Other Reactions.—In addition to the reactions which lead exclusively to the bis complexes, there are two other reactions which are worthy of note. The first is the equilibration of $Ni(\mathit{cis,cis}\text{-tach})_2^{2+}$ with an equivalent quantity of $Ni(H_2O)_6^{2+}$ to give, at least in solution, $Ni(\mathit{cis,cis}\text{-tach})(H_2O)_3^{2+}$. When the preparations of the Zn(II) and Cd(II) compounds were attempted, considerable quantities of the insoluble metal hydroxide were obtained. No attempt was made to prepare the Co(II) compound because of the ease of oxidation. The second reaction, which has been of considerable importance within this laboratory, is the acid decomposition of $Ni(\mathit{cis,cis}\text{-tach})_2^{2+}$. From this reaction isomerically pure ligand can readily be obtained. Earlier,[1] the decomposition of $Co(\mathit{cis,cis}\text{-tach})_2^{3+}$ in strong base was described. Although this reaction serves the same purpose, the kinetic stability of the Co(III) complex precludes utilization of this reaction as a preparative method. The lability of the Ni(II) complex in strong acid, however, facilitates the isolation of the pure ligand in large quantities, and additional studies which require the ligand uncontaminated with the *cis,trans* isomer have been possible. Some of these will be described in a subsequent publication.

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Anation of *cis*-$Co(en)_2NO_2dmso^{2+}$ Ion in Dimethyl Sulfoxide: Dissociative Interchange[1]

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Substantial evidence has accumulated to implicate bond breaking (dissociation) as the mode of activation in substitution reactions of octahedral complexes of cobalt(III).[3] However, several experiments[4-6] document the absence of a kinetically detectable five-coordinate intermediate in many cases. Of course, a dissociative mode of activation need not be accompanied by an intermediate. The point along the reaction coordinate with negligible bonding to either entering or leaving ligand may be merely the transition state. Such a situation has been termed dissociative interchange.[6-8] The entering group will appear in the rate law for dissociative interchange because it is a stoichiometric component of the transition state. However, all entering groups should react at the *same rate* if their encounters[9] with the substrate site are equally probable. In ion pairs between a cationic complex and an anionic entering group, different anions should have very similar probabilities for encounter with the reactive site on the substrate complex. However, the complex is simultaneously in encounter with several solvent molecules so that it is more probable that the crucial site on the complex is in encounter with a solvent molecule than an anion. Thus, we would expect the first-order rate constants for formation of inner-sphere complexes from ion pairs to be similar for all anions (dissociative mode of activation) but to lie below the rate constant for solvent exchange (since the probability of encounter with the solvent is higher).

The relationship between solvent-exchange rate and anation rate in ion pairs may distinguish dissociative interchange (I_d[10]) from the conventional dissociative pathway *via* an intermediate of reduced coordination number (D[10]). Recently, Watts and Lantzke[11] reported an elegant nmr experiment using a deuterium tracer to obtain the solvent-exchange rates of some dimethyl sulfoxide (dmso) complexes dissolved in dimethyl sulfoxide. For example, they report a rate constant of $3.07 \pm 0.07 \times 10^{-4}$ sec^{-1} at 35° for the reaction

$$\mathit{cis}\text{-}Co(en)_2NO_2dmso^{2+} + dmso^* = \mathit{cis}\text{-}Co(en)_2NO_2dmso^{*2+} + dmso \quad (1)$$

where the asterisk indicates labeled dmso and en is ethylenediamine. Tobe, Watts, and their coworkers have also shown that ion association between Co(III) complex cations and simple anions is quite pronounced at *low* electrolyte concentrations in dimethyl sulfoxide.[12,13] In this note, we report rates of the reactions

$$\mathit{cis}\text{-}Co(en)_2NO_2dmso^{2+} + X^- = \mathit{cis}\text{-}Co(en)_2NO_2X^{2+} + dmso \quad (2)$$

(where $X^- = Cl^-, NO_2^-$, and SCN^-) in dimethyl sulfoxide at 35.0° and at a constant ionic strength of 0.050 *M* maintained with $(C_6H_5)_4AsClO_4$. As anion concentrations are increased, the pseudo-first-order rate constants obtained approach a limit in two of the cases. This limiting rate is clearly associated with saturation of the equilibrium forming the ion pairs *cis*-$Co(en)_2NO_2dmso^{2+},X^-$. The rate of formation of *cis*-$Co(en)_2NO_2X^+$ from these ion pairs is the limiting rate. It may be compared to the solvent-exchange rate.

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(1) We gratefully acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society.

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Experimental Section

Dimethyl sulfoxide was Mallinckrodt reagent grade. $(C_6H_5)_4As^+$ salts were prepared by neutralization of $(C_6H_5)_4AsOH$ with the appropriate acid or by ion exchange. The cation was obtained as $(C_6H_5)_4AsCl$ in reagent grade from G. Frederick Smith Chemical Co. The salts were recrystallized from ethanol–water mixtures. The dmso complex was prepared by the method of Watts and Lantzke.[11] The product complexes and their *trans* isomers were prepared by the traditional methods.[14,15] Important spectral characteristics are as follows: *cis*-$[Co(en)_2NO_2dmso](ClO_4)_2$: λ 440, ε 87; λ 470, ε 115; λ 490, ε 125. *cis*-$[Co(en)_2NO_2Cl]DlO_4$: λ 490, ε 85. *cis*-$[Co(en)_2NO_2NCS]ClO_4$: λ 470, ε 274. *cis*-$[Co(en)_2(NO_2)_2]ClO_4$: λ 440, ε 180. λ is the wavelength in mμ and ε is the molar extinction coefficient.

The reactions were followed at two wavelengths in the visible region using a Beckman DU spectrophotometer with a Gilford absorbance indicator and equipped with a thermostated cell chamber maintained at 35.0 ± 0.1°. Anions were introduced as $(C_6H_5)_4As^+$ salts and the metal complex as its perchlorate. Ionic strength was maintained at 0.050 *M* with $(C_6H_5)_4AsClO_4$. The metal complex concentrations were chosen over the range $(1–4) \times 10^{-3}$ *M*, and reactive anion concentrations were chosen in the range 0.001–0.050 *M*.

First-order rates of approach to equilibrium (independent of complex concentration) are reported for each anion concentration. They are calculated from data collected over 3 half-lives of the reactions. Satisfactory agreement with a first-order rate law is not expected for the experiment in which Cl^- concentration equaled complex concentration (see Table I). A first-order plot was anomalously satisfactory. Comparison of "infinity time" spectra taken after 7 half-lives of the reactions with spectra of synthetic products shows that conversion to product was incomplete. However, percentage conversion to product calculated from data at the two different wavelengths suggests that the product formed was at least 95% *cis*. (No evidence for *trans* was obtained.)

Results

Table I displays rates of approach to equilibrium as a function of entering anion concentration along with percentage conversion to anionic product at equilibrium. All of these rates are pseudo-first order. Therefore, each rate of approach to equilibrium may be combined with the fraction of conversion *via* the formalism of opposed first-order reactions[16] to give the pseudo-first-order rate constants for anations (eq 2). These anation rate constants are shown in Figure 1 as a function of anion concentration. The rate of dimethyl sulfoxide exchange is shown as a broken line at the top of the figure.

TABLE I

RATES OF APPROACH TO EQUILIBRIUM (k_{eq}), ANATION RATES (k_{an}), AND THE EQUILIBRIUM PERCENTAGE OF CONVERSION OF COMPLEX TO THE ANIONIC FORM (%)[a]

	Anion concn, *M*							
	0.001	0.002	0.005	0.010	0.020	0.030	0.040	0.050
1. Chloride								
k_{eq}	3.6	6.5	9.7	9.3	7.0	7.8	8.3	9.2
k_{an}	(2.0)[b]	(3.6)	5.4	5.4	3.9	4.4	4.6	5.4
%[c]			56	56	56	56	56	56
2. Nitrite								
k_{eq}			6.0	8.9	11.1	15.3	15.7	15.8
k_{an}			4.5	6.6	8.4	11.5	11.8	11.9
%[c]			75	75	75	75	75	75
3. Thiocyanate								
k_{eq}				0.47	0.83	1.6	2.4	2.5
k_{an}				0.39	0.64	1.3	2.0	2.1
%[c]				80	80	81	82	82

[a] Note that the per cent conversion is independent of total complex concentration when the anion is in large excess. Rate constants are quoted in $sec^{-1} \times 10^5$. [b] The values in parentheses are to be considered less accurate. They were not expected to conform to a first-order rate plot but did so within the considerable experimental error. [c] This quantity is sufficient to determine the over-all equilibrium constant for the reaction. However, it is convenient not to tabulate constants since two different ones may be defined. At lower anion concentrations it would be convenient to treat the reactants as the free ions. At higher anion concentrations it would be convenient to treat the reactant as an ion pair. The two treatments are connected by the value of *K* from eq 4 which is given in the text.

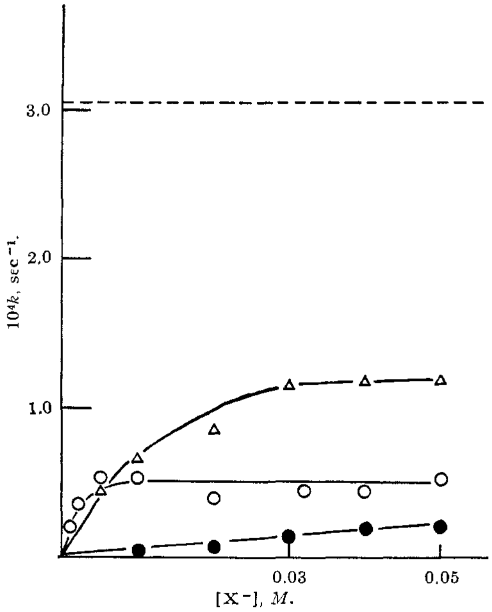

Figure 1.—Rate of anation of *cis*-$Co(en)_2NO_2dmso^{2+}$ ion as a function of the concentration of the entering anion X^-: △, $X^- = NO_2^-$; ○, $X^- = Cl^-$; ●, $X^- = SCN^-$. The broken line shows the rate of the dmso-exchange reaction.

Discussion

The rates of anation of *cis*-$Co(en)_2NO_2dmso^{2+}$ by chloride and nitrite reach limiting values at low anion concentration. The rate of reaction with thiocyanate does not reach a limit.[17] Clearly, the equilibrium constants for forming ion pairs between the complex and Cl^-, or NO_2^-, are larger than 10^2 where the corresponding constant for SCN^- is less than 20. Values of ion-pairing constants of 650 for Cl^- and 120 for NO_2^- fit the curvature of the low-concentration regions. The lack of curvature in the SCN^- data implies a value less than 20. (These are the *K*'s of eq 4 below.) This is consistent with Parker's ideas about anion solvation in dimethyl sulfoxide.[18]

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We resolve the anation reaction (eq 2) into two steps

$$cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+} + \text{X}^- \overset{K}{\rightleftharpoons} cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+},\text{X}^- \quad (3)$$

$$cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+},\text{X}^- \xrightarrow{k} cis\text{-Co(en)}_2\text{NO}_2\text{X}^+ + \text{dmso}$$

where K is the equilibrium constant for ion association and k is the first-order rate constant for anation. The observed pseudo-first-order rate constants, k_{obsd}, are related to k and K by

$$k_{\text{obsd}} = \frac{kK[\text{X}^-]}{1 + K[\text{X}^-]} \quad (4)$$

The brackets in (4) represent molar concentrations. It follows that the limiting rate observed with Cl^- and NO_2^- is k. The slope of the thiocyanate plot is kK. (The difficulty we experience in finding k for SCN^- is parallel to the results of Watts, Tobe, and coworkers.)

Values of k for Cl^-, NO_2^-, and SCN^- are, respectively, 5.0×10^{-4}, 1.2×10^{-4}, and $>5.0 \times 10^{-5}$ (probably $<1.0 \times 10^{-4}$; see ref 17). All these values are well below the solvent-exchange rate and span a range of little more than a factor of 2. If one admits that there would be a difference among the anions in the probability of occupancy of the *reactive* site in the ion pair (from the stereochemistry it seems that it would be adjacent to the leaving dmso), the results are accommodated by the I_d model. A model focusing on nucleophilic attack by the anions would face the difficulty that the equilibrium data imply a stronger cobalt–ligand bond to any of the anions than to dmso.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Four-, Five-, and Six-Coordinated Nickel(II) and Cobalt(II) Complexes of Schiff Bases Derived from Pyridine-2-carboxaldehyde and N,N-Substituted Ethylenediamines

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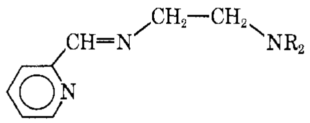
It has been found that tridentate Schiff bases derived from N,N-substituted ethylenediamines and *ortho*-substituted benzaldehydes form pentacoordinate complexes with nickel(II) salts when the terminal nitrogen atom of the ethylenediamine possesses appropriate steric hindrance. Examples of this are the complexes formed with the Schiff bases derived from N,N-diethyl- and N,N-dimethylethylenediamine and *o*-methylaminobenzaldehyde (set NNN),[2] *o*-methylthiobenzaldehyde (set SNN),[3] and *o*-methoxybenzaldehyde (set ONN),[4] respectively. In order to study the stereochemistry of the complexes formed when a heterocyclic nitrogen donor is substituted for a nitrogen donor attached to the ring, we have prepared a new ligand, which is the Schiff base formed from pyridine-2-carboxaldehyde and N,N-dimethyl- and N,N-diethylethylenediamine (I), indicated as PyAenR_2,



I

possessing the set of donor atoms NNN. We have also synthesized a similar ligand, derived from furan-2-carboxaldehyde and N,N-dimethylethylenediamine, indicated as FuAenR_2, and possessing the potential set of donor atoms ONN, in order to study its coordinating capacity toward cobalt(II). All of the complexes obtained have the general formula MLX_2 (M = Co, Ni; L = PyAenR_2, FuAenR_2; X = Cl, Br, I, NO_3). During the course of this work two papers regarding pentacoordinate complexes of cobalt(II)[5] and nickel(II)[6] with tridentate ligands containing the pyridyl group have appeared.

Experimental Section

Preparation of the Compounds.—The compounds were prepared by two methods and identical crystalline compounds were always obtained. In the first method equimolar quantities of pyridine-2-carboxaldehyde or furan-2-carboxaldehyde and the appropriate substituted ethylenediamine were heated under reflux for 0.5 hr using ethanol as a solvent. The Schiff base formed in this way was then distilled under vacuum and used without further purification. Samples of 10 mmol of the crude Schiff base and 10 mmol of the appropriate metal halide were dissolved in 50 ml of 1-butanol and heated to boiling. The mixture was concentrated and cooled slowly to obtain needlelike crystals. The complexes were filtered in an atmosphere of dry, pure nitrogen and then dried in a vacuum oven. In the second method of preparation the substituted ethylenediamine, pyridine-2-carboxaldehyde or furan-2-carboxaldehyde, and the metal halide were dissolved in 1-butanol (10 mmol of each compound in 50 ml of solvent); the solution was then heated, concentrated, and cooled. In both cases the yield was about 50–60%.

Physical Measurements.—The electronic spectra, magnetic measurements, and molecular weight and conductometric measurements were performed as reported in ref 2.

Results and Discussion

The analytical data and properties of the complexes are reported in Table I. The complexes are all of the high-spin type. The compounds are soluble in nitroethane and 1,2-dichloroethane and are insoluble in nonpolar solvents. Molecular weight and conductivity values (see Table I) indicate that the complexes are essentially monomeric and nonelectrolytic in solution in inert solvents.

The spectra of the solid compounds are practically identical with those in solution. The halide derivatives show three main peaks at *ca.* 6000, 14,000, and 22,000 cm^{-1} for the nickel complexes (see Figure 1) and

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