ported. In fact, no values calculated in the above fashion have been reported, probably because of the difficulty of determining r for a nonrigid structure. It is interesting that the $(\partial \ln D/\partial T)$ value obtained, -2.5×10^{-3} deg^{-1}, is of the same order of magnitude as that reported[17] for bulk water, -4.7×10^{-3} deg^{-1}.

The thermodynamic values determined in this study for $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ proton ionization were found not to fit the same linear $\Delta G°$–$\Delta S°$ relation found for other carboxylic acids.[2] The two points for $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ on a plot of $\Delta G°$ *vs.* $\Delta S°$ fall on a parallel line with a different intercept. It would now be of interest to study other boranocarboxylic acids to learn if this intercept is characteristic of the $\Delta H°$ values for ionization of carboxylic acids with the carboxyl group attached to a boron atom.

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The Equilibrium and Kinetic Properties of the Aqueous Hydroxide–Nitroprusside System

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A complete thermodynamic and kinetic investigation of the aqueous hydroxide–pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, system has been carried out. For the equilibrium

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2{}^{4-} + H_2O \qquad (1)$$

$\Delta H° = -16.2 \pm 0.9$ kcal/mole and $\Delta S° = -26.1 \pm 3.0$ gibbs/mole. The equilibrium constant, K_{12}, at 298°K is $(1.5 \pm 0.3) \times 10^6$. The mechanism postulated for the nitroprusside–hydroxide reaction is

$$(NC)_5FeNO^{2-} + OH^- \xrightarrow{k_{12}} (NC)_5FeNO_2H^{3-} \qquad (3)$$

$$(NC)_5FeNO_2H^{3-} + OH^- \longrightarrow (NC)_5FeNO_2{}^{4-} + H_2O \qquad (4)$$

where (4) is a rapid acid–base reaction and (3) is rate-determining. For k_{12}, $\Delta H^* = 12.6 \pm 0.2$ kcal/mole and $\Delta S^* = -17.5 \pm 0.7$ gibbs/mole. At 298°K $k_{12} = 0.55 \pm 0.01\ M^{-1}\ \text{sec}^{-1}$. For the equilibrium

$$(NC)_5FeNO_2{}^{4-} + H_2O \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} (NC)_5FeH_2O^{3-} + NO_2{}^- \qquad (2)$$

$\Delta H° = +12.3 \pm 0.2$ kcal/mole, $\Delta S° = 25.2 \pm 0.7$ gibbs/mole, and $\Delta G°_{298} = 4.81$ kcal/mole. The equilibrium constant, K_{23}, at 298°K is $(3.0 \pm 0.1) \times 10^{-4}$ For k_{23}, $(1.4 \pm 0.2) \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$ at 298°K, $\Delta H_{23}{}^* = 21.6 \pm 0.9$ kcal/mole and $\Delta S_{23}{}^* = -3.6 \pm 3.0$ gibbs/mole. At 298°K $k_{32} = 0.46 \pm 0.07\ M^{-1}\ \text{sec}^{-1}$, $\Delta H_{32}{}^* = 9.3 \pm 1.1$ kcal/mole, and $\Delta S_{32}{}^* = -28.8 \pm 3.7$ gibbs/mole.

Introduction

Cambi and Szegö[1] in their investigation of the reaction between pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, and hydroxide ions reported the existence of the equilibrium

$$(NC)_5FeNO^{2-} + 2OH^- \rightleftharpoons (NC)_5FeNO_2{}^{4-} + H_2O \qquad (1)$$

and obtained from spectrophotometric measurements $K_{12} = 0.74 \times 10^4$ (288°K). Kolthoff and Toren[2] reinvestigated reaction 1 and obtained $K_{12} = 1.0 \times 10^6$ (298°K). The latter investigators also reported the decomposition of $(NC)_5FeNO_2{}^{4-}$ to unspecified products and attempted to correct for this decomposition by extrapolation of their spectrophotometric data to zero time. Zuman and Kabát reported an equilibrium constant of 0.74×10^5 at 293°K.[3] We have found in this investigation that the reaction between nitroprusside and hydroxide ions is not as simple as has been supposed and that in fact there are two important equilibria established in this system, the first being reaction 1 and the second being

$$(NC)_5FeNO_2{}^{4-} + H_2O \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} (NC)_5FeOH_2{}^{3-} + NO_2{}^- \qquad (2)$$

We report here the results of a complete thermodynamic and kinetic investigation of reactions 1 and 2.

Experimental Section

Reagents.—Solutions were prepared from J. T. Baker reagent grade chemicals which were used without further purification; KCl (99.9%), $NaNO_2$ (98.9%), NaOH (98.7%), $Na_2Fe(CN)_5NO\cdot 2H_2O$ (99.6%), and NaCl (99.5%). Stock nitroprusside solutions were stored in the dark and all operations were carried out in darkened rooms to prevent any light-catalyzed reactions.[4] It was found that the presence of oxygen had no effect on the measurements made.

Instruments.—A Beckman Expandomatic pH meter and low

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[1] L. Cambi and L. Szegö, *Gazz. Chim. Ital.*, **58**, 71 (1928).

[2] I. M. Kolthoff and P. E. Toren, *J. Am. Chem. Soc.*, **75**, 1197 (1953).

[3] P. Zuman and M. Kabát, *Chem. Listy*, **48**, 358 (1954).

[4] O. Baudish, *Science*, **108**, 443 (1948).

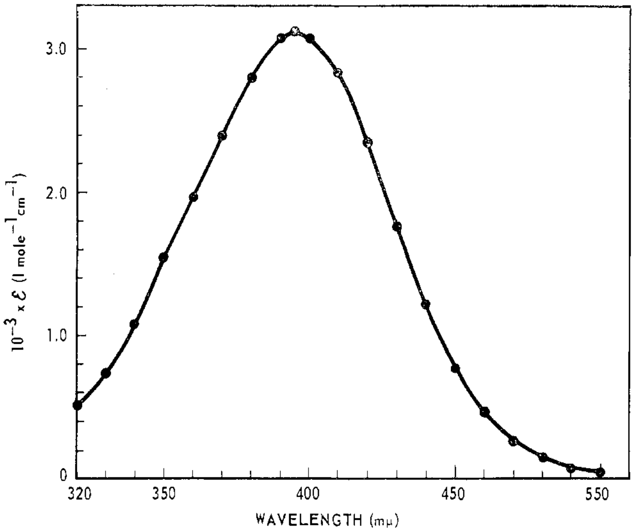

Figure 1.—Spectrum of $(NC)_5FeNO_2^{4-}$ at $\mu = 1.00$ (NaCl).

sodium ion error E-2 glass electrode were used for pH measurements. Spectrophotometric data were obtained with an Applied Physics Corp. Cary Model 14, recording spectrophotometer, equipped with a variable temperature cell block. The accuray of the temperature measurement was ±0.5°.

Results and Discussion

Thermodynamic Data.—Aqueous solutions of sodium nitroprusside (10^{-2} to 10^{-4} M) prepared with an ionic strength of 1.00 (using either NaCl or KCl) were found to obey Beer's law. If these same solutions are made alkaline with NaOH (0.1–0.5 M to ensure complete conversion of nitroprusside to the nitritopentacyanoferrate(II) complex) the total absorbance is no longer directly proportional to the total nitroprusside concentration. However, the absorbance for a given nitroprusside concentration is reproducible and shows no apparent tendency to change in the course of several hours. It was first observed in a preliminary kinetic run that the "decomposition" of $(NC)_5FeNO_2^{4-}$ could be prevented by carrying out reaction 1 in the presence of excess nitrite ion, and it was subsequently found that alkaline nitroprusside solutions containing added excess nitrite ion obey Beer's law. These observations imply that reactions 1 and 2 provide a satisfactory explanation of the behavior of alkaline nitroprusside solutions.

The visible absorption spectrum of the species $(NC)_5FeNO_2^{4-}$ obtained in the presence of excess nitrite (1.00×10^{-4} to 8.00×10^{-4} M nitroprusside, 0.20 M NaOH, 4.00×10^{-2} M $NaNO_2$, $\mu = 1.00$ (NaCl)) and corrected for the absorbance of nitrite in this region by means of a blank is given in Figure 1.

The equilibrium constant for reaction 1 was determined from the absorbance at 4000 A in solution, for which the "total" nitroprusside concentration (*i.e.*, $[(NC)_5FeNO^{2-}] + [(NC)_5FeNO_2^{4-}]$) was varied from 2×10^{-4} to 4×10^{-3} M and the hydroxide ion concentration was varied from 2×10^{-4} to 3×10^{-3} M. All solutions were made 3.00×10^{-2} M in $NaNO_2$, which is sufficient to ensure the presence of no more than about 1% of the species $(NC)_5FeOH_2^{3-}$ (*vide infra*). The total ionic strength was kept at 1.00 with KCl. The extinction coefficients used in analyzing the absorbance at 4000 A were: NO_2^- (1.0); $(NC)_5FeNO^{2-}$ (20.5); $(NC)_5FeNO_2^{4-}$ (3.075×10^3 M^{-1} cm^{-1}). The solutions were assumed sufficiently alkaline in all cases so that only unprotonated species are of significance (pK_a = 3.29 for HNO_2(aq) and pK_a = 4.17 for $HFe(CN)_6^{3-}$).[5,6]

Each value of K_{12} at a given temperature was an average of five determinations over the concentration ranges previously indicated. At 298°K the values obtained for K_{12} were: 1.2, 2.1, 1.4, 1.5, and 1.4×10^6, which yields an average value of $(1.5 \pm 0.3) \times 10^6$. The values of K_{12} obtained as a function of temperature were: $(4.2 \pm 1.0) \times 10^6$ (288°K); $(1.5 \pm 0.3) \times 10^6$ (298°K); $(0.69 \pm 0.12) \times 10^6$ (308°K). On recycling the temperature absorbances were found to check the previously obtained values within 5%. From a plot of log K_{12} *vs.* T^{-1} we compute for reaction 1: $\Delta H° = -16.2 \pm 0.9$ kcal/mole, $\Delta G°_{298} = -8.43$ kcal/mole, and $\Delta S° = -26.1 \pm 3.0$ gibbs/mole. These thermodynamic data are based on the arbitrarily chosen hypothetical 1 M [in $\mu = 1.00$ (KCl)] standard state.

The equilibrium constant K_{23} for reaction 2 was also determined as a function of temperature. Solutions having a total ionic strength of 1.00 (NaCl) which were 0.2 M in NaOH, in which the total nitroprusside concentration (*i.e.*, $[(NC)_5FeNO_2^{4-}] + [(NC)_5FeOH_2^{3-}]$) was varied from 1×10^{-4} to 8×10^{-4} M, and in which the $NaNO_2$ concentration ranged from 0 to 1×10^{-4} M, were used in the determination of K_{23}. The extinction coefficient of the aquopentacyanoferrate(II) ion was taken as 1.09×10^3 M^{-1} cm^{-1} at 4000 A.[7]

The value of K_{23} obtained at each temperature was an average of five determinations within the concentration ranges previously indicated. At 298°K the values for K_{23} were: 3.0, 3.0, 3.2, 2.8, and 3.0×10^{-4}, which yields an average value of $(3.0 \pm 0.1) \times 10^{-4}$. The values of K_{23} obtained were: $(1.1 \pm 0.1) \times 10^{-4}$ (283°K), $(3.0 \pm 0.1) \times 10^{-4}$ (298°K), and $(5.8 \pm 0.2) \times 10^{-4}$ (308°K). The reproducibility of the observed absorbances on cycling the temperature back to 25° was better than 1%. From a plot of log K_{23} *vs.* T^{-1} we compute for reaction 2: $\Delta H° = 12.3 \pm 0.2$ kcal/mole; $\Delta G°_{298} = +4.81$ kcal/mole, and $\Delta S° = +25.2 \pm 0.7$ gibbs/mole (in $\mu = 1.00$ (NaCl), standard state).

In order to check the assumption that reaction 2 is correct as written and that the reaction does not involve hydroxide ion the absorbance of a solution 4.00×10^{-4} M in nitroprusside was taken at four different hydroxide concentrations and the results obtained were: 0.1 M, 0.781; 0.2 M, 0.781; 0.3 M, 0.782; and 0.5 M, 0.773. The last value may indicate the onset of the formation of the $(NC)_5FeOH^{4-}$ species. At any rate, we conclude on the basis of these data that hydroxide

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(5) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, p 32.

(6) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

(7) S. Iimori, *Z. Anorg. Allgem. Chem.*, **167**, 145 (1927).

TABLE I

EQUILIBRIUM AND THERMODYNAMIC DATA

μ = 1.00 (NaCl)

Equilibrium	K_{298}	$\Delta H°$, kcal/mole	$\Delta S°$, gibbs/mole	$\Delta G°_{298}$, kcal/mole
$(NC)_5FeNO_2^- + 2OH^- \rightleftharpoons (NC)_5FeNO_2^{4-} + H_2O$	$(1.5 \pm 0.3) \times 10^6$	-16.2 ± 0.9	-26.1 ± 3.0	-8.43
$(NC)_5FeNO_2^{4-} + H_2O \rightleftharpoons (NC)_5FeNO_2^{4-} + NO_2^-$	$(3.0 \pm 0.1) \times 10^{-4}$	$+12.3 \pm 0.2$	$+25.2 \pm 0.7$	$+4.81$

ion is not involved in the reaction to any appreciable extent under our conditions.

Discussion of Thermodynamic Data.—Table I summarizes the thermodynamic data obtained.

The large difference between K_{12}, $(1.5 \pm 0.3) \times 10^6$ at 298°K, obtained in this investigation and values determined by other workers can be ascribed either to the failure of these workers to recognize the importance of reaction 2[1,3] or to obtain an accurate value for the extinction coefficient of the species $(NC)_5FeNO_2^{4-}$ by means of their extrapolation procedure.[2]

Kinetic Data.—The kinetics of both equilibria 1 and 2 were followed at 4000 A, where $(NC)_5FeNO_2^{4-}$ is essentially the only contributor to the absorbance. When $(NC)_5FeH_2O^{3-}$ was present the necessary corrections were made.

The rate law for the reaction of hydroxide with nitroprusside was found to be first order to both of the reactants. When nitroprusside was treated with excess hydroxide the pseudo-first-order plots were linear over at least two half-lives and the half-life was inversely proportional to the concentration of hydroxide between 2.5×10^{-2} and 5×10^{-1} M. At 286°K k_{12} as calculated from $\ln 2/t_{1/2}(OH^-)$ equals 0.21, 0.20, and 0.20 M^{-1} sec^{-1} when the excess hydroxide concentration equals 5.0×10^{-1}, 1.0×10^{-1}, and 2.5×10^{-2} M, respectively, and the initial concentration of nitroprusside equals 2.5×10^{-4} M. All runs were carried out in excess NO_2^- to prevent the aquation of $(NC)_5FeNO_2^{4-}$. If the mechanism is assumed to be

$$(NC)_5FeNO^{2-} + OH^- \xrightarrow{k_{12}} (NC)_5FeNO_2H^{3-} \quad (3)$$

$$(NC)_5FeNO_2H^{3-} + OH^- \longrightarrow (NC)_5FeNO_2^{4-} + H_2O \quad (4)$$

where step 4 is rapid compared to step 3, the values of k_{12} in units of M^{-1} sec^{-1} determined as a function of temperature are: 0.20 ± 0.01 (286°K), 0.55 ± 0.01 (298°K), and 0.92 ± 0.01 (306°K). The values of ΔH_{12}^* and ΔS_{12}^* computed from the $\ln k_{12}/T$ *vs.* $1/T$ plot were 12.6 ± 0.2 kcal/mole and -17.5 ± 0.7 gibbs/mole.

The kinetics of equilibrium 2 was studied at high base strengths so that the $(NC)_5FeNO_2^{4-}$ complex formed rapidly and the aquation reaction (2) could be studied conveniently. The disappearance of $(NC)_5FeNO_2^{4-}$ was followed at 4000 A. It was assumed that $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$ were the only contributors to the absorbance. Pseudo-first-order plots of the disappearance of $(NC)_5FeNO_2^{4-}$ were obtained, which were independent of hydroxide (0.25 M and 0.5 M) and showed linear behavior over at least one half-life. Table II summarizes typical kinetic data taken under various concentration conditions.

TABLE II

TYPICAL KINETIC DATA FOR AQUATION OF $(NC)_5FeNO_2^{4-}$

μ = 1.00 (NaCl), T = 298°K

$10^4[(NC)_5FeNO^{2-}]_{initial}$, M	$[OH^-]$, M	$10^4 k_{23}$,[a] M^{-1} sec^{-1}
2.50	0.50	1.5
1.25	0.50	1.3
2.50	0.25	1.4
1.25	0.25	1.5

[a] Average of three runs and calculated from $k_{23} = \ln 2/t_{1/2}[H_2O]$

At the lowest temperature (298°K) the plot became nonlinear after one half-life as might be expected from the observed decrease in K_{23} with decreasing temperature (see Thermodynamic Data). Values of k_{23} in units of M^{-1} sec^{-1} determined at various temperatures are: $(10.9 \pm 0.5) \times 10^{-4}$ (316°K), $(6.6 \pm 0.5) \times 10^{-4}$ (311°K), $(3.2 \pm 0.2) \times 10^{-4}$ (306°K), and $(1.4 \pm 0.2) \times 10^{-4}$ (298°K). ΔH_{23}^* is 21.6 ± 0.9 kcal/mole and ΔS_{23}^* is -3.6 ± 3.0 gibbs/mole. The activation parameters ΔH_{23}^* and ΔS_{32}^* for k_{32} using the thermodynamic $\Delta H°$ and $\Delta S°$ are 9.3 ± 1.1 kcal/mole and -28.8 ± 3.7 gibbs/mole.

Discussion of Kinetic Data.—Table III summarizes the kinetic data and activation parameters obtained.

The entropies of activation for k_{12} and k_{32} are in agreement with those predicted purely on the basis of electrostatics. Using $\Delta S^*_{el} = -10Z_1Z_2$, where ΔS^*_{el} is the electrostatic contribution to ΔS^* and Z_1 and Z_2 are the charges on the reactants,[8] ΔS^*_{el} are -20 and -30 gibbs/mole for k_{12} and k_{32}, respectively.

It is interesting to speculate as to the structure of the species involved in the mechanism represented by eq 3 and 4. On the basis of Mössbauer effect studies of nitroprusside it can be concluded that the NO group is bound to the iron as NO^+.[9] The most reasonable mechanism involves the attack of a hydroxide at the nitrogen forming $(NC)_5Fe^{II}NO_2H^{3-}$ in the rate-determining step. The second hydroxide removes the proton from the complex in a rapid acid–base reaction yielding $(NC)_5FeNO_2^{4-}$ and water.

The reaction of nitroprusside with bisulfide apparently involves a similar mechanism. It appears from stop-flow experiments that the rate of formation of the colored species initially formed in the reaction is first order in both of the reactants. The entropies of activation for the SH^- and OH^- reactions are nearly

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(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 145.

(9) J. Danon, *J. Chem. Phys.*, **41**, 3378 (1964).

TABLE III

KINETIC DATA AND ACTIVATION PARAMETERS, $\mu = 1.00$ (NaCl)

Reaction	Rate constant, M^{-1} sec^{-1} (298°K)	ΔH^*, kcal/mole	ΔS^*, gibbs/mole
$(NC)_5FeNO^{2-} + OH^- \xrightarrow{k_{12}} (NC)_5FeNO_2H^{3-}$	0.55 ± 0.01	12.6 ± 0.2	-17.5 ± 0.7
$(NC)_5FeNO_2^{4-} + H_2O \xrightarrow{k_{23}} (NC)_5FeOH_2^{3-} + NO_2^-$	$(1.4 \pm 0.2) \times 10^{-4}$	21.6 ± 0.9	-3.6 ± 3.0
$NO_2^- + (NC)_5FeOH_2^{3-} \xrightarrow{k_{32}} (NC)_5FeNO_2^{4-} + H_2O$	0.46 ± 0.07[a]	9.3 ± 1.1[a]	-28.3 ± 3.7[a]

[a] Values obtained from activation parameters for k_{23}, and $\Delta S°$ and $\Delta H°$ for equilibrium 2.

the same and the enthalpy of activation is about 5 kcal/mole smaller for the bisulfide reaction. A complete kinetic and thermodynamic investigation of the system is presently being carried out.

From the data obtained it is possible to comment on other reactions in which nitroprusside takes part. Cambi[10] has made observations on the reaction between nitroprusside and acetone. It is clear from our preliminary experiments that acetone does not react with the products of the hydroxide–nitroprusside reaction, $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$. Therefore the enolate form of acetone must be competing with hydroxide for the site on nitroprusside, the product in the acetone–nitroprusside reaction being $(NC)_5FeNO(C_3H_5O)^{3-}$. This species can then aquate as $(NC)_5FeNO_2^{4-}$ does in the hydroxide–nitroprusside reaction. In general base–nitroprusside reactions will involve equilibria of the type in reaction 1, and the species formed will depend on the competitive equilibria between the bases in the system for the site on nitroprusside. Reactions between bases and nitroprusside may provide an interesting route in the preparation of some unique compounds.

(10) L. Cambi, *Chem. Zent.*, **I**, 1756 (1913); *ibid.*, **II**, 1109 (1914).

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The Aqueous Solution Chemistry and Kinetic Behavior of a Pseudo-Octahedral Complex of Gold(III)

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The pseudo-octahedral complexes, $[Au(Et_4dien\text{-}H)X]PF_6$[2] (X = Cl, Br) have been synthesized and their aqueous solution chemistry investigated. Evidence is presented for hydrolytic and acid–base equilibria. In addition, rate constants for the reaction of $[Au(Et_4dien\text{-}H)Cl]^+$ with Br^- and OH^- and half-lives for the isotopic exchange of this substrate and its conjugate acid with Cl^- are reported. The rate of chloride ion replacement is almost independent of the nature and the concentration of the reagent. Other reagents such as N_3^-, I^-, and SCN^- replace not only the chloride ion but also the triamine to yield complexes of the type AuX_4^-.

Introduction

The rates of substitution reactions of square-planar metal complexes are usually dependent on the nature and concentration of the reagent.[3] Octahedral complexes in aqueous solution generally react at rates that do not depend on the entering ligand, except for anation reactions.[4] The square-planar, low-spin, d^8 complex $[Pd(Et_4dien)Cl]^+$ has been found to react like an octahedral substrate.[5] This anomalous result was ascribed to the structure of this ion and suggests the difference in behavior between octahedral and square-planar complexes is due in part to steric considerations. Because it behaves like an octahedral complex, the complex was designated a pseudo-octahedral complex.

Investigations of some reactions of $[Au(dien)Cl]^{2+}$ in aqueous solution show that these proceed almost entirely by the path that is first order in reagent.[6] Because of this strong dependence of the rate of reaction on the entering ligand, it seems of interest to test the importance of steric factors using the analogous sterically hindered system. This paper reports the results of such a study on the complex ions $[Au(Et_4dien\text{-}H)Cl]^+$ and $[Au(Et_4dien)Cl]^{2+}$.

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(2) dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$, Et_4dien = $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$, Et_4dien-H = $(C_2H_5)_2NCH_2CH_2NCH_2CH_2N(C_2H_5)_2$.

(3) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(4) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 3.

(5) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

(6) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).