	8.97	2.02	0.86	
7.37	4.378	1.21	4.29	5.84	10.8	2.00	1.25	
8.95	4.354	1.12	4.55	7.15	12.5	2.18	1.67	
			T-Jump Data ($\mu = 0.1$ *M*)					
63.6	3.652	860	26.8	61.0	18.1	0.53	3.49	7.93
106	3.656	840	26.6	101	30.1	0.90	9.74	7.88
176	3.662	750	26.2	165	50.1	1.52	26.9	7.82
269	3.673	682	25.6	248	77.1	2.39	63.7	7.70
490	3.636	610	27.9	443	126	3.60	171	8.10
490	3.390	835	49.1	470	76.0	1.23	62.0	10.9
560	3.659	560	26.4	497	149	4.49	239	7.85

[a] Total molar concentration of scandium(III) perchlorate. [b] Glass electrode pH of the sample solution. [c] Average of six independent measurements of the chemical relaxation time at each concentration. Estimated error in each value of τ is approximately ±10%. [d] Molar concentrations calculated from eq 16–19 (and eq 20–22 in the case of the *E*-jump data) using $^*K_1 = 10^{-5.1}$, $^*K_2 = 10^{-5.1}$, and $^*K_{22} = 10^{4.03}$.

The precipitate was then recovered on a sintered-glass filter and dried for several hours at 70° and 0.1 Torr. A room-temperature aqueous stock solution was titrated with EDTA using Eriochrome Black T indicator.[3]

Sample solutions for the dissociation field effect or electric field jump (*E*-jump) relaxation method[4] experiments were prepared by adding, under nitrogen, small aliquots of stock solution to 10^{-7} ohm^{-1} cm^{-1} water at room temperature prepared by an electrophoretic ion-exclusion technique.[5] A Beckman 1019 pH meter was used to measure the pH of each sample solution.

Our *E*-jump apparatus has been described elsewhere.[6,7] Sudden application of a square, high-voltage wave of up to 12-μsec duration to the sample solution located between two bright platinum electrodes rapidly changes the electric field intensity *E* in the interelectrode region from 0 to ~10^5 V/cm. If the species on one side of the sample chemical equilibrium conduct electricity better than those on the other, the chemical equilibrium shifts in the direction of greater conductivity. Should it lie between ~0.3 and ~10.0 μsec, the time constant τ for this displacement, called the relaxation time, can be measured with an oscilloscope and a Wheatstone bridge, one arm of which is the sample solution cell.

Preparation of aqueous scandium(III) perchlorate solutions for Joule heating temperature jump (*T*-jump) relaxation method[8] experiments differed only slightly from the above: it was necessary to make the sample solutions 2×10^{-5} *M* in methyl orange to permit spectrophotometric measurements of τ at 520 mμ and also 0.1 *M* in $NaClO_4$ to permit rapid heating from 17 to 25 ± 1°. Our *T*-jump apparatus closely resembles that of Hammes and Fasella[9] modified for single-beam operation.[10]

Our experimental relaxation times, total scandium(III) perchlorate concentrations c_0, and measured values of pH are shown in Table I.

Results and Discussion

Kilpatrick and Pokras[2,11] measured hydrogen ion concentrations in ~2×10^{-2} *M* aqueous scandium(III) perchlorate solutions and interpreted their results in terms of a monomeric acid dissociation

$$Sc(H_2O)_6^{3+} \underset{}{\overset{k_1}{\rightleftharpoons}} Sc(H_2O)_5OH^{2+} + H^+ \quad (^*K_1 = k_1/k_{-1}) \quad (1)$$

and the dimerization

$$2Sc(H_2O)_5OH^{2+} \overset{k_2}{\rightleftharpoons} Sc_2(H_2O)_{10}(OH)_2^{4+} \quad (^*K_{22} = k_2/k_{-2}) \quad (2)$$

They explicitly excluded a second stage of monomeric hydrolysis

$$Sc(H_2O)_5OH^{2+} \overset{k_3}{\rightleftharpoons} Sc(H_2O)_4(OH)_2^+ + H^+ \quad (^*K_2 = k_3/k_{-3}) \quad (3)$$

They later collaborated with Biedermann and Sillén in a reinterpreation[12] of their data that invoked all three of the above equilibria plus formation of $Sc_3(OH)_4^{5+}$ and higher polymers. At 25° and at the ionic strengths shown in parentheses Kilpatrick and Pokras[2,11] reported $p(^*K_1) = 4.90$, $p(^\dagger K_{22}) = -3.90$ (0.5 *M*); $p(^*K_1) = 4.74$, $p(^\dagger K_{22}) = -3.82$ (0.1 *M*); and $p(^*K_1) = 4.61$, $p(^\dagger K_{22}) = -3.87$ (0.01 *M*). At 25° and 1.0 *M* ionic strength Biedermann, *et al.*,[12] reported that $^*K_1 = 10^{-5.1\pm0.2}$, $^*K_1{}^*K_2 = 10^{-10.2\pm0.5}$, and $^\dagger K_{22} = {}^*\beta_{22}/{}^*K_1{}^2 = 10^{-6.17}/10^{-10.2} = 10^{4.03}$. To simplify the notation we denote $Sc(H_2O)_6^{3+}$ hereafter by Sc^{3+}, $Sc(H_2O)_5OH^{2+}$ by $ScOH^{2+}$, etc.

Let us begin the interpretation of the kinetic data of Table I by assuming that we have all three equilibria, eq 1–3, present in our sample *T*-jump solutions as well as the methyl orange equilibrium. Then

$$HIn \overset{k_4}{\rightleftharpoons} H^+ + In^- \quad (K_{In} = k_4/k_{-4}) \quad (4)$$

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(8) See ref 4, p 969.

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for which Kolthoff[13] reported $pK_{In} = 3.39$ at $\mu = 0.1$ *M* and 25°. Assuming that the protolytic equilibria 1, 3, and 4 are rapidly established following a temperature jump compared to the dimerization equilibrium, eq 2, we derive for the relaxation time of this slow equilibrium

$$\tau^{-1} = 4k_2\alpha[\mathrm{ScOH^{2+}}] + k_{-2} \tag{5}$$

where

$$\frac{1}{\alpha} = 1 + \frac{[\mathrm{ScOH^{2+}}]\beta + [\mathrm{H^+}]}{{}^*K_1} + \frac{{}^*K_2 - [\mathrm{Sc(OH)_2{}^+}]\beta}{[\mathrm{H^+}]} \tag{6}$$

and

$$\beta = \frac{\dfrac{{}^*K_2}{[\mathrm{H^+}]} - \dfrac{[\mathrm{H^+}]}{{}^*K_1}}{1 + \dfrac{[\mathrm{In^-}]}{K_{In} + [\mathrm{H^+}]} + \dfrac{[\mathrm{ScOH^{2+}}]}{{}^*K_1} + \dfrac{[\mathrm{Sc(OH)_2{}^+}]}{[\mathrm{H^+}]}} \tag{7}$$

To calculate concentrations we use ${}^*K_1 = 10^{-5.1}$, ${}^*K_2 = 10^{-5.1}$, $\dagger K_{22} = 10^{4.03}$, $K_{In} = 10^{-3.39}$, and $[\mathrm{H^+}] = 10^{-pH}/0.83$, where the denominator of this last relation is the Debye–Hückel limiting law activity coefficient for H^+ at 25° and $\mu = 0.1$ *M*. Figure 1 is a τ^{-1} *vs.* $4\alpha[\mathrm{ScOH^{2+}}]$ plot of the data of Table I. The least-squares straight line through the data points has a slope $k_2 = 3.0 \times 10^6\ M^{-1}\ \mathrm{sec^{-1}}$ and an intercept $k_{-2} = 1.1 \times 10^3\ \mathrm{sec^{-1}}$. The quotient $\dagger K_{22} = k_2/k_{-2} = 10^{3.44}$ (titrimetric[12] $\dagger K_{22} = 10^{4.03}$). The reported uncertainty[12] in $p({}^*K_1)$, 5.1 ± 0.2, may account for this discrepancy in $\dagger K_{22}$ since $\dagger K_{22}$ involves ${}^*K_1$ to the reciprocal second power.

The magnitude of k_2 does not depend critically upon the above choice of equilibrium constants. To show this we assume instead, as did Kilpatrick and Pokras originally, that the second monomeric hydrolysis, eq 3, is not present and use ${}^*K_1 = 10^{-4.74}$, $\dagger K_{22} = 10^{3.82}$, and $K_{In} = 10^{-3.39}$. We require eq 5 again but now

$$\frac{1}{\alpha} = 1 + \frac{[\mathrm{ScOH^{2+}}]\beta' + [\mathrm{H^+}]}{{}^*K_1} \tag{8}$$

and

$$\beta' = \frac{-\dfrac{[\mathrm{H^+}]}{{}^*K_1}}{1 + \dfrac{[\mathrm{In^-}]}{K_{In} + [\mathrm{H^+}]} + \dfrac{[\mathrm{ScOH^{2+}}]}{{}^*K_1}} \tag{9}$$

A slope–intercept plot yields this time $k_2 = 8.5 \times 10^5\ M^{-1}\ \mathrm{sec^{-1}}$, $k_2 = 1.1 \times 10^3\ \mathrm{sec^{-1}}$, and $\dagger K_{22} = k_2/k_{-2} = 10^{2.89}$ (titrimetric[2,11] $\dagger K_{22} = 10^{3.82}$). The discrepancy in $\dagger K_{22}$ values is greater than that found in the preceding calculation but is insufficient to warrant rejecting the two-equilibrium interpretation[2,11] in favor of the multiple-equilibrium interpretation of Biedermann, *et al.*[12] Thus we assign k_2 the average value $2 \times 10^6\ M^{-1}\ \mathrm{sec^{-1}}$.

Eventually, the rate constant $k_2 = 2 \times 10^6\ M^{-1}\ \mathrm{sec^{-1}}$ may prove useful in testing the suggestion[14] that the specific rate of dimer formation could be predicted once the water-exchange rate for the monomeric form, in this case $\mathrm{ScOH^{2+}}$, is known. The fact that this k_2 is not a great deal smaller as rate constants go than the specific rate[15] $k_2' \cong 4.8 \times 10^7\ M^{-1}\ \mathrm{sec^{-1}}$ for the reaction

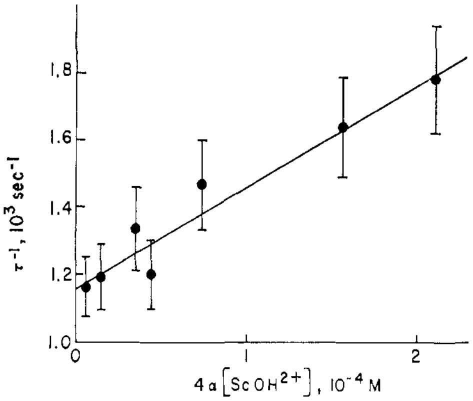

Figure 1.—Plot of the reciprocal of the temperature-jump relaxation time *vs.* the product $4\alpha[\mathrm{ScOH^{2+}}]$ where α is defined by eq 6 of the text. The diagonal through the experimental points is a least-squares straight line of slope $k_2 = 3.0 \times 10^6\ M^{-1}\ \mathrm{sec^{-1}}$.

$$\mathrm{Sc^{3+}} + \mathrm{L^-} \underset{}{\overset{k_2'}{\rightleftharpoons}} \mathrm{ScL^{2+}} \tag{10}$$

where L^- is the monovalent murexide anion and $\mu = 0.1$ *M* at 12°, suggests that the two reactions, eq 2 and 10, may have a common rate-determining step. However, such a step is not necessarily the splitting out of a first-coordination-sphere water molecule since in the similar case of gallium(III) the first-order ligand-penetration rate constant for reaction of $SO_4{}^{2-}$ with Ga(III) is only 30 sec^{-1} [16] whereas the water-exchange rate is 10^4 sec^{-1}.[17]

Having related the *T*-jump relaxation times of Table I to dimerization of $\mathrm{ScOH^{2+}}$, let us turn now to the reactions responsible for the much shorter *E*-jump relaxation times also given in Table I. If two monomeric hydrolysis steps occur with the values of ${}^*K_1$ and ${}^*K_2$ reported by Biedermann, *et al.*,[12] their relaxation times could be approximated using estimated values of the diffusion-controlled rate constants k_{-1} and k_{-3} along with the equation

$$\tau_{1,2}{}^{-1} = \frac{\alpha_{11} + \alpha_{22}}{2}\left[1 \pm \sqrt{1 - \frac{4(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})}{(\alpha_{11} + \alpha_{22})^2}}\right] \tag{11}$$

where

$$\alpha_{11} = k_1 + k_{-1}([\mathrm{H^+}] + [\mathrm{ScOH^{2+}}]) \tag{12}$$

$$\alpha_{12} = k_{-1}([\mathrm{H^+}] + [\mathrm{ScOH^{2+}}]) \tag{13}$$

$$\alpha_{21} = k_3 - k_{-3}[\mathrm{Sc(OH)_2{}^+}] \tag{14}$$

$$\alpha_{22} = k_3 + k_{-3}([\mathrm{H^+}] + [\mathrm{Sc(OH)_2{}^+}]) \tag{15}$$

For instance, for $c_0 = 5.26 \times 10^{-5}$ *M* and pH 4.46, we proceed with the iterative solution of the equations

$${}^*K_1 = \frac{[\mathrm{ScOH^{2+}}][\mathrm{H^+}]}{[\mathrm{Sc^{3+}}]} \tag{16}$$

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$$^*K_2 = \frac{[\mathrm{Sc(OH)_2}^+][\mathrm{H}^+]}{[\mathrm{ScOH}^{2+}]} \tag{17}$$

$$^\dagger K_{22} = \frac{[\mathrm{Sc_2(OH)_2}^{4+}]}{[\mathrm{ScOH}^{2+}]^2} \tag{18}$$

$$c_0 = [\mathrm{Sc}^{3+}] + [\mathrm{ScOH}^{2+}] + [\mathrm{Sc(OH)_2}^+] + 2[\mathrm{Sc_2(OH)_2}^{4+}] \tag{19}$$

$$\mu = \frac{1}{2}(9[\mathrm{Sc}^{3+}] + 4[\mathrm{ScOH}^{2+}] + [\mathrm{Sc(OH)_2}^+] + 16[\mathrm{Sc_2(OH)_2}^{4+}] + [\mathrm{H}^+] + 3c_0) \tag{20}$$

$$-\log \gamma_{\mathrm{H}^+} = 0.509\sqrt{\mu} \tag{21}$$

$$[\mathrm{H}^+] = \frac{10^{-\mathrm{pH}}}{\gamma_{\mathrm{H}^+}} \tag{22}$$

Using $^*K_1 = 10^{-5.1}$, $^*K_2 = 10^{-5.1}$, and $^\dagger K_{22} = 10^{4.03}$ we find that $\mu = 3.01 \times 10^{-4}\ M$, $[\mathrm{H}^+] = 3.53 \times 10^{-5}\ M$, $[\mathrm{Sc}^{3+}] = 3.99 \times 10^{-5}\ M$, $[\mathrm{ScOH}^{2+}] = 8.97 \times 10^{-6}\ M$, $[\mathrm{Sc(OH)_2}^+] = 2.02 \times 10^{-6}\ M$, and $[\mathrm{Sc_2(OH)_2}^{4+}] = 8.57 \times 10^{-7}\ M$. Now suppose we have the unfavorable case in which the ion-recombination rate constants have the plausible, nearly equal values $k_{-1} = 1.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{-3} = 1.7 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$. From eq 11–15 we would then calculate $\tau_1 = 1.12\ \mu\mathrm{sec}$ and $\tau_2 = 2.48\ \mu\mathrm{sec}$. Two relaxation times differing by even less than the present factor of 2.2 have been reported so our observation of only one τ in the microsecond time range cannot reasonably be ascribed to the two relaxations characterizing this system being too close to one another in time to be resolved.

There is however, another more plausible explanation for observing a single microsecond time range relaxation. The amplitude of one of the two relaxation effects is indetectably small. Thus Hammes and Steinfeld[10] noted that for a coupled system of two equilibria one of the two so-called normal variables y, which are proportional to the amplitudes of the respective signal voltage changes, is a sum of two large terms in the reactant concentrations, specific rates, reciprocal relaxation times, derivatives of the equilibrium constants with respect to the electric field intensity, etc. The other normal concentration variable is a difference of two such terms. It follows that the amplitude of this latter relaxation may be very small. Tentatively accepting this explanation for our E-jump data, we calculate concentrations from eq 16–22 and plot our data first in terms of

$$\tau^{-1} = k_1 + k_{-1}([\mathrm{H}^+] + [\mathrm{ScOH}^{2+}]) \tag{23}$$

and then in terms of

$$\tau^{-1} = k_3 + k_{-3}([\mathrm{H}^+] + [\mathrm{Sc(OH)_2}^+]) \tag{24}$$

Iterating to a constant value of $k_1/k_{-1} = {}^*K_1$, the least-squares plot of eq 23 yields $k_1 = 2.9 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-1} = 9.7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, and $^*K_1 = k_1/k_{-1} = 10^{-4.52}$ (titrimetric[12] $^*K = 10^{-5.1}$). A similar calculation using eq 24 yields $k_3 = 2.7 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-3} = 1.2 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, and $^*K_2 = k_3/k^{-3} = 10^{-4.65}$ (titrimetric[12] $^*K_2 = 10^{-5.1}$). Evidently it is impossible on the basis of this calculation to say which of the two hydrolysis equilibria, eq 1 and 3, is responsible for the observed E-jump relaxation.

Another explanation for an indetectable second microsecond time range relaxation would be a vanishingly small $\mathrm{Sc(OH)_2}^+$ concentration. This suggests a recalculation of specific rates from eq 23 using concentrations calculated from eq 16 and 18–22, deleting terms in $[\mathrm{Sc(OH)_2}^+]$ from eq 19 and 20, and using $^*K_1 = 10^{-4.61}$ and $^\dagger K_{22} = 10^{3.87}$. Iterating to a constant $^*K_1$, we obtain from a least-squares plot of τ^{-1} *vs.* $([\mathrm{H}^+] + [\mathrm{ScOH}^{2+}])$ the values $k_1 = 1.7 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-1} = 1.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, and $^*K_1 = k_1/k_{-1} = 10^{-4.78}$ (titrimetric[2,11] $^*K_1 = 10^{-4.61}$). The agreement of the $^*K_1$ values is good. Applying "Occam's razor," the kinetic data of Table I do not require eq 3 for their successful interpretation and the rate constant $k_{-1} = 1 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$.

From our similar values of k_1 for scandium and aluminum,[18] $k_1 \cong 10^5\ \mathrm{sec}^{-1}$, we predict that a linear relation between k_1 and ionic radius r ranging over many powers of 10 in k_1 for d^0 and d^{10} trivalent metal ions will not be found. Considering the superficial similarity of the splitting off of a proton and of a water molecule from the first coordination sphere of these ions, such a trend in k_1 analogous to that observed[19] for the rate-determining inner coordination sphere water loss in complex ion formation might have been expected.

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Naphthyridine Complexes of Group VIb Metal Carbonyls[1]

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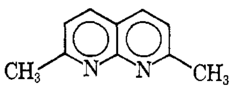
The coordination chemistries of the bidentate nitrogen heterocyclic ligands 1,10-phenanthroline and 2,2′-bipyridine which form five-member chelate ring systems have been extensively studied.[3–5] We wish to report the preparation and characterization of group VIb metal carbonyl complexes with the bidentate nitrogen heterocycle 2,7-dimethyl-1,8-naphthyridine (I). These complexes present a rare example of a four-



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(1) Presented at the 1st Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 9, 1968.

(2) NASA Graduate Trainee.

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