low level (12 ev) in order to minimize hydrogen loss in the spectrometer. The methyliodo derivative, which undoubtedly resulted from iodination of $CH_3LiC_2B_4H_4$ by I_2 formed from LiI and Br_2, was identified from its mass spectroscopic cutoff at *m/e* 214, corresponding to the $^{127}I^{12}C_3{}^{11}B_4{}^{1}H_7{}^{+}$ parent ion, and its fragmentation pattern, which closely matches the profile calculated for the composition indicated.

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Activation Parameters for Substitution Kinetics of Methyl(aquo)bis(dimethylglyoximato)cobalt(III)

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Crumbliss and Wilmarth[1] (see also ref 2) have reported that the substitution kinetics of methyl(aquo)bis(dimethylglyoximato)cobalt(III) with various ligands are quite rapid compared to other bis(dimethylglyoximato)cobalt(III) complexes.[3-7] The rates were found to be as much as 10^5 times faster than the comparable reactions with a nitrite[3] ion in place of the methyl group showing that the methyl group exhibits a very large trans effect. Because of the interest in these compounds as models for vitamin B_{12}[8] and because of this large rate enhancement by the methyl group we wish to report the activation parameters of two of these reactions, the reactions with thiocyanate and with pyridine.

Experimental Section

Kinetic Measurements.—Chemicals used for kinetic measurements were reagent grade. Sodium thiocyanate was once recrystallized and the pyridine used was spectroquality grade (Matheson Coleman and Bell). Deionized water was used for preparation of solutions. Methyl(aquo)bis(dimethylglyoximato)cobalt(III) (abbreviated as $CH_3Co(DH)_2OH_2$) was prepared by the method of Schrauzer and Windgassen.[9]

The rate of ligand substitution was observed spectrophotometrically at 445 nm with a Beckman Model 260 kinetic system employing a stopped-flow apparatus. At this wavelength the molar extinction coefficient of the aquo derivative is 1430, of the pyridine derivative is 465, and of the thiocyanate derivative is 827.

Kinetic observations were carried out under pseudo-first-order kinetic conditions; *i.e.*, the concentration of NCS^- or pyridine was 50–100 times that of $CH_3Co(DH)_2OH_2$. The concentration of $CH_3Co(DH)_2OH_2$ was in the range 2.0×10^{-4} to 5.0×10^{-4} *M*. Solutions of $CH_3Co(DH)_2OH_2$ were rapidly mixed with solutions of pyridine or NCS^-. The temperature was maintained constant to within ±0.5° and was reproducible to within ±1°. Observed pseudo-first-order rate constants, k_{obsd}, were estimated directly from the slope of a plot of log (absorbance) *vs.* time stored on the instrument oscilloscope and the appropriate circuit constants. The total error in the rate constants, k_{obsd}, was estimated from the total absorbance change during the reaction to be 10%. Second-order rate constants, k_1, M^{-1} sec^{-1}, for pyridine substitution were obtained by the relationship $k_1 = k_{obsd}/[py]$. The standard deviation of values for k_1 was ±5% for several observations at three different pyridine concentrations. The rate constants for thiocyanate substitution were obtained from the slope and intercept of plots of k_{obsd} *vs.* $[NCS^-]$ for five concentrations of thiocyanate. The error in the rate constants was graphically estimated to be ±3%.

Formation Constants.—Equilibrium constants for the formation of methyl(pyridinato)bis(dimethylglyoximato)cobalt(III) were determined spectrophotometrically at 445 nm by a Cary recording spectrophotometer, Model 14, maintained at constant temperature with a circulating water bath. Equilibrium constants *K* were determined from linear plots of $(A - B)/B$ *vs.*

$$K = \frac{[CH_3Co^{III}(DH)_2py]}{[CH_3Co^{III}(DH)_2OH][py]}$$

[py], where *A* is the difference in absorption between $CH_3(DH)_2OH_2$ only and $CH_3Co(DH)_2OH_2$ in the presence of a 1000-fold excess of pyridine, and *B* is the difference in absorption between $CH_3Co(DH)_2OH_2$ only and $CH_3Co(DH)_2OH_2$ in the presence of an equilibrium pyridine concentration. The error in the equilibrium constants was estimated graphically to be ±5%.

Results and Discussion

The formation constants K_f, M^{-1}, for methyl(pyridinato)bis(dimethylglyoximato)cobalt(III) at various temperatures are presented in Table I. The standard enthalpy and entropy for the reaction were -5.1 ± 0.4 kcal mol^{-1} and -2 ± 1.5 eu, respectviely, as estimated from the slope and intercept of a plot of log K_f *vs.* $1/T$.

TABLE I

THERMODYNAMIC DATA FOR THE

$$CH_3Co(DH)_2OH_2 + py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Co(DH)_2py$$

EQUILIBRIUM IN WATER[a]

Temp, °C	$10^{-3}K_f$, M^{-1}	Temp, °C	$10^{-3}K_f$, M^{-1}	Temp, °C	$10^{-3}K_f$, M^{-1}
10	4.81[b]	30	1.58	40	1.12
20	1.90	35	1.24	45	0.96
25	1.66				

[a] The concentration of $CH_3Co(DH)_2OH_2$ was 2.0×10^{-4} *M* and the concentration of pyridine was in the range 2.0×10^{-3} to 1.6×10^{-2} *M*. ΔH^* and ΔS^* estimated from the slope and intercept of a plot of log K_f *vs.* $1/T$ were -5.1 ± 0.4 kcal mol^{-1} and -2 ± 1.5 eu, respectively. [b] Data of Crumbliss and Wilmarth[1] at unit ionic strength added for comparison.

For the substitution reaction

$$CH_3Co(DH)_2OH_2 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Co(DH)_2X + H_2O$$

the observed rate constants, k_{obsd}, are related to the individual rate constants by the relationship $k_{obsd} = k_1[X] + K_{-1}$. If $k_1[X] > k_{-1}$, then k_1 may be obtained from the relationship $k_1 = k_{obsd}/[X]$. Second-order rate constants for pyridine substitution were calculated by this method. However, for the thiocyanate reaction k_{-1} is not negligible compared to the value of $k_1(NCS^-)$. Therefore, k_1 and k_{-1} were estimated from the slope and intercept of a plot of k_{obsd} *vs.* $[NCS^-]$. The rate

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constants, k_{-1}, for pyridine were calculated from the equilibrium constants. Table II lists the calculated rate constants, k_1 and k_{-1}, for the pyridine and thiocyanate reactions at various temperatures.

TABLE II

RATE CONSTANTS FOR THE LIGAND SUBSTITUTION REACTIONS IN WATER[a]

$$CH_3Co(DH)_2OH_2 + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Co(DH)_2L$$

L = py			L⁻ = NCS⁻ [b]		
Temp, °C	$10^{-1}k_1$, M^{-1} sec^{-1}	10^2k_{-1},[c] sec^{-1}	Temp, °C	$10^{-1}k_1$, M^{-1} sec^{-1}	k_{-1}, sec^{-1}
10	2.99[d]				
11	1.2	0.47	10	4.96[d]	
15	2.0	0.88	15	5.2	0.70
19	3.2	1.6	20	8.9	1.3
25	6.8	4.1	25	15	2.6
31	12	8.7	30	26	4.3
34	21	17	35	43	7.3
47	88	98	40	63	14

[a] The concentration of $CH_3Co(DH)_2OH_2$ in these experiments was 2.0×10^{-4} to 5.0×10^{-4} M. The concentration of ligand was 50–100 times that of the $CH_3Co(DH)_2OH_2$ concentration. [b] Kinetic data for NCS^- substitution were estimated from plots of k_{obsd} *vs.* $[NCS^-]$. [c] Obtained from $k_{-1} = k_1/K_f$. [d] Data of Crumbliss and Wilmarth[1] at unit ionic strength added for comparison.

TABLE III

ACTIVATION PARAMETERS FOR THE SUBSTITUTION REACTION[a]

$$CH_3Co(DH)_2OH_2 + L \rightleftharpoons CH_3Co(DH)_2L$$

Ligand	ΔH^*, kcal mol^{-1}	ΔS^*, eu
Pyridine	20.5 ± 0.4	19 ± 1.5
NCS^-	17.5 ± 0.4	10 ± 1.5

[a] ΔH^* and ΔS^* were obtained from the slope and intercept, respectively, of a plot of log k_1/T *vs.* $1/T$.

The activation parameters listed in Table III are low for most substitution reactions on cobalt(III) complexes[10] and even low for bis(dimethylglyoximato)cobalt(III) complexes.[3] Hague and Halpern[3] found $\Delta H^* = 19.1 \pm 1.2$ kcal mol^{-1} and $\Delta S^* = -9 \pm 4$ eu for the reaction of thiocyanate ion with nitro(aquo)bis(dimethylglyoximato)cobalt(III). In contrast to these results the entropy of activation for methyl(aquo)bis(dimethylglyoximato)cobalt(III) is positive instead of negative and this factor contributes more to the rate enhancement than the decrease in the enthalpy of activation by the trans effect of the methyl group. Tobe[11] has proposed that a relatively low entropy of activation in a unimolecular reaction may represent a square-pyramidal transition state and a relatively high entropy of activation a trigonal-bipyramidal transition state. This could apply here if the mechanism is dissociative. However, if the process for these reactions is of the dissociative interchange mechanism (Id) as has been argued,[1,12] then the positive entropy of activation probably merely represents a more flexible transition state in which the dimethylglyoxime ligands are less rigidly held in a plane than that for the nitro(aquo)bis(dimethylglyoximato)cobalt(III).

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Correspondence

Rate Constants and Activation Parameters for the Formation of Monosubstituted Chromium(III) Complexes

Sir:

The recent compilation of CrX^{2+} formation rate constants[1] prompts us to communicate the results of related calculations made on the same reaction series. The present data supplement those of Espenson[1] in that activation parameters in addition to rate constants are reported. Also considered is the competition between complex formation and the $CrOH_2^{3+}$ water-exchange reaction.

Activation parameters for the reactions of eq 1 and 2 were obtained from aquation activation enthalpies and entropies and the appropriate thermodynamic data.[2–17]

$$CrOH_2^{3+} + X^- \xrightarrow{k} CrX^{2+} + H_2O \qquad (1)$$

$$CrOH^{2+} + X^- \xrightarrow{k_{OH}} Cr(OH)X^+ \qquad (2)$$

$$H^+ + Cr(OH)X^+ \xrightarrow{\text{fast}} CrX^{2+} + H_2O$$

Since most of the experimental work had been performed at elevated temperatures, formation rate constants at 25° were usually calculated directly from the tabulated activation parameters.[18]

Consider the ligands NCS^- through I^- in Table I. Espenson[1] has discussed the ligand-dependent nature of these reactions in light of the free energy correlation found by Swaddle and Guastalla[16] for the CrX^{2+} aquation reactions. It was suggested[1] that bond formation plays a role in the anation reactions, albeit one subordinate to the dissociative loss of water. The activation parameters of Table I (NCS^- through I^-) indicate that the ligand reactivity order is controlled by both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, although it can be said that the fastest

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