trans-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ and *trans*-$[Co((\pm)pn)_2Cl_2](H_5O_2)Cl_2$ exhibit different rate laws for dehydration *in vacuo*, they appear to possess virtually identical activation energies for this process. This seems to indicate that the same activation process occurs in both compounds. One possible means of activation would be through vibration of the $H_5O_2^+$ ion. The infrared spectra of these compounds have been reported in the literature.[20] The high-frequency vibration (the so-called "band I" in ref 20) occurs at 2850 cm^{-1} (8.16 kcal mol^{-1}) for the ethylenediamine complex and at 2920 cm^{-1} (8.36 kcal mol^{-1}) for the propylenediamine complex. The first overtone of this band would be of the same energy (16.3–16.7 kcal mol^{-1}) as the activation energy for dehydration.

Although the activation energies for the dehydration *in vacuo* of both the ethylenediamine and the propylenediamine complexes are the same (or nearly the same), these two compounds clearly differ in their ease of dehydration in static air. This difference can be traced to the fact that the ethylenediamine complex can lose HCl and H_2O from all faces while the propylenediamine complex resists dehydration from the (100) face. The rate of dehydration depends in part on the rate of diffusion of water from the solid. This is a temperature-dependent process which will be of greater importance in static air than *in vacuo*. Consequently, it is logical that the rate of dehydration of the propylenediamine complex is lower than that of the ethylenediamine complex where diffusion is apparently freer and not restricted in direction. The different activation energies exhibited by these two compounds in static air seem to reflect this difference in ease of diffusion.

The fact that the ethylenediamine complex undergoes dehydration from all faces while the propylenediamine complex resists dehydration from the (100) face may be due to some subtle difference in the manner in which the complex cations are packed within the (100) layers. Loss of HCl and H_2O from all faces of the ethylenediamine complex may provide an opportunity for recrystallization which is lacking in the propylenediamine complex where the (100) layers of complex cations are apparently not penetrated by the evolved HCl and H_2O.

Acknowledgment.—The author wishes to thank the Desert Research Institute of the University of Nevada for financial assistance.

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[20] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1640 (1964).

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Rate and Equilibrium Studies of the Displacement of Water in *trans*-Sulfitoaquobis(dimethylglyoximato)cobalt(III) by Various Nucleophiles[1]

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Ligation studies have been made of the rate of displacement of H_2O in $Co(DH)_2(SO_3)OH_2^-$, the symbol DH being used to represent the dimethylglyoxime anion. At 25° and unit ionic strength numerical values of the second-order rate constants (M^{-1} sec^{-1}) for the various nucleophiles are: thiourea (tu), 8.34; N_3^-, 7.30; HSO_3^-, 6.06; I^-, 5.50; py, 5.00; $S_2O_3^{2-}$, 1.45. Ligation by SO_3^{2-}, in contrast to the behavior of the other nucleophiles, appears to react in a limiting SN1 mechanism with maximum value of the rate constant of 0.56 sec^{-1}, independent of the SO_3^{2-} concentration above 0.10 *M*. Ligation by SCN^-, which is about as reactive as N_3^-, seems to occur by parallel reaction paths. The equilibrium quotient for formation of $Co(DH)_2(SO_3)I^{2-}$ is 2.56, a value larger than that for formation of $Co(DH)_2(SO)_3Br^{2-}$ (class b behavior). The equilibrium quotient for formation of $Co(DH)_2(SO_3)SCN^{2-}$ is 227. The acidity quotient of $Co(DH)_2(SO_3)OH_2$ at unit ionic strength is approximately 5.8×10^{-11}. The conjugate base $Co(DH)_2(SO_3)OH^{2-}$ does not react at an appreciable rate with SCN^- and probably not with the other nucleophiles listed above.

Introduction

It has recently been shown that the substitution reactions of Co(III) complexes may be markedly influenced by the presence of an SO_3^{2-} ligand.[2,3] Two aspects of the kinetic behavior of these sulfito complexes are of interest. First, the substitution reactions are remarkably rapid, the half-life at 25° being of the order of seconds or less. Since the available evidence indicates that substitution occurs in the *trans* position, this rapidity of reaction will be referred to below as *trans* activation. Second, the reactions which have been studied thus far proceed by a limiting type of SN1 mechanism with strong evidence for the generation of a five-coordinate reactive intermediate with a lifetime long enough to discriminate between the various nucleophiles present in the system.

Although only two studies[2,3] of the sort described above have been reported, the work involved complexes as dissimilar in structure as $Co(CN)_4(SO_3)OH_2^{3-}$ and

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[1] This work was supported by the Atomic Energy Commission and the National Science Foundation.

[2] J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

[3] P. H. Tewari, R. H. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967).

$Co(NH_3)_4(SO_3)X^{(1-n)+}$, where X^{n-} represents a variety of neutral or negatively charged ligands. Consequently, it seemed not unlikely that similar kinetic behavior might be observed for all Co(III) complexes containing the SO_3^{2-} ligand and perhaps other octahedral metal sulfito complexes as well.

To test further the generality of the phenomena under consideration, a kinetic study was made of the rate of substitution of H_2O in $Co(DH)_2(SO_3)OH_2^-$, where the symbol DH has been used to represent the conjugate base of dimethylglyoxime. The dimethylglyoxime complex was chosen for study for several reasons. First, it seemed likely that it would have the desired *trans* configuration, as in the case of other bis-dimethylglyoxime complexes.[4] Second, the negative charge should minimize the possibility of ion-pair formation with neutral or negatively charged ligands, thus simplifying the interpretation of kinetic studies. Third, the weak acidity of the H_2O ligand, with a pK of approximately 10.2, permitted studies using anions of relatively weak acids without the formation of the conjugate base of the complex, a feature which also simplifies the kinetic behavior.

By way of summary of the results to be described below, it can be stated that in our studies of $Co(DH)_2(SO_3)OH_2^-$, *trans* activation was observed with a variety of nucleophiles, but most of the reactions did not proceed by limiting SN1 mechanism. However, displacement of H_2O by SO_3^{2-} does appear to involve the expected limiting SN1 mechanism.

Experimental Section

Reagents and Solutions.—All commercial chemicals were of reagent grade and were used without further purification, except as specified below. Stock solutions of $NaClO_4$ were prepared by dissolving anhydrous Na_2CO_3 in 70% $HClO_4$, boiling to remove CO_2, and then adjusting the final pH to 6.5–7.0. Pyridine was purified by distillation, using an all-glass 15-plate Oldershaw perforated-plate fractionating column. A center cut of the distillate boiling within the range 113.8–114.0° was used in the kinetic experiments. NaSCN solutions were standardized by titration with aqueous $AgNO_3$ using eosin as an indicator.[5] NaN_3 solutions were standardized by an established iodometric procedure.[6]

Preparations. (1) **$Na[Co(DH)_2(SO_3)OH_2]\cdot 5H_2O$.**—A 5.0-g sample of $Co(DH)_2(Cl)OH_2$, prepared by the method[7] of Ablov and Samus, and an equimolar amount of Na_2SO_3 were added to 3.0 ml of H_2O and the suspension was heated to 50° for 10 min. On cooling to room temperature the poorly soluble by-product $[Co(DH)_2(OH_2)_2]Cl$ was removed by filtration. The solution was then evaporated at approximately 50° until the volume was decreased to approximately half of the original and $NaCo[(DH)_2(SO_3)OH_2]\cdot 5H_2O$ was removed by filtration at room temperature. After five recrystallizations the reddish brown product was obtained in a pure state with an over-all yield of approximately 20%. Later work indicated that a pure product could probably be obtained with less than five recrystallizations. *Anal.* Calcd for $NaCoC_8H_{26}N_4O_{13}S$: Co, 11.78; C, 19.20; N, 11.20; H, 5.24; S, 6.40; hydrate H_2O, 19.00. Found: Co, 11.76; C, 19.45; N, 11.24; H, 5.08; S, 6.25; hydrate H_2O, determined by weight loss under evacuation for 6 hr at 100°, 19.09.

(2) **$Na_2[Co(DH)_2(SO_3)(SCN)]\cdot 5H_2O$.**—Equimolar amounts of $Na[Co(DH)_2(SO_3)OH_2]\cdot 5H_2O$ and NaSCN were dissolved in a minimum amount of H_2O. The solution was then evaporated to dryness in a rotary evaporator under vacuum at 25°. Visual observation indicated that the light yellow solid product was contaminated with a small amount of the dark red reactant $Na[Co(DH)_2(SO_3)OH_2]\cdot 5H_2O$. Presumably, there was also an equivalent amount of unreacted NaSCN present, but no white solid was visible. In exploratory studies it was found that the solid, after being finely ground, could be purified by decantation from diethyl ether, the separation presumably depending on differences in density or particle size of the products. In this procedure the finely ground impure product was first suspended by rapid stirring in diethyl ether. Approximately 1.0 min after the stirring was terminated, the top three-fourths of the ether suspension was removed by decantation, leaving the bulk of the red impurity in the remaining quarter of the ether suspension. In obtaining the final product, the decantation procedure was repeated a second time. *Anal.* Calcd for $Na_2CoC_9H_{24}O_{12}N_5S_2$: C, 19.18; H, 4.30; N, 12.42; S, 11.40. Found: C, 18.99; H, 4.05; N, 12.13; S, 12.12.

In view of the preparative method employed, it is clear that the above analytical data do not constitute very reliable criteria of purity. Purification by the decantation procedure was employed only because rapid aquation prevented recrystallization. Fortunately, extreme purity was not essential, since the compound was used only in infrared studies where the results were insensitive to trace impurities.

(3) **$Na[Co(DH)_2(SO_3)(SCN_2H_4)]\cdot 2H_2O$.**—Equimolar amounts (0.005 mol) of thiourea and $Na[Co(DH)_2(SO_3)OH_2]\cdot 5H_2O$ were dissolved in the minimum of water and the solution was evaporated to dryness at 50°. Visual examination of the solid yellow product suggested that the reaction had proceeded to completion, but, as a precaution, the decantation method of purification described above was employed. Again, the product was desired only for infrared studies and extreme purity was not essential. *Anal.* Calcd for $NaCoC_9H_{23}O_9N_6S_2$: C, 21.42; H, 4.40; N, 16.65; S, 12.69. Found: C, 21.48; H, 4.85; N, 16.66; S, 12.95.

(4) **$Co(DH)_2(NCS)(OH_2)\cdot H_2O$.**—The compound was prepared by the method[8] of Ablov, Samus, and Popov in a procedure which involved the reaction of equivalent amounts of NaSCN and $Co(DH)_2(NO_2)OH_2$, the latter complex being prepared by the method[9] of Chugaev. *Anal.* Calcd for $CoC_9H_{18}O_6H_5S$: Co, 15.38; hydrate H_2O, 4.70. Found: Co, 15.41; hydrate H_2O determined by weight loss, 4.75.

Apparatus.—Spectrophotometric measurements were made using a Beckman DU or a Cary Model 14 spectrophotometer. The stopped-flow apparatus was purchased from Atom-Mech Machine Co. and has been described in detail elsewhere.[3] A Beckman Research Model pH meter equipped with an E3 glass electrode and a fritted reference electrode, No. 39071, was used in the pH measurements. The saturated KCl solution in the reference electrode was removed and replaced by 3.0 M NaCl, a procedure which prevented clogging of the fritted disk by precipitation of $KClO_4$ when measurements were made in solutions containing ClO_4^-. Infrared measurements were made using either a Beckman IR-7 or a Perkin-Elmer Model 137 instrument. The samples were prepared as Nujol mulls or as KBr disks, the two techniques yielding identical results.

Kinetic Measurements.—In each system the kinetic measurements were carried out at a wavelength where there was a favorable change in absorbancy. The wavelengths and absorbancy indices of interest for the various compounds are listed in Table I.

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(4) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 6041 (1963).

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 455.

(6) I. M. Kolthoff and T. Belcher, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p 312.

(7) A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, **4**, 410 (1960).

(8) A. V. Ablov, N. M. Samus, and M. S. Popov, *Dokl. Akad. Nauk SSSR*, **106**, 665 (1956).

(9) L. A. Chugaev, *Ber.*, **41**, 2226 (1908).

TABLE I

ABSORBANCY INDICES OF THE COMPLEXES

Species	Wave-length, mμ	Absorbancy Index, M^{-1} cm^{-1}	Species	Wave length, mμ	Absorbancy index, M^{-1} cm^{-1}
$Co(DH)_2(SO_3)(OH_2)^-$	320	7.08×10^3	$Co(DH)_2(SO_3)I^{2-}$	380	1.15×10^4
	325	5.45×10^3	$Co(DH)_2(SO_3)_2^{3-}$	325	2.62×10^4
	380	9.92×10^2			
	460	3.04×10^2	$Co(DH)_2(SO_3)S_2O_3^{3-}$	320	2.67×10^4
$Co(DH)_2(SO_3)SCN^{2-}$	325	2.33×10^4			
			$Co(DH)_2(SO_3)tu^-$	325	2.61×10^4
$Co(DH)_2(SO_3)N_3^{2-}$	325	2.41×10^4			
			$Co(DH)_2(SO_3)py^-$	460	1.42×10^2

Results

Stoichiometry.—In the results to be presented below, the general assumption will be made that displacement of H_2O in $Co(DH)_2(SO_3)OH_2^-$ is not accompanied by rapid aquation of either an SO_3^{2-} or a DH ligand. The assumption seems to us to be inherently plausible and, fortunately, with some ligands there is experimental support for its validity.

The strongest evidence is based on the preparative conversion of aqueous $Co(DH)_2(SO_3)OH_2^-$ to $Na_2[Co(DH)_2(SO_3)SCN]\cdot 5H_2O$ and $Na[Co(DH)_2(SO_3)SC(NH_2)_2]\cdot 2H_2O$. Analysis of the reaction products indicates the correctness of the assigned formulas. In addition, in anation reactions with the nucleophiles SO_3^{2-} and HSO_3^-, the absorption spectra after reaction are in quantitative agreement with that of a solution of $Na_3[Co(DH)_2(SO_3)_2]\cdot 12H_2O$. In view of these results, it seems very unlikely that any of the ligation reactions involve anything other than the displacement of H_2O in the complex.

Equilibrium Quotients.—The equilibrium quotient for reaction 1 was determined by measurement of the pH during a titration of 0.01 M $Co(DH)_2(SO_3)OH_2^-$ with 0.10 M NaOH, with both solutions containing added $NaClO_4$ so that the ionic strength was maintained at unity throughout the titration. The OH^- concentrations were calculated from the measured pH values by "calibration" of the pH meter using solutions of unit ionic strength containing NaOH in the concentration range 10^{-4}–10^{-1} M. The results are presented in Figure 1 as a plot of log $[(A^{2-})/(HA^-)]$ *vs.* $-\log (OH^-)$, where the symbols A^{2-} and HA^- have been used to represent $Co(DH)_2(SO_3)OH^{2-}$ and $Co(DH)_2(SO_3)OH_2^-$, respectively. In terms of theory, the points in Figure 1 should lie on a line of unit slope, but in actuality they lie closer to the line in the figure which has a slope of 1.08. The reason for this discrepancy is not understood. At the midpoint of the titration, where $-\log (OH^-)$ should equal log K_1, the position of the line corresponds to $K_1 = 2.89 \pm 10^3$. Assumption of an ionization quotient[10] for H_2O in 1.0 M $NaClO_4$ of 2×10^{-14}, the known value for 1.0 M NaCl, leads to an acidity quotient for ionization of $Co(DH)_2(SO_3)OH_2^-$ of 5.78×10^{-11}.

$$Co(DH)_2(SO_3)OH_2^- + OH^- \xrightleftharpoons{K_1} Co(DH)_2(SO_3)OH^{2-} + H_2O \qquad (1)$$

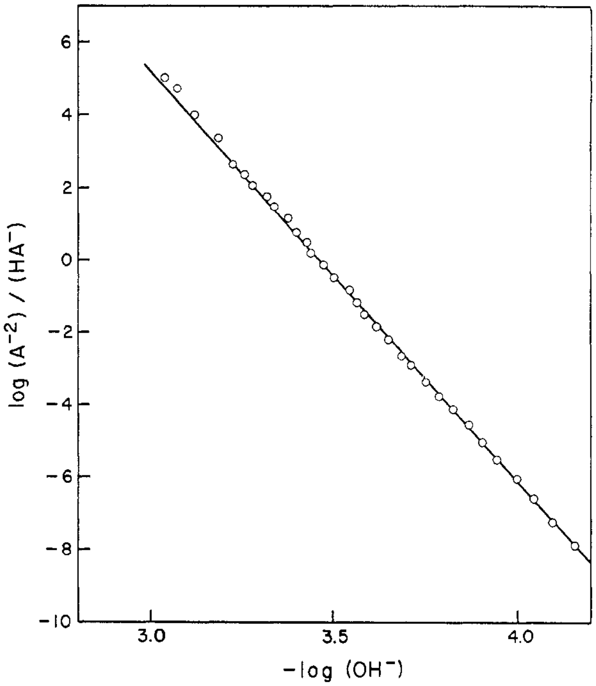

Figure 1.—Evaluation of the acidity quotient of $Co(DH)_2(SO_3)OH_2^-$. A plot of log $[(A^{2-})/(HA^-)]$ where (A^{2-}) and (HA^-) are the concentrations of $Co(DH)_2(SO_3)OH^{2-}$ and $Co(DH)_2(SO_3)OH_2^-$, respectively.

In the displacement of H_2O in $Co(DH)_2(SO_3)OH_2^-$ by X^-, where the symbol X^- has been used to represent any one of several uninegative ligands, the reactions with I^-, and to an even greater extent with Br^-, do not proceed to completion. This is also true with SCN^- in solutions alkaline enough so that neutralization of $Co(DH)_2(SO_3)OH_2^-$ occurs. In a solution at equilibrium the spectrophotometric parameters are related to the formation quotients of reaction 2 by

$$Co(DH)_2(SO_3)OH_2^- + X^- \rightleftharpoons Co(DH)_2(SO_3)X^{2-} + H_2O \qquad (2)$$

$$\frac{A_0 - A_\infty}{[Co(III)]l} = \frac{(\mathcal{E}_{ROH_2} - \mathcal{E}_{RX})K(X^-)}{1 + K(X^-)} \qquad (3)$$

Here [Co(III)] is used to represent the total concentrations of Co(III), $\mathcal{E}_{ROH_2}$ and $\mathcal{E}_{RX}$ are the absorbancy indices of $Co(DH)_2(SO_3)OH_2^-$ and $Co(DH)(SO_3)X^{2-}$, l is the path length, A_∞ is the measured absorbancy at equilibrium in the presence of the ligand X^-, A_0 is the absorbancy in the absence of the ligand at the same total Co(III) concentration, and K is the desired formation quotient.

The experimental data for anation by I^- and SCN^- are presented in Figure 2 as a plot of $10^{-3}(A_0 - A_\infty)/[Co(III)]$ *vs.* the ligand concentration. The solid lines drawn through the points represent a nonlinear least-squares evaluation of the data and correspond to formation quotients of SCN^- and I^- of 227 ± 7 and 2.54 ± 0.03, respectively. The indicated uncertainties here and elsewhere in this article represent standard deviations. A plot of the Br^- data similar to Figure 2 yielded only a straight line, indicating that $K(Br^-)$

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[10] The ionization quotient for H_2O in 1.0 M $NaClO_4$ has not been measured.

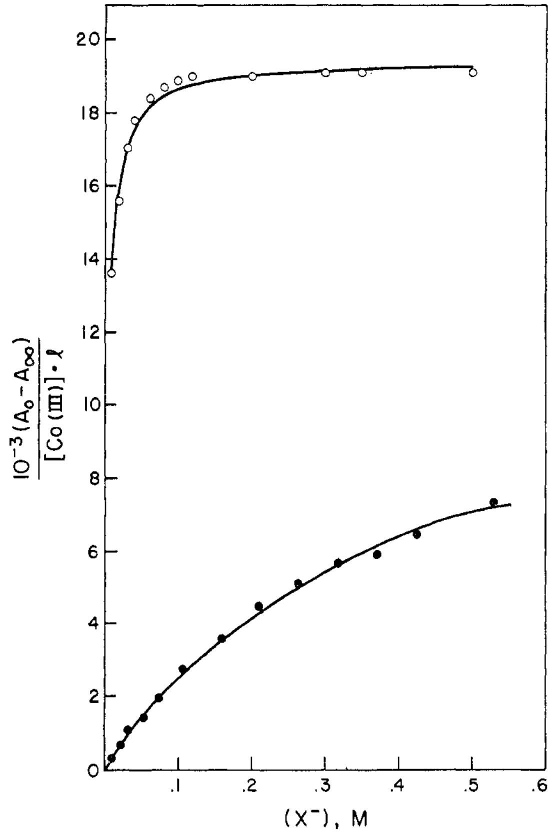

Figure 2.—Evaluation of the formation quotient of $Co(DH)_2(SO_3)SCN^{2-}$ and $Co(DH)_2(SO_3)I^{2-}$ at 25° and μ = 1.0 *M*: O, $X^- = SCN^-$; ●, $X^- = I^-$.

<<1. As inspection of eq 3 will show, it is not possible to evaluate the desired formation quotient under these conditions.[11]

Kinetics of Ligation of $Co(DH)_2(SO_3)OH_2^-$.—The rate of displacement of H_2O in $Co(DH)_2(SO_3)OH_2^-$ by a variety of ligands has been studied at 25° in solutions where the ionic strength has been adjusted to unity with added $NaClO_4$. See eq 4. Apart from certain experiments with SCN^-, to be discussed below, the solutions were acidic enough so that the concentration of $Co(DH)_2(SO_3)OH^{2-}$ was negligible but not acidic enough to protonate the ligand. The ligands which were investigated in detail include SCN^-, SO_3^{2-}, HSO_3^-, thiourea, I^-, N_3^-, py, and $S_2O_3^{2-}$. The reactions were studied using the stopped-flow technique, since they were too rapid to follow using conventional mixing procedures. In any given experiment, carried out in the presence of a large excess of X^{n-}, the rate was evaluated as a pseudo-first-order rate constant *k*, obtainable from the linear plot of log $(A - A_\infty)$ *vs.* time.

$$Co(DH)_2(SO_3)OH_2^- + X^{n-} \longrightarrow Co(DH)_2(SO_3)X^{(n+1)-} \quad (4)$$

The results obtained with SO_3^{2-} will be considered first since they differed markedly from those obtained with the other ligands. In each experiment a small and fixed concentration of HSO_3^- was added to prevent hydrolysis of SO_3^{2-} and formation of a significant concentration of $Co(DH)_2(SO_3)OH^{2-}$. In these studies the solutions were deaerated with oxygen-free nitrogen and exposure to air was minimized. Iodometric analysis provided an independent verification that aerial oxidation of SO_3^{2-} was insignificant. In one series of experiments represented by the upper points in Figure 3, the SO_3^{2-} concentration was varied at a fixed concentration of HSO_3^- of 0.10 *M*. The lower set of points constitutes a similar series of experiments except that the HSO_3^- concentration was 0.05 *M*. The dotted line is an empirical curve drawn through the points. The significance of the solid line will be discussed below. In both series of experiments the rate becomes zero order in SO_3^{2-} above a concentration of approximately 0.10 *M*. The value of *k* at zero SO_3^{2-} represents the contribution to the rate arising from the presence of the HSO_3^- at the two concentrations indicated.

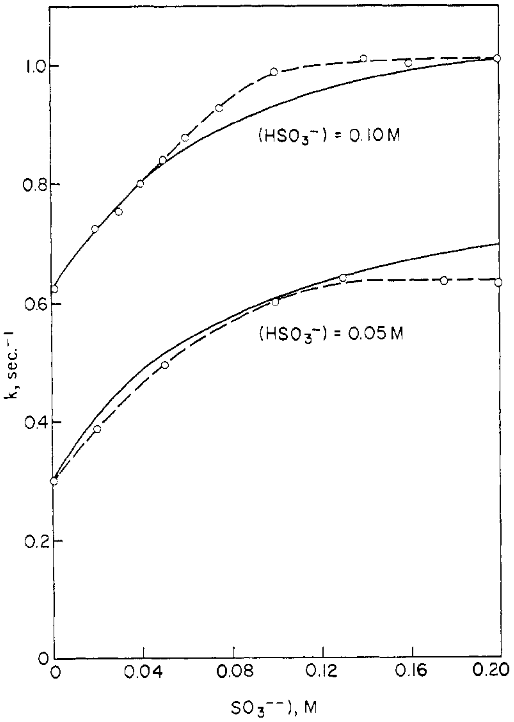

Figure 3.—Rate constants for the reaction of $Co(DH)_2(SO_3)OH_2^-$ with SO_3^{2-} at 25° and μ = 1.0.

The kinetic data for the anation reactions of thiourea, N_3^-, py, $S_2O_3^{2-}$, SCN^-, and I^- are presented in Figure 4 as plots of *k vs.* the ligand concentration. The nonzero intercept of I^- arises because in this instance the reaction does not proceed to completion.

To determine the effect of variation of pH upon rate, a series of experiments was carried out at a constant concentration of 0.10 *M* SCN^- and variable acidity. The variation of *k vs.* $-\log (H^+)$ may be seen in Figure 5 where $-\log (H^+)$ has been obtained from measured pH values by the pH meter calibration procedure referred to above. To calculate the H^+ concentration in alkaline solution it has again been necessary to assume that the ionization quotient of H_2O at unit ionic

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[11] Under these conditions one can obtain only the product $\varepsilon_{RX}K$.

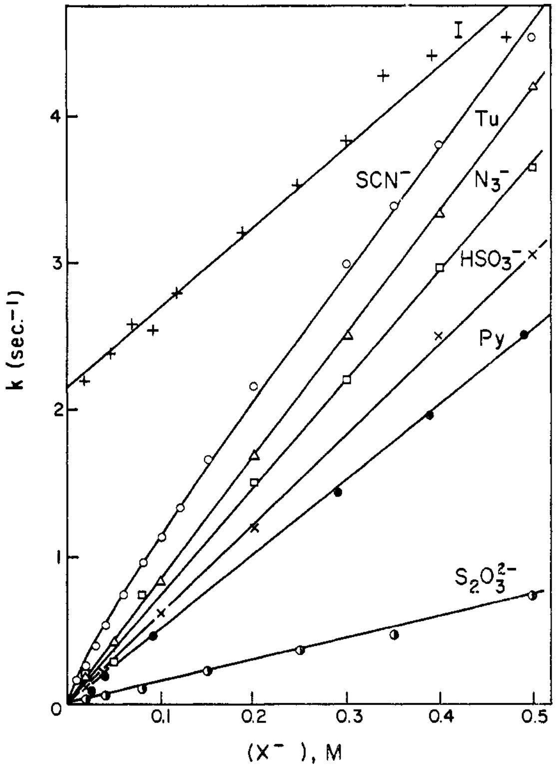

Figure 4.—Rate constants for the reaction of $Co(DH)_2(SO_3)OH_2^-$ with a variety of nucleophiles; Tu = Thiourea; Py = pyridine.

strength is 2×10^{-14}. It is evident from Figure 5 that the rate is independent of the acidity in acidic solutions but that there is a marked decrease in rate in alkaline solutions where $Co(DH)_2(SO_3)OH_2^-$ is converted to $Co(DH)_2(SO_3)OH^{2-}$.

Infrared Measurements.—Infrared measurements were carried out in an effort to determine which of the possible isomers were formed in the reaction of $Co(DH)_2(SO_3)OH_2^-$ with SCN^- and thiourea. The infrared spectra of $Co(DH)_2(NCS)OH_2$ and $Co(DH)_2(SO_3)OH_2^-$ were also examined. The results in the region of wavelengths of interest are presented in Table II.

Various authors have discussed the use of infrared spectra to identify Co–NCS and Co–SCN linkages. The absorption arising from the C–S stretching frequency has been most widely used.[12–14] In a metal–NCS linkage the absorption band is sharp, is medium in strength, and falls in the region 780–860 cm^{-1}. By contrast, the absorption band arising from a metal–SCN linkage is frequently very weak and is in the 670–740 cm^{-1} region.

More recently it has been proposed that the N–C–S bending vibration might be diagnostic[15] of the nature of the bonding. Metal–NCS and metal–SCN linkages appear to absorb at approximately 475 and 400–440 cm^{-1}, respectively. The available data presented in Table II provide strong evidence for the presence of a Co–NCS linkage in $Co(DH)_2(OH_2)NCS$. In the complex $Co(DH)_2(SO_3)SCN^{2-}$ the absorption bands listed at 710 and 425 cm^{-1} are not very well defined, but the total absence of any absorption in the 780–860-cm^{-1} region which might be attributed to a Co–NCS linkage strongly suggests that the bonding is Co–SCN. In view of the great differences in lability in substitution reactions of the two complexes, an indication that the Co(III) ions in the two complexes are chemically dissimilar, it is perhaps not too surprising that the mode of bonding of the SCN^- ligand is also different.

In a recent publication[16] Swaminathan and Irving discussed the current status of the infrared spectra of thiourea complexes. They concluded that, when metal–$SC(NH_2)_2$ bonds are present, the C–S stretching frequency of free thiourea at 730 cm^{-1} should be split and shifted to lower frequencies. By contrast it was

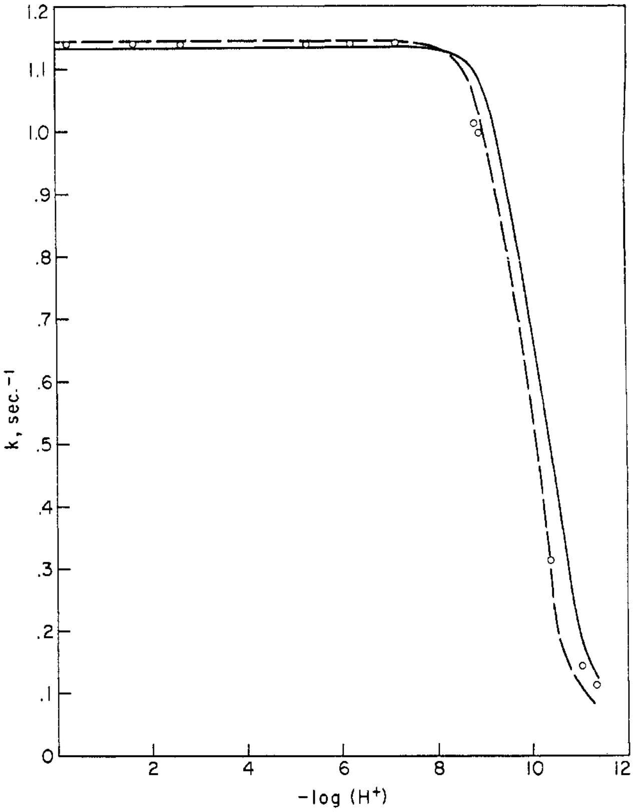

Figure 5.—Variation of *k* with −log (H^+) in the reaction of $Co(DH)_2(SO_3)OH_2^-$ with SCN^- at 25°, μ = 1.0, and [SCN^-] = 0.10 *M*.

TABLE II

INFRARED SPECTRA[a]

Compound	Ligand assignment		
	CS str	NCS bend	O–H–O str, bend
$Na_2[Co(DH)_2(SO_3)SCN] \cdot 5H_2O$	710(?) sh	425 w, sh	2350 br 1750 br
$Co(DH)_2(OH_2)NCS$	820 m	465 w	2370(?) vw
$NaCo(DH)_2(SO_2)tu$	711 m		2350 w
$NaCo(DH)_2(SO_3)OH_2 \cdot 5H_2O$			2350 w 1770(?) sh

[a] sh, shoulder; m, medium; w, weak; vw, very weak; br, broad.

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[12] The original proposal was made by M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

[13] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

[14] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[15] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965). See also R. H. Toeniskoetter and S. Solomon, *ibid.*, **7**, 617 (1968).

[16] K. Swaminathan and H. M. H. Irving, *J. Inorg. Nucl. Chem.*, **26**, 1291 (1964).

predicted that bonding of the metal atom to nitrogen would increase the C–S stretching frequency. In our complex a DH ligand absorption occurs at approximately 730 cm^{-1}, so possible splitting at 730 cm^{-1} is obscured, but a well-defined absorption band is observed at 711 cm^{-1}, an indication of sulfur bonding.

The two absorption bands arising from OH stretching[17] frequencies in *trans*-bis(dimethylglyoximato) complexes containing intramolecular hydrogen bonds are at approximately 2350 cm^{-1} and in the region 1600–1800 cm^{-1}. In our complexes the OH absorption in the 1600–1800-cm^{-1} region was not easily identified without deuteration experiments because of extensive overlap with other absorption bands. For most of the complexes the absorption at 2350 cm^{-1} was rather weak but definitely present. Occasionally it was not observable, perhaps merely because it was too weak to identify. In $Co(DH)(SO_3)OH_2^-$, the ion of major interest, deuteration experiments carried out by recrystallizing the complex from D_2O definitely confirmed that the absorption at 2350 cm^{-1} arose from an OH stretching frequency and led to a tentative identification of a second OH absorption as a very weak shoulder at 1770 cm^{-1}. The measurement provides evidence that the ion $Co(DH)_2(SO_3)OH_2^-$ has a *trans* configuration,[17] as anticipated.

Discussion

The zero-order dependence of rate on SO_3^{2-} concentration observable at high SO_3^{2-} concentration in Figure 3 may be plausibly understood, at least qualitatively, in terms of a mechanism based on reactions 5 and 6. In addition to reactions 5 and 6, it is necessary to add

$$Co(DH)_2(SO_3)OH_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(DH)_2SO_3^- + H_2O \qquad (5)$$

$$Co(DH)_2SO_3^- + SO_3^{2-} \xrightarrow{k_2} Co(DH)_2(SO_3)_2^{3-} \qquad (6)$$

reactions 7 and 8 to account for the contribution to

$$Co(DH)_2(SO_3)OH_2^- + HSO_3^- \xrightarrow{k_3} Co(DH)_2(SO_3)_2^{3+} + H^+ \qquad (7)$$

$$H^+ + SO_3^{2-} \longrightarrow HSO_3^{2-} \qquad (8)$$

product formation by added HSO_3^-. At the SO_3^{2-} concentrations employed, the reactions proceed to completion and the reverse of reactions 6 and 7 may be neglected.

A mechanism based on reactions 5–8 leads to the prediction that the observed pseudo-first-order rate constant k is related to the other kinetic parameters by eq 9. In testing the applicability of eq 9, we have used

$$k = k_3(HSO_3^-) + \frac{k_1(SO_3^{2-})}{(k_{-1}/k_2) + (SO_3^{2-})} \qquad (9)$$

the values of $k_3(HSO_3^-)$ which are given in Figure 4 and will be discussed below. The basis for assuming that the first term on the left should be of the form $k_3(HSO_3^-)$ will also become clear from this discussion.

A nonlinear least-squares evaluation of the data yielded the numerical values of $k_1 = 0.557 \pm 0.030$ and $k_{-1}/k_2 = 0.081 \pm 0.005$. In the computation the individual values of k were weighted as $1/k^2$, a procedure which assumes the same percentage error in all experiments. Assuming a water concentration of 55 M, the value of k_{-1}/k_2 corresponds to a relative reactivity of $SO_3^{2-}:H_2O$ of 650:1.

The solid lines in Figure 3 represent the predicted values of k based on the values of the kinetic parameters listed above. In quantitative terms the mechanism does not quite seem to reproduce the experimental data to within our estimate of the experimental error. In particular, the calculated values of k are too low at intermediate SO_3^{2-} concentration in the experiments at 0.10 M HSO_3^- and are too high at the highest SO_3^{2-} concentration in the experiments at 0.05 M HSO_3^-. At present we have no satisfactory explanation for this discrepancy.

As Figure 4 indicates, k varies linearly with the concentration for the nucleophiles thiourea, N_3^-, py, $S_2O_3^{2-}$, I^-, and HSO_3^-, an indication that the limiting SN1 mechanism does not play a detectable role in these reactions. In addition the observed rates are considerably faster than the maximum value observed at high SO_3^{2-} concentrations. The bimolecular rate constants, k_3 (M^{-1} sec^{-1}), obtained from the slope of the straight lines in Figure 4 are: thiourea, 8.34; N_3^-, 7.30; HSO_3^-, 6.06; I^-, 5.50; py, 5.00; $S_2O_3^{2-}$, 1.45. The rate constant for HSO_3^- was found to be independent of the acidity over a 30-fold change in acidity in the range 3×10^{-6} to 9×10^{-5} M, an indication that SO_2 was not contributing appreciably to the reaction in the HSO_3^- solutions.

The intercept at zero I^- in Figure 4 corresponds to a rate constant k_{-3} for aquation of $Co(DH)_2(SO_3)I^{2-}$ of 2.15 sec^{-1}. The calculated value of the formation quotient of $Co(DH)_2(SO_3)I^{2-}$ of 2.56 using the relationship $K = k_3/k_{-3}$ may be compared with the value 2.54 ± 0.03 obtained from the data of Figure 2.

The over-all variation of k_3 for the nucleophiles under consideration is only a factor of 5.8, an indication that bond breaking is probably much more important than bond making in the activated complex. In the nomenclature[18] of Langford and Gray, the mechanism would be classified as I_d. The difference in mechanism between that of SO_3^{2-} and that of the other nucleophiles under consideration is, therefore, not as extreme as the differences in rate laws might, at first, seem to suggest.

Perhaps the most surprising aspect of the data is the difference in rate laws found for SO_3^{2-} and HSO_3^-. It is possible, of course, that the HSO_3^- reaction does not involve rupture of the $Co–OH_2$ bond but instead involves breaking of an S–OH bond, a process which would lead to addition of SO_2 to the oxygen atom of the $Co–OH_2$ linkage followed by rapid or simultaneous deprotonation of the oxygen atom. This latter mechanism would presumably require a rapid rearrangement of the $Co–OSO_2$ linkage to form $Co–SO_3$.

In this discussion it has been assumed that $Co(DH)_2$-

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[17] R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958). For a later discussion, see K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

[18] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

$(SO_3)_2^{3-}$, the product of the SO_3^{2-} and HSO_3^- reaction, contains two Co–SO_3 linkages. It is possible that this assumption is incorrect, but in our opinion the available evidence provides little support for the existence of a Co–OSO_2 linkage in any inert octahedral complex ion. This topic has been discussed in more detail in an earlier publication.[19]

The best line drawn through the points for SCN^- in Figure 4 shows a small but distinct curvature. The results are consistent with displacement of H_2O by parallel reaction paths, one being the limiting SN1 mechanism analogous to that of the SO_3^{2-} reaction and a second being the bimolecular process adopted by the other nucleophiles. The effect of variation of rate with pH was carried out only with SCN^-, the first nucleophile which was studied. The marked decrease in rate observable at high pH in Figure 5 suggests that the rate of anation of $Co(DH)_2(SO_3)OH^{2-}$ is negligible compared to that of $Co(DH)_2(SO_3)OH_2^-$, at least for the nucleophile SCN^-. Quantitative calculations presented below support this viewpoint.

Assumption of parallel reaction paths and microscopic reversibility implies that k is related to the other kinetic parameters by

$$k = \frac{k_3(SCN^-)}{1 + K_1(OH^-)} + \frac{k_1(SCN^-)}{(k_{-1}/k_2) + (SCN^-)}\,\frac{1}{1 + K_1(OH^-)} + \frac{k_3}{K_2} + \frac{k_1/K_2}{(k_{-1}/k_2) + (SCN^-)} \quad (10)$$

For this equation, K_1 is the equilibrium quotient for reaction 1, the neutralization of $Co(DH)_2(SO_3)OH_2^-$, and K_2 is the formation quotient for the SCN^- reaction.

Equation 10 is more complex than the equations previously discussed for two reasons. In itself, the assumption of parallel reaction paths would result in a two-term rate law, assuming that the reaction was quantitative. However, in alkaline solution the reaction does not proceed to completion, a feature which necessitates the inclusion of the last two terms on the left side of eq 10 as well as the factor $1 + K_1(OH^-)$ in the denominator of the first two terms.

Least-squares curve fitting using eq 10 was carried out in two ways. In the first the only fixed parameter was $k_1 = 0.557$, the value obtained from the SO_3^{2-} kinetic data. The dashed line in Figure 5 and the solid line in Figure 4 represent the results of this procedure and correspond to the values $k_1/k_{-1} = 0.102 \pm 0.020$, $k_3 = 8.31 \pm 0.060$, $K_{SCN^-} = 267 \pm 62$, and $K_{OH^-} = 6727 \pm 1300$. In an alternative procedure the fixed parameters included $K_{SCN^-} = 229$ and $K_{OH^-} = 2880$, the values obtained independently from the equilibrium measurements. The solid line is based on this procedure and yields the values $k_1/k_{-1} = 0.119 \pm 0.017$ and $k_3 = 8.31 \pm 0.090$. As one might expect, the first method of curve fitting, with the greater number of adjustable parameters, yields a slightly better prediction of the rate constants in Figure 5, but the difference between the two methods of computation is small. For the results in weakly acidic solution presented in Figure 4, the difference in results of the two methods of computation lies within the limit of error of the data.

The quite accurate prediction of the rate constants of Figure 5 in strongly alkaline solution supports the conclusion presented above that ligation of $Co(DH)(SO_3)OH^{2-}$ by SCN^- is, at most, a relatively unimportant reaction. Analogous results were obtained in our study of the ligation reactions[3] of $Co(CN)_4(SO_3)OH_2^{3-}$. By contrast, the kinetic studies[2] of the ligation reactions of $Co(NH_3)_4(SO_3)OH_2^+$ in alkaline solution provide evidence for a limiting SN1 mechanism in which an important path for generation of the reactive intermediate $Co(NH_3)_4SO_3^+$ is loss of OH^- from $Co(NH_3)_4(SO_3)OH$.

A comparison of our rate constants with those for the displacement of H_2O in $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ by various nucleophiles indicates the order of magnitude of the *trans* activation arising from the presence of a SO_3^{2-} ligand.[20] As a rough generality, based on data for the nucleophiles SCN^-, N_3^-, HSO_3^-, and I^- at 25°, the reactions of $Co(DH)_2(SO_3)OH_2^-$ are faster by a factor of approximately 10^4 than those of the other two dimethylglyoxime complexes.

A detailed understanding of the unique features of the substitutional behavior of Co(III) complexes containing an SO_3^{2-} ligand is not available at present. It does not seem to arise from strong metal-to-ligand π bonding, since such bonding would probably be more important in $Co(DH)_2(NO_2)OH_2$ than it is in $Co(DH)_2(SO_3)OH_2^-$. The relatively low reactivity of $Co(DH)_2(I)OH_2$ indicates that the presence of a ligand of low electronegativity and high polarizing ability is also not the essential feature. Various other tentative suggestions might be made, but in the absence of more evidence, such discussion seems premature.

Apart from the marked differences in the rates of reaction, the available evidence suggests that the chemical behavior of $Co(DH)_2(NO_2)OH_2$, $Co(DH)_2(1)OH_2$, and $Co(DH)_2(SO_3)OH_2^-$ is rather similar. With respect to both rate and equilibrium constants, the Co(III) ions in the first two complexes[20] act as borderline class b ions or soft acids.[21] The formation quotient for reaction of $Co(DH)_2(SO_3)OH_2^-$ with I^- is larger than that for reaction with Br^-, an indication of class b behavior in this complex as well. The ratio of the two formation quotients for reaction of I^- and Br^- is not known, but the available data suggest the class b behavior of $Co(DH)_2(SO_3)OH_2^-$ may be somewhat more pronounced than in $Co(DH)(NO_2)OH_2$ or $Co(DH)_2(1)OH_2$ but probably not greatly so.

There is at least one other noteworthy instance where complexes with otherwise similar chemical behavior differ markedly in rate of reaction. As Schrauzer has pointed out, the chemistry of aquocobalamin is very

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(19) H. H. Chen, M. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966). The mechanism of the acid-catalyzed aquation of $Co(DH)_2(SO_3)_2^{3-}$ follows a rate law entirely analogous to that reported for $Co(CN)_4(SO_3)_2^{5-}$ in the above publication.

(20) D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

(21) For a general discussion of these classifications, see F. Basolo and R. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 1.

like that of the dimethylglyoxime complexes.[22] However, the displacement of H_2O in aquocobalamin[23] by various nucleophiles is more rapid by a factor of approximately 10^2 than it is in $Co(DH)_2(SO_3)OH_2^-$. The rapidity of reaction of aquocobalamin is not well understood, but it seems doubtful that it arises largely from the *trans* effect of an imidazole ligand.

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(22) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

(23) W. C. Randall and R. A. Alberty, *Biochemistry*, **5**, 3189 (1966); **6**, 1520 (1967).

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π-Cyclopentadienyl(1,4-tetraazendiyl)cobalt

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The reaction of organic azides with $\pi\text{-}C_5H_5Co(CO)_2$ gave air-stable complexes of a molecular formula $\pi\text{-}C_5H_5CoN_4R_2$ ($R = CH_3$, C_6H_5). Physical measurements as well as chemical reactions of these complexes suggest a structure involving a 1,4-tetraazendiyl ($R\underset{|}{N}N{=}N\underset{|}{N}R$) ligand.

In a systematic study[1] on the interaction of a variety of heterocumulenes or -dienes with transition metal compounds, we have investigated the interaction of organic azides. During the course of our study, the reaction of methyl azide with iron carbonyl has been reported.[2] We found that the reaction of methyl azide with π-cyclopentadienylcobalt dicarbonyl occurred at the reflux temperature of *n*-hexane. A deep green crystalline complex (**1**) of a molecular formula $C_5H_5CoN_4(CH_3)_2$ was isolated in 69% yield by cooling the reaction mixture. It is soluble in common organic solvents and slightly soluble in water to give air-stable green solutions. It sublimes at 70–80° (5 mm). Phenyl azide reacted very readily with $\pi\text{-}C_5H_5Co(CO)_2$ even at room temperature with vigorous evolution of gas and heat. An air-stable deep brown complex, $C_5H_5CoN_4(C_6H_5)_2$ (**2**), was obtained in 36% yield through repeated recrystallizations. The complex **2** was soluble in benzene, tetrahydrofuran, and methylene chloride but insoluble in water. The solution was stable in air. Compound **2** was sublimable at 180° (1 mm). The ir spectra (*cf.* Experimental Section) of these complexes showed the presence of the π-cyclopentadienyl group. No prominent bands are observed in the region of 2500–1600 cm^{-1}, implying the absence of triple-bond systems (such as $C{\equiv}O$, $-N{\equiv}N$, $C{\equiv}N$), cumulene systems ($-N{=}N{=}N$, $-N{=}C{=}O$), and double-bond systems ($C{=}O$, $C{=}N$). The phenyl derivative (**2**) exhibited characteristic bands due to a monosubstituted phenyl group. The far-infrared bands at 393 and 430 cm^{-1} for **1** and at 360, 400, and 403 (sh) cm^{-1} for **2** may be due to the π-cyclopentadienyl group. Bands at 489, 582, and 599 cm^{-1} for **1** and at 563 cm^{-1} for **2** probably have some connection to ν_{Co-N}. The electronic spectrum of **1** in C_2H_5OH showed maxima at 227 (ε 18,000), 258 (ε 9850), 337 (ε 1260), 430 (ε 6800), and 660 mμ (ε 470). The two bands in the visible region are similar to those of chlorophyll a (λ_{max} at 432 and 663 mμ in methanol). The absorption maxima of **1** may be compared with those of the phenyl derivative occurring at 270 (ε 19,000), 470 (ε 7700), and 660 mμ (ε 750).

The nmr spectrum of **1** (in $CDCl_3$) showed two singlets at τ 5.11 and 5.87 in a ratio of 5:6, which are assigned, respectively, to $\pi\text{-}C_5H_5$ and two equivalent CH_3 protons. The chemical shift of the methyl protons is near the value for the recently reported iron carbonyl complex $(CH_3)_2N_4Fe(CO)_3$[2] (τ 5.6), for which resonance structures involving 1,4-dimethyltetrazadiene and 1,4-dimethyltetraazendiyl groups are proposed. In comparison with the chemical shift of the $N{-}CH_3$ group in aliphatic or aromatic amines (τ 7.1–7.8), the observed value (τ 5.87) is low. Somewhat related complexes, $[(CH_3N{=}CHCH{=}NCH_3)_3Fe^{II}]^{2+}$ and $(CH_3\underset{|}{N}N{=}NCH_3)_3Al$, have their methyl resonances[3] at τ 6.8 in D_2O[4a] and at τ 6.8 in benzene,[4b] respectively. Although the chemical shift value of the free ligand 1,4-dimethyltetraazadiene is not available, the τ value of **1** is considered to be quite low and the downfield shift may be caused by the complex formation. In many cases the downfield shift of N-alkyl or S-alkyl protons upon lone-pair coordination has been observed.[5,6] In a few particular examples,[7] it was observed that the "metal atom field effect" caused a considerable downfield shift.[8] Therefore, until the effect is

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(1) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometal. Chem.* (Amsterdam), **7**, 339 (1966); *Inorg. Chem.*, **7**, 261 (1968).

(2) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

(3) Converted to τ values (reported values: 3.21 ppm from sodium 2,2-dimethyl-2-silapentane-5-sulfonate and 4.03 ppm from benzene, respectively).

(4) (a) N. Tanaka and T. Ito, private communication; (b) F. E. Brinckman, H. S. Haiss, and R. A. Robb, *Inorg. Chem.*, **4**, 936 (1965).

(5) R. R. Holmes and R. P. Carter, *ibid.*, **2**, 1146 (1963).

(6) R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965); **5**, 293 (1966).

(7) (a) R. B. King, *J. Am. Chem. Soc.*, **85**, 1922 (1963); (b) S. Trofimenko, *ibid.*, **89**, 6288 (1967).

(8) The authors are grateful to a referee who pointed out these examples.