these considerations and much intense experimental effort, no unequivocal conclusions can be drawn with regard to the structural difference between the $\alpha(1)$ and $\alpha(2)$ isomers at the present time. We recognize the possibility of other sources for the isomerism; *e.g.*, different modes of oxalate coordination, etc.

The stereochemical relationships in the multiform system $[Co^{III}(CRH)X_2](ClO_4)]$ are summarized in Figure 12.

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Kinetics of the Reactions between 1,2-Diaminocyclohexanetetraacetatocobaltate(II) Ion and Cyanide Ion

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Cyanide ion reacts very rapidly with cobalt(II)–CyDTA to form a 1:1 mixed complex. The formation rate, studied from 5 to 25° by the temperature-jump relaxation technique, is first order in cobalt–CyDTA and first order in cyanide ion with a rate constant of $k_1 = 1.8 \times 10^6\ M^{-1}\ sec^{-1}$ at 25°. The activation energy, 0.8 kcal/mol, and the fact that k_1 is about 5000 times larger than expected from the characteristic water-exchange value of Co(II), suggest that cobalt–CyDTA–cyanide is a seven-coordinate complex. The stability constant of $CoCyCN^{3-}$ at 25° is 39 M^{-1} as determined by both temperature-jump and spectrophotometric techniques. The rate of complete replacement of CyDTA by cyanide to give $Co(CN)_5^{3-}$ (and its oxidized products) is slow. The reaction is first order in $CoCyCN^{3-}$ and second order in CN^- with a rate constant equal to $9.5 \times 10^{-3}\ M^{-2}\ sec^{-1}$. The mechanism for the replacement of CyDTA from cobalt by cyanide ion is the same as that observed for the reactions of cyanide ion with $NiEDTA^{2-}$ and $CoEDTA^{2-}$, which also involve three cyanide ions. The cyanide ion displacement of CyDTA from cobalt(II) is 1.2×10^5 times slower than the corresponding displacement of EDTA.

Introduction

There is a rapid reaction between *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetatocobaltate(II) ion, $CoCy^{2-}$, and cyanide ion to form a 1:1 mixed complex

$$CoCy^{2-} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CoCyCN^{3-} \qquad (1)$$

The reaction is sufficiently fast that it was necessary to use the temperature-jump relaxation method to study it. The rate was more than 1000 times that predicted from the characteristic water-exchange rate constant for the aquocobalt(II) ion after correction for outer-sphere repulsion.

With a large excess of cyanide ion a second much slower reaction occurs with the displacement of the CyDTA and the formation of $Co(CN)_5^{3-}$ and its air-oxidized products.

$$CoCyCN^{3-} + 2CN^- \xrightarrow[\text{rate-detn}]{k_2} \text{(intermediate species)} \qquad (2)$$

$$\text{(intermediate species)} + 2CN^- + H^+ \xrightarrow{\text{fast}} Co(CN)_5^{3-} + HCy^{3-} \qquad (3)$$

$$Co(CN)_5^{3-} \xrightarrow{O_2} [Co(CN)_5]_2O_2^{6-},\ Co(CN)_5(H_2O)^{2-}, \text{etc.} \qquad (4)$$

The kinetic dependence is given by eq 2; a total of only three cyanide ions, including the one in eq 1, is needed in the rate-determining step. The nature of the intermediate species is not known and might be $Co(CN)_3Cy^{5-}$ or $(Co(CN)_3^- + Cy^{4-})$, but the cobalt species is a kinetic intermediate without appreciable concentration and it reacts rapidly with additional cyanide ion. The rate of release of HCy^{3-} in eq 3 equals the rate of disappearance of $CoCyCN^{3-} + CoCy^{2-}$. A mixture of products is formed after the rapid reaction of O_2 with $Co(CN)_5^{3-}$.

Experimental Section

The acid form of CyDTA was obtained from LaMont Laboratories and was purified by recrystallization from water.

Standard solutions of cobalt–CyDTA, 0.018–0.054 M, were prepared by adding an excess of cobalt(II) perchlorate to a standard CyDTA solution and removing the excess cobalt by hydroxide precipitation at pH 10.

Sodium cyanide solutions were standardized before use by titration with silver nitrate in the presence of iodide ion.

Absorption spectra were recorded on a Cary 14 spectrophotometer. The spectrum of $CoCy^{2-}$ had absorption maxima at 608, 510, and 460 mμ with extinction coefficients of 1, 7, and 8 $M^{-1}\ cm^{-1}$, respectively. Air oxidation of $CoCy^{2-}$ to give the Co(III)–CyDTA complex is extremely slow and could not be detected spectrophotometrically over a period of several months. The Co(III) complex, obtained by H_2O_2 oxidation, has absorption maxima at 550 and 380 mμ. The mixed Co(II)–CyDTA–cyanide complex, with an absorption maximum at 487 mμ (ϵ 72.5 $M^{-1}\ cm^{-1}$) and a shoulder at 510 mμ, also was stable to air oxidation.

Kinetic Measurements Using Temperature-Jump Relaxation.—The apparatus used was described earlier.[2] The temperature-

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[1] Correspondence to be addressed to this author.

[2] D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).

jump cell was thermostated to ±0.1° and the magnitude of the jump was 5.7° using a 40-kV discharge. A time of 5–7 min was allowed between jumps for the solution to attain temperature equilibrium. The absorbance change after the temperature jump was followed at 487 mμ, the absorbance maximum of the mixed complex, $CoCyCN^{3-}$. An indicator was not necessary. A solution of $CoCy^{2-}$ and $NaClO_4$ without NaCN showed no relaxation. The concentration ranges used in the study were: $[CoCy^{2-}] = (5\text{–}10) \times 10^{-3}$ *M* and $[CN^-] = (1\text{–}5) \times 10^{-2}$ *M*. The ionic strength was maintained at 0.10 with $NaClO_4$ and all solutions were adjusted to pH 11.50 ± 0.02 with NaOH.

Large relaxation signals were observed and the curves obeyed the expression for a single-step relaxation.[3] The relaxation expression for eq 1 is

$$\tau^{-1} = k_{-1} + k_1(\overline{[CoCy^{2-}]} + \overline{[CN^-]}) \qquad (5)$$

where τ is the observed relaxation time and the mean concentrations are those after the temperature jump. Each τ value was obtained from an average of four or more individual relaxation experiments. The average standard deviation for the τ values is 7%. The best values of k_1, k_{-1}, and K_1 $(= k_1/k_{-1})$ were calculated using an iterative computer program which gave the least-squares fit for eq 5 by correcting the reactant concentrations for the amount of $CoCyCN^{3-}$ formed.[2]

Kinetics of Replacement of CyDTA by Cyanide Ion.—Attempts to study reactions 2–4 spectrophotometrically by monitoring the disappearance of reactants or the appearance of products were not successful, because several species such as $(CN)_5Co\text{–}O\text{–}O\text{–}Co(CN)_5{}^{6-}$, $Co(CN)_5H_2O^{2-}$, and $Co(CN)_5OH^{3-}$, which result from the oxidation of $Co(CN)_5{}^{3-}$, form and disappear during the reaction. These species have absorption spectra which overlap with those of $CoCyCN^{3-}$ and $Co(CN)_5{}^{3-}$.

A complexometric method was developed to determine the amount of uncomplexed CyDTA in the presence of $CoCy^{2-}$, CN^-, and the oxidation products of $Co(CN)_5{}^{3-}$. The reaction solutions were kept saturated with oxygen in order to ensure rapid oxidation of $Co(CN)_5{}^{3-}$. For the kinetic measurements, 10-ml aliquots of the reaction mixture were withdrawn at hourly intervals, added to 90 ml of 0.01 *M* NaOH, and immediately titrated with Ca^{2+} using methylthymol blue indicator. The dilution quenched the cyanide reaction and the total elapsed time from dilution of the sample to the end of the titration was only 3–5 min in order to give negligible reaction after the dilution. The reactions were maintained at 25.0 ± 0.02° with 0.10 ionic strength ($NaClO_4$) and adjusted to pH 11.50 ± 0.02 with NaOH. The initial $CoCy^{2-}$ concentration was 4.52×10^{-3} *M* and the NaCN concentration was varied from 0.04 to 0.08 *M* in five different runs.

Results and Discussion

I. Equilibrium and Kinetics of $CoCyCN^{3-}$

Determination of the Stability Constant of the Cobalt(II)–CyDTA–Cyanide Complex.—A spectrophotometric mole ratio study (of CN^- to $CoCy^{2-}$) did not give a definite break and the absorbance did not reach a constant value up to 0.1 *M* CN^-. Nevertheless, large absorbance changes occurred at 487 mμ and the data give a consistent stability constant for a 1:1 stoichiometry as shown in Table I. Equation 6 was used for

$$K_1 = \frac{[CoCyCN^{3-}]}{[CoCy^{2-}][CN^-]} = \frac{\Delta A/\Delta\epsilon}{\{[CoCy]_T - (\Delta A/\Delta\epsilon)\}\{[CN]_T - (\Delta A/\Delta\epsilon)\}} \qquad (6)$$

these calculations where $\Delta A = A - A_0$, A_0 is the absorbance of $CoCy^{2-}$ in absence of CN^-, and $\Delta\epsilon = \epsilon_{CoCyCN} - \epsilon_{CoCy}$.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF THE STABILITY CONSTANT OF $CoCyCN^{3-}$

$10^3[CoCy^{2-}]$, *M*	$10^3[CN^-]$, *M*	Absorbance (487 mμ, 1-cm cell)	K_1, M^{-1} [a,b]
3.67	1.85	0.045	48.6
	3.69	0.057	42.9
	5.54	0.070	43.9
	9.23	0.088	40.7
	18.5	0.127	42.1
	18.8	0.115	32.9
	27.7	0.151	41.6
7.30	1.88	0.083	41.4
	3.76	0.105	38.5
	5.65	0.121	34.1
	9.40	0.161	36.6
	18.8	0.228	35.5
	28.2	0.281	36.8
	28.2	0.284	37.7
18.3	0.00	0.142	...
	3.76	0.230	33.4
	5.60	0.275	35.5
	9.40	0.357	36.4
	18.8	0.541	40.1
	28.2	0.669	39.9
	110	1.075	38.6
		Av	38.9
		σ	3.9

[a] The ϵ and K_1 values for $CoCyCN^{3-}$ were obtained by reiteration of all of the data and the individual K_1 values are based on ϵ 72.5 M^{-1} cm^{-1}. [b] pH 11.5, μ 0.10, and 25°. [c] A_0 value.

A computer program was written which calculated both K_1 and ϵ_{CoCyCN} from the 20 data points by iteration until successive K_1 values agreed within 0.5%. The values obtained from this calculation are $\epsilon_{CoCyCN} = 72.5\ M^{-1}$ at 487 mμ and $K_1 = 39 \pm 4\ M^{-1}$.

Magnetic Measurements.—The magnetic susceptibility of the 1:1 complex in aqueous solution was determined using a Faraday balance. There was no significant difference between the magnetic moment of $CoCy^{2-}$ and $CoCyCN^{3-}$; both were approximately 5.0 BM. Thus, it requires more than one cyanide to cause a transition from high spin to low spin.

Kinetics.—The relaxation times for reaction 1 were very short with values of 10–30 μsec at 5.7° under the conditions studied. These fast relaxation times are close to the limiting response time of our instrument. Figure 1 shows the plot of eq 4 where the mean concentrations, the slope, and the intercept were calculated by the program described. As the temperature was increased, fewer and fewer τ values could be obtained over the concentration range needed to observe the complex. Hence there are only three points at 15° and two points at 25°. Table II summarizes the constants obtained from Figure 1. Although only two relaxation times were obtained at 25°, the calculated value for K_1 is 40 M^{-1} which is in excellent agreement with the value of 39 M^{-1} obtained from equilibrium studies.

The temperature dependence of the forward and reverse rate constants is described by the Arrhenius equations: $k_1 = 6.8 \times 10^6 \exp(-800/RT)$ and $k_{-1} =$

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(3) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Part II, p 902.

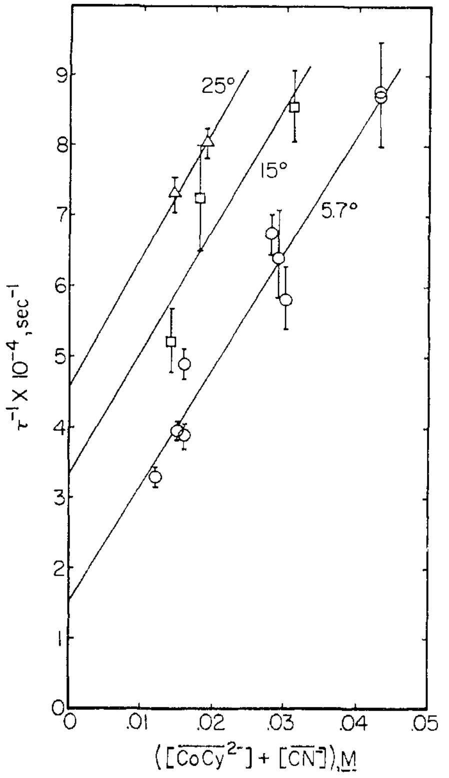

Figure 1.—Reciprocal of the relaxation times for the reaction $CoCy^{2-} + CN^- \rightleftarrows CoCyCN^{3-}$.

Table II

Kinetics of Formation and Dissociation of $CoCyCN^{3-}$ as a Function of Temperature at pH 11.50 and μ = 0.10

Temp, °C	$10^{-6}k_1$, M^{-1} sec^{-1}	$10^{-4}k_{-1}$ sec^{-1}	K_{CoCyCN}, M^{-1}
5.7	1.66	1.53	108
15.0	1.72	3.35	51
25.0	1.82	4.56	40

$3.7 \times 10^{11} \exp(-9400/RT)$. At 25.0° for the forward reaction $\Delta H^{\ddagger}$ = 0.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −29.3 cal deg^{-1} mol^{-1} and for the reverse reaction $\Delta H^{\ddagger}$ = 8.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −7.6 cal deg^{-1} mol^{-1}. Although the $\Delta H^{\ddagger}$ value for the forward rate constant, k_1, is nearly zero, the τ values are sensitive to temperature changes because eq 5 also depends on the reverse rate constant.

The differences in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for k_1 and k_{-1} give ΔH = −8.6 kcal mol^{-1} and ΔS = −21.7 cal deg^{-1} mol^{-1} for reaction 1. These values corresponded to a K_1 value of 38 M^{-1} at 25° which again is in excellent agreement with the value of 39 M^{-1} obtained from equilibrium studies. The consistency of the K_1 value obtained from the different sets of data tends to confirm the reliability of the kinetic data although only a few points are available. The $\Delta S^{\ddagger}$ value for the forward reaction has the expected sign and magnitude for the reaction of like-charged ions in aqueous solution.

Discussion of the Low Activation Energy and the High Rate of Formation of $CoCyCN^{3-}$.—The experimental activation energy, 0.8 kcal/mol, is much less than the generally accepted value of 3.5 ± 0.4 kcal/mol for diffusion-controlled reactions in aqueous solutions.[4,5] Few reactions have this low an activation energy. Reactions of the hydrated electron with H^+ and NO_2^- have values of 2.6 and 1.7 kcal/mol, respectively.[6] Huchital and Wilkins[7] encountered a zero activation energy for the reaction

$$Co^{II}(EDTA)^{2-} + Fe^{III}(CN)_6^{3-} \rightleftarrows (EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5^{5-} \quad (7)$$

Their explanation for the zero activation energy was that the forward rate constant for the reaction is a composite of cyanide bridge formation and an electron-transfer process.

In the present case the reaction appears to be so simple that the only way to account for the extremely low value of the activation enthalpy is that the energy required for diffusion is offset by a large degree of cyanide bonding before the transition state. Appreciable bonding of the incoming ligand before the transition state is not typical for octahedral substitution reactions of divalent metals. Indeed the value for k_1 is far greater than would be expected for "normal" cobalt(II) substitution reactions between ions of the same charge. The characteristic water-exchange value[8] for Co(II) is 3.8×10^5 sec^{-1} and the outer-sphere "association constant", K_{os}, for a −2 ion and a −1 ion is calculated[9] to be 0.005 for an interaction distance of 4.0 Å. If the water-exchange value were not affected by CyDTA, a k_1 value of 1.9×10^3 M^{-1} sec $^{-1}$ would be predicted. The experimental value of k_1 is much larger and equals 1.8×10^6 M^{-1} sec^{-1} at 25°. In the case of nickel(II) its coordination with CyDTA slows down the rate of its reaction with CN^-. The rate constant for the formation[10] of $NiCyCN^{3-}$ is only 27 M^{-1} sec^{-1}, which is a factor of 5 less than would be predicted using the characteristic water exchange of the aquonickel ion and a K_{os} value of 0.005. This agrees with the observation that the coordination of EDTA to nickel decreases the water-substitution rate constant with NH_3 by a factor of 6. [The K_{os} value of 0.005 also can be calculated from experimental data for the water–ammonia exchange rate constant of $NiEDTA^{2-}$ and the rate of formation of $Ni(EDTA)CN^{3-}$.] Hence the formation rate constant for $CoCyCN^{3-}$ is about 4700 times larger than expected. However, k_1 is much less than the value of 7×10^8 M^{-1} sec^{-1} which would be calculated for a diffusion-controlled reaction of a −2 ion with a −1 ion with an interaction distance of 4.0 Å.[11]

A comparison of the ratio of rate constants for Co(II) and Ni(II) complexed to the same ligand with identical

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[4] M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, **2**, 287 (1964).

[5] M. Anbar, Z. B. Alfasse, and H. Bregman-Reisler, *J. Am. Chem. Soc.*, **89**, 1263 (1967).

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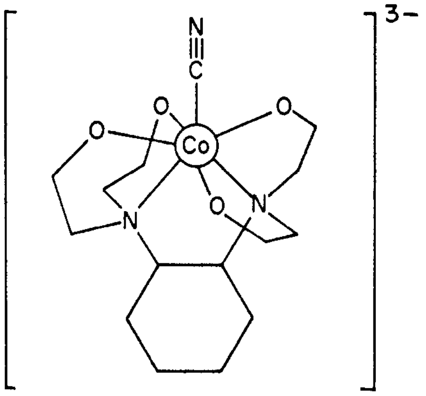
bonding has been used as a measure of their difference in activation energies[12]

$$\Delta E_a = E_a(\mathrm{Ni}) - E_a(\mathrm{Co}) = RT \ln(k_{\mathrm{Co}}/k_{\mathrm{Ni}})$$

Hammes and Steinfeld studied the glycine, diglycine, and imidazole reactions and found a value of 1.9 kcal/mol for ΔE_a. By contrast the ΔE_a calculated in this way is 6.6 kcal/mol for the $CoCy^{2-}$ and $NiCy^{2-}$ reactions with CN^-. This indicates that there is a significant difference in the bonding and mechanism for the cyanide reaction with the cobalt and nickel CyDTA complexes. There is reason to believe that the $CoCyCN^{3-}$ complex is seven-coordinate. Wilkins has shown that EDTA bonds all six of its coordinating groups to cobalt(II) in aqueous solutions.[13] CyDTA should do the same and a $\Delta H^{\ddagger}$ value of nearly zero is extremely unlikely if a carboxylate group has to be broken in order for the cyanide complex to form.

There are several examples of seven-coordinate EDTA and CyDTA complexes. Both the Mn(II)[14]- and the Fe(III)[15]-EDTA complexes have been shown to be sexadentate seven-coordinate aquo complexes in X-ray studies of their crystalline salts. The calcium salt of Fe(III)-CyDTA, $Ca[Fe(OH_2)Cy]_2 \cdot 9H_2O$, also is seven-coordinate with one water molecule and six groups from CyDTA coordinated.[16] A suggested structure for $CoCyCN^{3-}$ paralleling the seven-coordinate iron(III)-CyDTA complex is shown in structure I.



I

The low activation energy and the high value for k_1 could be explained by the reaction of a six-coordinate cobalt complex ($CoCy^{2-}$) forming a seven-coordinate complex ($CoCyCN^{3-}$).

II. Kinetics of the Complete Displacement of CyDTA by Cyanide Ion

In the presence of excess cyanide ion CyDTA is completely replaced from cobalt to give $Co(CN)_5^{3-}$ as described in eq 2 and 3. The rate of release of CyDTA followed eq 8 where $[CoCy]_T = [CoCy^{2-}] + [CoCyCN^{3-}]$, provided the cyanide ion was in sufficient excess to remain constant during the reaction.

$$\frac{d[HCy^{3-}]}{dt} = k_0[CoCy]_T \tag{8}$$

Good first-order plots were obtained in following the reaction to the release of 80% of the CyDTA from the cobalt. Table III shows the dependence of k_0 on the cyanide concentration. In this range of cyanide concentration, the $CoCyCN^{3-}$ complex is only partially formed, and when k_0 is corrected for this as shown in eq 9, the total cyanide

$$(1 + K_1[CN^-])k_0 = k_2K_1[CN^-]^3 \tag{9}$$

dependence is third order. The graph of eq 9 gave a good straight line with a zero intercept. A value for k_2 of 9.5×10^{-3} M^{-2} sec^{-1} was determined from the slope.

TABLE III

DEPENDENCE OF k_0 ON THE CONCENTRATION OF EXCESS CYANIDE ION AT $[CoCy]_T = 4.5 \times 10^{-3}$ M, $\mu = 0.10$, pH 11.50, AND 25 ± 0.02°

10^2[NaCN], M	10^5k_0, sec^{-1}
7.97	3.31 ± 0.08[a]
7.97	3.31 ± 0.10
6.38	2.31 ± 0.11
3.98	0.82 ± 0.00
3.98	0.82 ± 0.14

[a] Standard deviations are given using four to seven points.

Comparison with Other Systems.—Cyanide reactions with the nickel and cobalt complexes of EDTA and CyDTA now can be compared. All four complexes form 1:1 mixed complexes with cyanide. The stability constants and experimental conditions of measurement for these complexes are shown in Table IV.[10,17,18]

TABLE IV

STABILITY OF 1:1 MIXED COMPLEXES AT 25°

Complex	pH	μ	K_1, M^{-1}	Ref
$Ni(EDTA)CN^{3-}$	11.0	0.10	1.2×10^4	10
$Ni(CyDTA)CN^{3-}$	11.4	0.10	310	17
$Co(EDTA)CN^{3-}$	11.7	0.20	2×10^3	18
$Co(CyDTA)CN^{3-}$	11.5	0.10	39	This work

The ratio of the K_1 value of NiEDTA to that of NiCyDTA is 39 and the ratio of the value for CoEDTA to that of CoCyDTA is 51. The ratios are very similar and show that for both metal ions the $M(CyDTA)CN^{3-}$ mixed complex is less stable than the $M(EDTA)CN^{3-}$ complex by the same factor.

The mechanism in eq 1 and 2 is the same as that found for the cyanide ion replacement of EDTA from nickel.[19] Nakamura[18] also proposed this mechanism for the stopped-flow studies of $CoEDTA^{2-}$ reacting with cyanide ion. In each of these three cases, a total of three cyanide ions is present in the rate-determining step. The values for k_2, the third-order rate constant for the reaction of two cyanide ions with $M(EDTA)CN^{3-}$, are 4.2 M^{-2} sec^{-1} for nickel and 1.1×10^3 M^{-2} sec^{-1} for cobalt. Thus the effect of using cobalt in place of

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[18] S. Nakamura, Ph.D. Thesis, The University of Chicago, 1964.

[19] D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Am. Chem. Soc.* **83**, 1791 (1961).

nickel in the EDTA complexes is to increase the k_2 value by a factor of 260. The effect of using EDTA in place of CyDTA with the cobalt complexes is to increase the k_2 value by a factor of 1.2×10^5. On the basis of these ratios, the k_2 value for $NiCyCN^{3-}$ can be predicted to be 3.5×10^{-5} M^{-2} sec^{-1} if direct proportionality is valid. A very small value of k_2 is in agreement with the observation[17] that over a period of 2 months no displacement of CyDTA from nickel occurred using 0.01 *M* cyanide ion and, in fact, k_2 must be less than 3×10^{-5} M^{-2} sec^{-1}.

Ligand replacement reactions for EDTA complexes compared to CyDTA complexes are much faster in general. The rate constants of the polyamine reactions of $CuEDTA^{2-}$ were found[20] to be about 5×10^4 greater than for the corresponding reaction with $CuCyDTA.^{2-}$

The diminished reactivity of the CyDTA complexes is attributed in part to steric effects due to interference of the cyclohexane ring and in part to the greater initial stability of the complexes. In the case of cobalt(II) $\log K_1 = 19.6$ for CyDTA[21] compared to $\log K_1 = 16.3$ for EDTA[22] at 20°. The greater thermodynamic and kinetic stability is due to the more basic nitrogen atoms and the cagelike structure of the CyDTA complex.

In each of these polyaminocarboxylate systems, an over-all third-order cyanide dependence was found in contrast to the fourth-order dependence found for the formation of tetracyanonickelate(II) from the aquonickel ion[23] and from triethylenetetraminenickel(II).[24]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WOOLWICH POLYTECHNIC, NORTHERN POLYTECHNIC,
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Metal Complexes of Azopyridines. II. Complexes of Bivalent Cobalt, Nickel, and Copper with 3,3′- and 4,4′-Azopyridines

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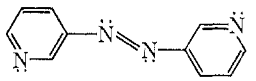
4,4′-Azopyridine (L′) and 3,3′-azopyridine (L″) have been used to prepare complexes of the type $MX_2 \cdot L$ (L = L′ or L″; M = Co, X = Cl, Br, I; M = Ni, Cu, X = Cl, Br), of the type $MSO_4 \cdot nH_2O \cdot L'$ (M = Cu, $n = 4$; M = Co, $n = 2, 6$), and $CuSO_4 \cdot L'$. Structures are suggested on the basis of diffuse reflectance spectra, infrared spectra (450–80 cm^{-1}), and magnetic properties. Except for $CoBr_2 \cdot L'$, $CoI_2 \cdot L'$, and CoI_2L'' which are pseudotetrahedral, the halide complexes have distorted octahedral structures involving halogen and azopyridine bridges. The oxyanion complexes appear to have the metal atom in a tetragonal environment.

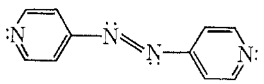
Introduction

The base 2,2′-azopyridine and its 3,3′ and 4,4′ isomers are stable in solution in their *trans* configurations.[2] Models show that of the three isomers only 2,2′-azopyridine will chelate without undue strain. Preliminary experimental work showed that 2,2′-azopyridine could form more than one type of complex when different mole ratios of reactants were used, but that the other two organic bases always gave 1:1 complexes. A brief report on the preparation of some of the 2,2′- and 4,4′-azopyridines has been made previously.[3]

The work has now been extended and a clearer picture of the coordination behavior of these ligands has been obtained. We report here the results for the complexes of 3,3′-azopyridine (=L″) and 4,4′-azopyridine (=L′)



L″



L′

Experimental Section

Preparation of Compounds.—The 3,3′- and 4,4′-azopyridines were prepared from 3- and 4-aminopyridine, respectively, by a modified method of Kirpal and Reiter and the products[4] were purified by partition chromatography.[5]

Recrystallization of 3,3′-azopyridine from petroleum ether (bp 60–80°) gave orange needles, mp 142°, and the 4,4′ isomer formed yellow-brown needles, mp 109°.

The complexes were prepared by mixing ethanolic solutions of metal salts and ligands. The precipitates were isolated by centrifugation, washed with ethanol and then with dry ether, and dried *in vacuo* at room temperature over silica gel. Attempts to obtain complexes other than the 1:1 type failed. Analytical results are given in Table I.

Physical Measurements.—Magnetic susceptibility measurements at room temperature were made by the Gouy method using $HgCo(NCS)_4$ as the calibrant. The diamagnetic correction for

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