

assumption is supported by the fact that it yields values of σ for PPh₂(OPh) and PPh(OPh)₂ which also correlate quite closely with the carbonyl chemical shifts.

It is tempting to suggest that the extent of transition metal \rightarrow carbonyl π back-donation is therefore dependent predominantly upon the σ basicity of the phosphorus ligand. While this may indeed be true, we must conclude that an increased electron density at the phosphorus may be reflected at the transition metal via either an increased σ basicity or a decreased π acidity of the phosphorus ligand. The data in Table I may thus be interpreted in terms of a relative order of the electron donor:acceptor ratios for various ligands toward Ni(CO)₃.

Registry No. [PCl₃]Ni(CO)₃, 18474-97-0; Ni(CO)₄, 13463-39-3; [PPhCl₂]Ni(CO)₃, 18474-95-8; [PPhCl₂]₂Ni(CO)₂, 55333-53-4; [P(OPh)₃]Ni(CO)₃, 18474-92-5; [P(OPh)₃]₂Ni(CO)₂, 14653-44-2; [PPh₂Cl]Ni(CO)₃, 18559-01-8; [PPh₂Cl]₂Ni(CO)₂, 35824-48-7; [PPh(OPh)₂]Ni(CO)₃, 55333-54-5; [P(OMe)₃]Ni(CO)₃, 17099-58-0; [P(OMe)₃]₂Ni(CO)₂, 16787-28-3; [P(OMe)₃]₃Ni(CO), 17084-87-6; [PPh₂(OPh)]Ni(CO)₃, 55333-39-6; [PPh(OMe)₂]Ni(CO)₃, 55333-40-9; [P(OEt)₃]Ni(CO)₃, 18558-97-9; [P(OEt)₃]₂Ni(CO)₂, 16787-36-3; [P(OEt)₃]₃Ni(CO), 25945-15-7; [P(O-*i*-Pr)₃]Ni(CO)₃, 55333-41-0; [P(O-*i*-Pr)₃]₂Ni(CO)₂, 55333-42-1; [PPh₂(OMe)]Ni(CO)₃, 55333-43-2; [AsPh₃]Ni(CO)₃, 37757-32-7; [PPh₃]Ni(CO)₃, 14917-13-6; [PPh₃]₂Ni(CO)₂, 13007-90-4; [PPh₂Me]Ni(CO)₃, 55333-44-3; [P(*p*-tol)₃]Ni(CO)₃, 52729-09-6; [PPhMe₂]Ni(CO)₃, 55333-45-4; [SbPh₃]Ni(CO)₃, 52151-12-9; [PMe₃]Ni(CO)₃, 16406-99-8; [PEt₃]Ni(CO)₃, 18555-45-8; [PEt₃]₂Ni(CO)₂, 16787-33-0; [PBu₃]Ni(CO)₃, 15698-54-1; [PBu₃]₂Ni(CO)₂, 20658-46-2; [Ph₂PCH₂CH₂PPh₂]Ni(CO)₂, 15793-01-8; [PPh₃]-[PBu₃]Ni(CO)₂, 55333-46-5; [PBu₃][P(OMe)₃]Ni(CO)₂, 55333-47-6; [PPh₃][P(OMe)₃]Ni(CO)₂, 55333-48-7; [PBu₃][P(OPh)₃]Ni(CO)₂, 55400-72-1; [PPh₃][P(OPh)₃]Ni(CO)₂, 55333-49-8; [P(OPh)₃]-[P(OMe)₃]Ni(CO)₂, 55333-50-1; ¹³C, 14762-74-4.

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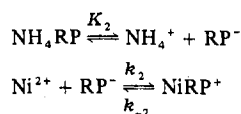
Kinetics of Nickel(II) Complexation Reactions in Nonaqueous Solvents. II. Ammonium Salt of 2,2'-Nitrilodi-1,3-indandione (Ruhemann's Purple) and 4-(2-Pyridylazo)resorcinol (PAR)

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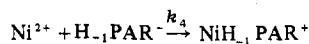
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The kinetics of the reactions of nickel(II) with the ammonium salt of 2,2'-nitrilodi-1,3-indandione, Ruhemann's Purple (NH₄RP), in pyridine and with 4-(2-pyridylazo)resorcinol (PAR) in 0.0125 M pyridine in nitromethane have been investigated. For the Ni^{II}-NH₄RP reaction the mechanism is assumed to be



The rate constants K_2k_2 and k_{-2} at 25° and their Arrhenius activation energies, E_a , are $2.1 \times 10^4 \text{ sec}^{-1}$, $19.6 \pm 0.2 \text{ kcal/mol}$, and 15.8 sec^{-1} , $13.3 \pm 0.4 \text{ kcal/mol}$, respectively. For the Ni^{II}-PAR reaction the mechanism is assumed to be



The rate constant k_4 at 25° and E_a are $1.4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and $13.5 \pm 0.5 \text{ kcal/mol}$, respectively.

The kinetics of nickel(II) complexation reactions have been widely studied.^{1,2} Most of these kinetic studies have dealt with reactions in water. For those reactions which are not sterically controlled, the available data are consistent with the Eigen-Wilkins mechanisms.^{1,2} A restrictive Eigen-Wilkins mech-

anism requires that the second-order rate constants for metal ion complexation reactions be equal to an ion-pairing constant multiplied by the rate constant for solvent exchange at the metal center. The rate-determining step is the elimination of a solvent molecule from the primary coordination sphere of

the metal ion. To understand the role of the solvent in complexation reactions, the reactions must be studied in different solvents. For many metal ion complexation reactions in nonaqueous solvents, the data are not obviously consistent with the Eigen-Wilkins model.³⁻¹¹ In some cases it has been shown that a property of the ligand is responsible for such behavior, for example, the work of Hoffmann et al.¹² In an effort to elucidate the mechanism for metal ion complexation reactions in nonaqueous solvents, a study of the kinetics of the reactions of Ni(II) with the neutral ligand 2-(4-dimethylaminophenylazo)pyridine (DPAP) in pyridine and in pyridine-nitromethane was carried out.¹³ Reported here is a kinetic study of the reactions of Ni(II) with the ammonium salt of 2,2'-nitrilodi-1,3-indandione, Ruhemann's Purple (NH₄RP), in pyridine and with 4-(2-pyridylazo)resorcinol (PAR) in 0.0125 *M* pyridine in nitromethane.

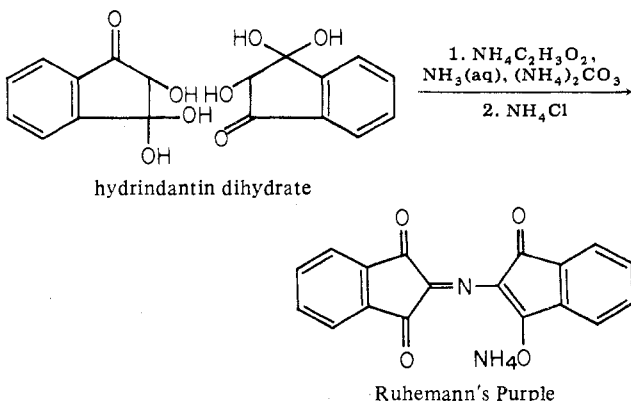
Ruhemann's Purple, NH₄RP, was chosen as a ligand because it forms a 1:1 complex with Ni(II) in pyridine, a large spectral change accompanies the reaction, and the reactive form of the ligand has no titratable protons. 4-(2-Pyridylazo)-resorcinol was chosen because the reactive form of the ligand is a monoanion, a 1:1 complex is formed with Ni(II), no acid-base equilibrium occurs in the solvent system studied, and the complexation process causes a large spectral change. Both PAR and DPAP¹³ probably coordinate to Ni(II) through a pyridine nitrogen and an azo nitrogen forming five-membered chelate rings. One reason for studying Ni(II) complexation reactions in pyridine and in pyridine-nitromethane is that the nature of the solvated Ni(II) cation has been reported.^{14,15} Knowledge of the composition of the solvation spheres of cations is important in understanding the effects of bulk solvent and mixed coordination spheres on metal ion complexation reactions.

Experimental Section

Reagents and Solutions. Bis(tetrafluoroborate)tetrakis(pyridine)nickel(II). Ni(py)₄(BF₄)₂ was prepared according to the synthesis devised by Rosenthal and Drago.¹⁴ Anal. Calcd for C₂₀H₂₀N₄B₂F₈Ni: C, 43.78; H, 3.67; N, 10.21. Found: C, 43.69; H, 3.73; N, 10.01.

This compound was stored in a desiccator and the purity was checked periodically by recording the spectrum of a solution of Ni(py)₄(BF₄)₂ in 6.20 *M* pyridine in nitromethane. The extinction coefficient at 605 mμ is 15 *M*⁻¹ cm⁻¹ which is identical with the value reported by Rosenthal and Drago.¹⁴

The Ammonium Salt of 2,2'-Nitrilodi-1,3-indandione, Ruhemann's Purple, NH₄RP. The ammonium salt of Ruhemann's Purple, NH₄RP, was prepared by treating hydrindantin dihydrate, prepared according to a procedure reported by Ruhemann,¹⁶ with an ammonium buffer solution.¹⁷ Anal. Calcd for C₁₈H₁₂O₄N₂: C, 67.5; H, 3.78; N, 8.74.



Found: C, 66.31; H, 4.04; N, 8.99.

Aqueous solutions of Ruhemann's Purple absorb at 565 and 420 mμ with extinction coefficients of 2.4 × 10⁴ *M*⁻¹ cm⁻¹ at both wavelengths. Schwarzenbach and Gysling¹⁸ reported these extinction coefficients to be 2.3 × 10⁴ *M*⁻¹ cm⁻¹.

4-(2-Pyridylazo)resorcinol, PAR. Eastman 4-(2-pyridylazo)res-

orcinol was used without further purification. The melting point of the Eastman PAR was 183° which agrees with the literature value of 182°.¹⁹

Ammonium Tetrafluoroborate. NH₃(aq) was neutralized with HBF₄ to make NH₄BF₄. The solid NH₄BF₄ was recrystallized from water and dried at 110°.

Tetraethylammonium Tetrafluoroborate. N(C₂H₅)₄OH (Matheson Coleman and Bell) was neutralized with HBF₄ to form N(C₂H₅)₄BF₄ which was recrystallized from water and dried at 110°.

Reagent grade pyridine (py) was dried over barium oxide and distilled in a distillation apparatus protected from the atmosphere with calcium chloride drying tubes. The boiling point of the dried pyridine was 115.2°. Reagent grade Spectroquality nitromethane (nm) was dried over Drierite and distilled in a one-piece distillation apparatus under reduced pressure (50-100 Torr). The water content of the solutions used was determined by the Karl Fischer method. The lowest attainable water concentration was 0.002 *M*.

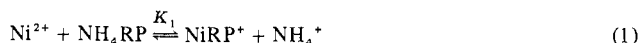
Solutions used for equilibrium and kinetic measurements were prepared from stock solutions of Ni(py)₄(BF₄)₂, PAR, and NH₄RP. The pyridine-nitromethane solutions had pyridine concentrations of 0.0125 *M* (0.1% pyridine-99.9% nitromethane by volume). The concentration of pyridine in the 0.0125 *M* pyridine in nitromethane solution was in at least 200-fold excess over the Ni(II) concentration. All solutions were protected from atmospheric water and were periodically monitored for water content using the Karl Fischer method.

Instruments. Visible and ultraviolet spectra were recorded with a Cary 14 recording spectrophotometer. Kinetic runs were made on a stopped-flow instrument manufactured by the Durrum Instrument Co. Temperature control was to ±0.2°. Relaxation experiments were carried out on a temperature-jump instrument manufactured by Messanlagen Studiengesellschaft, GmbH. The temperature control for the temperature-jump instrument was accurate to ±0.5°. A 20-kV discharge was used for pyridine solutions containing 0.10 *M* NH₄BF₄ to achieve a temperature-jump of 3.0 ± 0.5°. Discharges greater than 30 kV caused serious cavitation effects in pyridine solutions.

The analog voltage signals from the temperature-jump and stopped-flow instruments were converted to digital signals and punched on paper tape.¹³ The paper tape records of the kinetic runs were then analyzed on a PDP-8/I computer to give relaxation times or rate constants.

Results and Discussion

Ni^{II}-NH₄RP Reaction in Pyridine. In pyridine solutions containing 0.10 *M* NH₄BF₄, Ni(II) reacts with NH₄RP according to reaction 1. The nature of the solvated cation



is not included in this equation for simplicity. The stoichiometry of reaction 1 was determined by the method of Job.^{20,21} Addition of ammonium ion to a solution of Ni(II) and NH₄RP at equilibrium causes dissociation of the NiRP⁺ complex. The complex absorbs at 497 mμ (ϵ 4.5 × 10⁴ *M*⁻¹ cm⁻¹) and the uncomplexed ligand absorbs at 420 mμ (ϵ 2.4 × 10⁴ *M*⁻¹ cm⁻¹) and 570 mμ (ϵ 2.1 × 10⁴ *M*⁻¹ cm⁻¹). The ligand spectrum does not obey Beer's law unless a large excess of ammonium ion is added to the pyridine solutions. Addition of the N(C₂H₅)₄⁺ cation does not cause a pyridine solution of NH₄RP to obey Beer's law. For these reasons, all kinetic and spectral studies were carried out on solutions containing at least 0.10 *M* NH₄BF₄.

The kinetics of reaction 1 were studied using temperature-jump techniques. The relaxation times were determined as a function of [Ni²⁺], [NH₄RP], [NH₄BF₄], [H₂O], wavelength, and temperature. Since the relaxation times did not vary as a function of wavelength, most of the kinetic runs were monitored at 497 mμ. The data are consistent with mechanism 2 and are shown in Table I. If [NH₄⁺] >



Table I. Temperature-Jump Data for the Ni^{II}-NH₄RP Reaction in Pyridine^a

10 ⁴ [Ni ²⁺], M	10 ⁴ [NH ₄ RP], M	T, °C	[H ₂ O], M	1/τ, °C sec ⁻¹	10 ³ X ^e
0.40	0.20	3.0	0.018	3.4	0.53
1.60	0.20	3.0	0.018	4.4	1.61
2.80	0.20	3.0	0.018	7.4	2.75
4.00	0.20	3.0	0.018	8.3	3.92
0.21	0.20	13.0	0.010	7.6	0.35
0.54	0.20	13.0	0.010	8.9	0.62
1.06	0.20	13.0	0.010	11.0	1.07
2.12	0.20	13.0	0.010	18.1	2.06
4.24	0.20	13.0	0.010	25.8	4.13
0.20	0.20	23.0	0.010	18.6	0.33
0.50	0.20	23.0	0.010	21.9	0.56
1.00	0.20	23.0	0.010	29.4	0.99
2.00	0.20	23.0	0.010	44.9	1.92
2.00	0.40	23.0	0.010	43.9	1.85
1.00	0.40	23.0	0.010	28.3	1.00
4.00	0.20	23.0	0.020	40.7 ^d	1.96
2.00	0.20	23.0	0.015	25.6 ^d	1.00
3.00	0.20	23.0	0.015	37.2 ^d	1.48
4.80	0.20	23.0	0.015	44.2 ^d	2.35
1.00	0.20	23.0	0.006	27.7	1.06
1.00	0.20	23.0	0.054	24.5	1.06
2.00	0.20	23.0	0.054	35.4	1.99
4.00	0.20	23.0	0.054	51.5	3.92
0.20	0.20	33.0	0.005	39.9	0.31
0.80	0.20	33.0	0.015	58.2	0.77
1.40	0.20	33.0	0.015	87.7	1.32
2.00	0.20	33.0	0.015	116	1.89

^a 0.10 M NH₄BF₄. ^b ±1.0°. ^c ±10%. ^d 0.20 M NH₄BF₄.
^e ([Ni²⁺] + [NH₄RP])/[NH₄⁺].

Table II. Rate Constants for the Ni^{II}-NH₄RP Reaction in Pyridine^a

T, °C	10 ⁻³ k ₂ K ₂ , sec ⁻¹	k ₋₂ , sec ⁻¹	10 ⁻³ K ₁
3	1.5 ± 0.2	2.5 ± 0.2	0.60
13	5.2 ± 0.3	5.8 ± 0.2	0.89
23	16.6 ± 0.1	12.9 ± 0.1	1.28
25	21 ^c	15.8 ^c	1.4 ^c
33	47 ± 1	24.5 ± 0.8	1.9

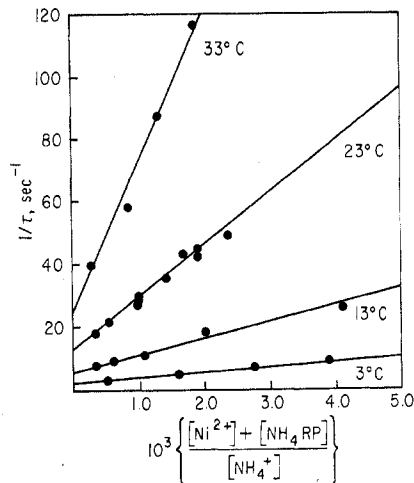
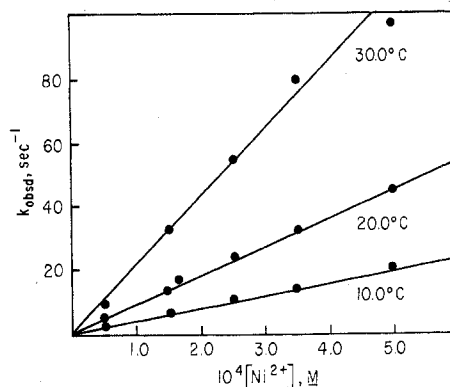
^a [NH₄⁺] = 0.10 M; [H₂O] = 0.01 M. ^b ±1°. ^c Determined graphically.

K₂ and [RP⁻] and if K₂ > [RP⁻], both of which are reasonable assumptions, the expression for the relaxation time simplifies to

$$\frac{1}{\tau} = k_2 K_2 \left\{ \frac{[\text{Ni}^{2+}] + [\text{NH}_4\text{RP}]}{[\text{NH}_4^+]} \right\} + k_{-2} \quad (2')$$

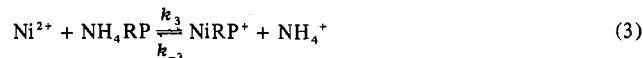
$$X = \frac{[\text{Ni}^{2+}] + [\text{NH}_4\text{RP}]}{[\text{NH}_4^+]}$$

Plots of 1/τ vs. X have slopes equal to k₂K₂ and intercepts equal to k₋₂. The equilibrium constant K₁, k₂K₂/k₋₂, is large (1.4 × 10³ at 25°), and values for K₁ at various temperatures were not determined independently. An iterating computer program was used to calculate values for [Ni²⁺] and [NH₄RP] (Table I) from [Ni²⁺]_{total}, [NH₄RP]_{total}, and successive values of k₂K₂/k₋₂. The program stopped when two successive calculations of k₂K₂/k₋₂ agreed within 5%. Table I contains a tabulation of the relaxation times, 1/τ, vs. the concentrations [Ni²⁺], [NH₄RP], and [H₂O] and temperature. Up to [H₂O] = 0.02 M the effect of water on 1/τ is small, and all points with [H₂O] ≤ 0.02 M are included in Figure 1, which contains plots of 1/τ vs. the computer value of ([Ni²⁺] + [NH₄RP])/[NH₄⁺] at various temperatures. When [H₂O] = 0.054 M values of 1/τ are substantially different from those at lower contents (see Table I). Table II contains a summary of the values of k₂K₂ and k₋₂ determined from Figure 1. The

Figure 1. Plots of 1/τ vs. ([Ni²⁺] + [NH₄RP])/[NH₄⁺] at various various temperatures for the Ni^{II}-NH₄RP reaction in pyridine.Figure 2. Plots of the observed first-order rate constant k_{obsd} vs. the Ni(II) concentration at various temperatures for the Ni^{II}-PAR reaction in 0.0125 M pyridine in nitromethane.

Arrhenius activation energies, E_a , for k_2K_2 and k_{-2} are 19.6 ± 0.2 and 13.3 ± 0.4 kcal/mol, respectively. For subsequent discussions of the mechanism, values of ΔH^\ddagger and ΔS^\ddagger were calculated for k_2K_2 and k_{-2} and are 19.0 ± 0.2 kcal/mol, 25 ± 1 eu, and 12.7 ± 0.4 kcal/mol, -10 ± 2 eu, respectively.

The kinetic data for the reaction of Ni(II) with NH₄RP are not consistent with a rate law for the mechanism

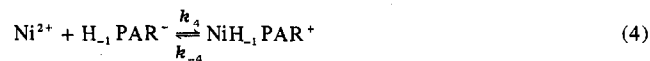


The relaxation expression for this mechanism is

$$1/\tau = k_3([\text{Ni}^{2+}] + [\text{NH}_4\text{RP}]) + k_{-3}([\text{NiRP}^+] + [\text{NH}_4^+])$$

Since [NH₄⁺] ≫ [NiRP⁺] in all kinetic experiments, the intercepts of plots of 1/τ vs. ([Ni²⁺] + [NH₄RP]) for different [NH₄⁺] should have different intercepts, which is not the case.

Ni^{II}-PAR Reaction in 0.0125 M Pyridine in Nitromethane. The reaction of Ni(II) with PAR in 0.0125 M pyridine in nitromethane proceeds according to eq 4. H₋₁PAR⁻ is used



to represent 4-(2-pyridylazo)resorcinol, PAR, that has lost one proton. Pyridine is a strong enough base to remove one proton from PAR but not two. The complex absorbs at 525 mμ (ε 1.6 × 10⁴ M⁻¹ cm⁻¹) and 397 mμ (ε 1.35 × 10⁴ M⁻¹ cm⁻¹) with a shoulder at 550 mμ. The uncomplexed ligand absorbs at 383 mμ (ε 1.7 × 10⁴ M⁻¹ cm⁻¹). The kinetics of reaction 4 were studied at 530 mμ using a stopped-flow spectropho-

Table III. Kinetic Data for the Ni^{II}-PAR Reaction in 0.0125 M Pyridine in Nitromethane^a

[Ni ²⁺], M	[PAR], M	T, °C	[H ₂ O], M	k _{obsd} , sec ⁻¹
0.50	5.0	10.0	0.01	2.14
1.50	5.0	10.0	0.01	5.59
2.50	5.0	10.0	0.01	10.8
3.50	5.0	10.0	0.01	14.0
5.00	5.0	10.0	0.01	20.3
0.50	5.0	20.0	0.01	3.03
1.50	5.0	20.0	0.01	13.6
2.50	5.0	20.0	0.01	24.2
3.50	5.0	20.0	0.01	33.3
5.00	5.0	20.0	0.01	44.9
1.66	3.8	23.0	0.01	17.5
1.66	7.5	23.0	0.01	17.0
0.50	5.0	30.0	0.01	8.8
1.50	5.0	30.0	0.01	33.4
2.50	5.0	30.0	0.01	55.0
3.50	5.0	30.0	0.01	79.4
5.00	5.0	30.0	0.01	96.8
2.62	5.0	20.0	0.01	29.1
2.62	5.0	20.0	0.04	26.1
2.62	5.0	20.0	0.05	23.8

^a 530 μm. ^b ±0.2°. ^c Each value is the average of at least three experiments, ±5%.

Table IV. Rate Constants for the Ni^{II}-PAR Reaction in 0.0125 M Pyridine in Nitromethane^a

T, °C	10 ⁻⁴ k ₄ , M ⁻¹ sec ⁻¹
10.0	4.1 ± 0.1
20.0	9.2 ± 0.4
30.0	20 ± 1

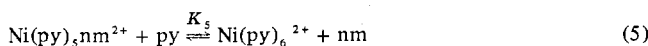
^a [H₂O] = 0.01 M. ^b ±0.2°.

tometer. When [Ni²⁺] >> [H₋₁PAR⁻], the reaction kinetics are pseudo first order. The rate law is

$$\frac{d[H_{-1}PAR^{-}]}{dt} = k_4[Ni^{2+}][H_{-1}PAR^{-}]$$

which is consistent with mechanism 4 if the reverse process is negligible. Table III is a tabulation of the observed pseudo-first-order rate constant, k_{obsd}, as a function of reactant and water concentrations and temperature. Figure 2 contains plots of k_{obsd} vs. [Ni²⁺] at various temperatures. The slopes of these lines are the second-order rate constants, k₄, which are tabulated in Table IV. The intercept, k₋₄, is zero within experimental error. The value of E_a for k₄ is 13.5 ± 0.5 kcal/mol, and ΔH[‡] and ΔS[‡] are 12.9 ± 0.5 kcal/mol and 8 ± 2 eu, respectively.

Rosenthal and Drago¹⁴ implied that when solid Ni(py)₄(BF₄)₂ is dissolved in pyridine, Ni(py)₆²⁺ is formed. It has also been suggested that the species present is Ni(py)₄(BF₄)₂.¹⁵ In nitromethane solutions containing a small amount of added pyridine ([py] > [Ni²⁺]), equilibrium 5 is established.¹⁴ The



value for K₅ at 28° is 8.9 M⁻¹. When the concentration of added pyridine is 0.0125 M and [py] >> [Ni²⁺], the ratio of Ni(py)₃nm²⁺ to Ni(py)₆²⁺ is 9. Temperature-jump experiments to measure the rate constants for reaction 5 were unsuccessful because the ΔH[‡] for the reaction is near zero and the time constant for the reaction is less than the temperature-jump instrumental time constant.

The nature of the interaction between Ni(II) and Ruhemann's Purple, RP⁻, is of interest in interpreting the kinetics. RP⁻ is potentially a tridentate ligand, coordinating to metals through a nitrogen and two oxygen atoms. The chromophore of the ligand is identical with the chromophore of the monoanionic murexide ion.¹⁸ Murexide most probably functions

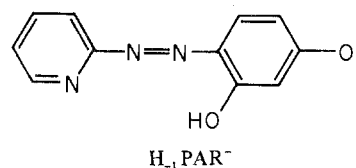
as a tridentate ligand toward 2+ metal cations in water.²² The visible electronic spectra of nickel(II) murexide and Ni^{II}-RP⁻ in water are similar suggesting that the ligands are coordinated in the same way. Thus, RP⁻ is probably also a tridentate ligand in water. Because the spectrum of NiRP⁺ in water is like the spectrum of NiPR⁺ in pyridine, the ligand is assumed to act as a tridentate ligand in pyridine.

Values of K₂ for the reaction NH₄RP ⇌ NH₄⁺ + RP⁻ were not determined independently. However, limits can be set on K₂ by the following analysis. If substantial amounts of RP⁻ exist when [NH₄⁺] = 0.10 M, plots of 1/τ vs. ([Ni²⁺] + [NH₄RP])/[NH₄⁺] would not be linear in the region where [Ni²⁺] ≈ [NH₄RP]. The exact relaxation expression for mechanism 2 is

$$\frac{1}{\tau} = k_2 \left\{ \frac{[Ni^{2+}](K_2 + [RP^{-}])}{K_2 + [RP^{-}] + [NH_4^{+}]} + [RP^{-}] \right\} + k_{-2}$$

If [NH₄⁺] > K₂ and [RP⁻], [NH₄⁺] exceeds [NH₄RP] and the relaxation expression simplifies to expression 2'. The linearity of the plots in Figure 1 shows that the assumption that K₂ << [NH₄⁺] is valid. Thus, K₂ must be less than 10% of [NH₄⁺] or less than or equal to 10⁻² M.

In 0.0125 M pyridine in nitromethane solutions, 4-(2-pyridylazo)resorcinol, PAR, probably exists as the monoanion



The para phenolic proton is more acidic than the ortho proton because the ortho proton is hydrogen bonded to the azo linkage.²³

The statement that PAR exists as a monoanion is based on the observation that at large pyridine concentration or in the presence of the stronger base piperidine two separate spectral changes are observable during the course of the complexation reaction compared to one when [py] is 0.0125 M. It is likely that the first spectral change represents the formation of a bidentate complex with Ni(II). The second slower spectral change is present only at large pyridine concentrations or when piperidine is present and could be associated with the removal of the ortho proton and subsequent tridentate chelate formation. The kinetic studies reported in this paper deal only with the formation of the presumed bidentate chelate, in which H₋₁PAR⁻ would bond through the pyridine nitrogen and an azo nitrogen.

Since both of the ligands used in the studies reported in this paper are multidentate, the rate-determining step in the complexation process can be either formation of the first metal-ligand bond or ring closure forming the chelate. It is difficult on the basis of studies with only a few ligands to determine which process is rate determining. To answer this question, it will be necessary to compare the kinetic data for the complexation of Ni(II) with many monodentate and multidentate ligands in nonaqueous solvents. If multidentate ligands react with the same rate constants as monodentate ligands, the rate-determining step in multidentate complex formation must be the formation of the first metal-ligand bond. Another alternative is that monodentate ligands may not complex Ni(II) in pyridine and in pyridine-nitromethane with the same rate constants. If such is the case, the complexation process is no longer being controlled by the metal ion and determination of the rate-determining step in multidentate chelate formation would be difficult.

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Registry No. NH₄RP, 1237-31-6; PAR, 1141-59-9; Ni²⁺, 14701-22-5.

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Enthalpy of Chelation of a Series of Poly(1-pyrazolyl)borates with Some Divalent Transition Metal Ions in Water and Acetonitrile

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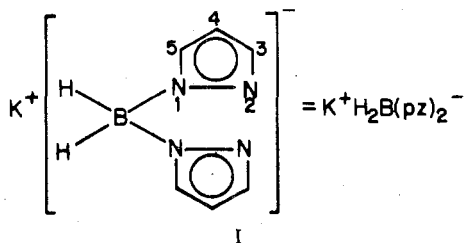
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The enthalpy of chelation of Co(II), Ni(II), Cu(II), and Zn(II) with four poly(1-pyrazolyl)borate ligands is reported in water and acetonitrile media. Whereas precipitation of the chelates occurs in every case in water, all product species are soluble in acetonitrile. Enthalpy results suggest that six-coordinate Cu(II) complexes may be tetragonal rather than octahedral. Evidence is presented which indicates the formation of six-coordinate, anionic chelates of Co(II) and Ni(II) with the bidentate, monoanionic dihydrobis(1-pyrazolyl)borate ligand in acetonitrile solution. Substitution of a methyl group in the pyrazole rings of this ligand molecule prevents chelate anion formation as a result of steric hindrance. Enthalpy values for the substituted ligand are lower than for the unsubstituted one in those cases where a steric effect is expected. Replacement of the remaining boron hydrogen of hydrotris(1-pyrazolyl)borate by a fourth pyrazole group results in substantially decreased enthalpies of reaction in both water and acetonitrile media, most likely because of coordination competition with the uncomplexed pyrazole ring. The much larger enthalpy values obtained in acetonitrile in all cases are attributed to the markedly weaker solvation of the metal and ligand ions by this solvent than by water.

Introduction

A series of ligands has been reported by Trofimenko, Jesson, and Eaton²⁻⁵ which offers unique opportunities for thermodynamic and stereochemical study of chelation reactions. The poly(1-pyrazolyl)borates are uninegative ligands of the general formula H_nB(pz)_{4-n}⁻, where *n* is 0, 1, and 2 and the "pz" stands for the 1-pyrazolyl moiety. Potassium dihydrobis(1-pyrazolyl)borate is shown in I. This ligand molecule is bi-



dentate, coordination taking place through the pyrazole nitrogen atoms. Further replacement of the remaining borate hydrogens by pyrazole groups to form tri- and tetradentate compounds provides a series of chelating ligands, all of which react readily with the divalent first-row transition metal ions.^{3,5} Both the ligand salts and the transition metal chelates are quite stable in the solid form (with the exception of some Mn(II) and Fe(II) chelates, which are air sensitive).⁵ Aqueous solutions of the ligands exhibit lower and varying stabilities.⁵

Systematic studies of the stoichiometry and structure of the first-row transition metal complexes have shown that mixing

aqueous solutions of the divalent metal ion and the poly(1-pyrazolyl)borate ligand yields neutral, anhydrous precipitates.³ In all cases the stoichiometry is one metal ion to two ligand molecules. With the H₂B(pz)₂⁻ ligand, either tetrahedral or planar complexes are formed with the transition metals, while the HB(pz)₃⁻ and B(pz)₄⁻ ligands are reported to form six-coordinate complexes.⁵

In order to compare the thermodynamic properties of a series of monoanionic bi-, tri-, and tetradentate ligands which have identical coordination sites and very similar reaction stoichiometry with a series of divalent metal ions, enthalpies of aqueous precipitation of cobalt(II), nickel(II), copper(II), and zinc(II) with four poly(1-pyrazolyl)borates were determined. An attempt was made to gain some information concerning the relative degrees of solvation of the metal and ligand ions by analysis of thermodynamic and conformational results of chelate formation in water and acetonitrile (MeCN). In contrast to water, soluble chelates were formed in this aprotic nonaqueous solvent, and therefore the heat of chelate formation is absent from the reaction enthalpy.

Where geometries of the reaction product are the same for a particular ligand, differences between the aqueous and MeCN data for the same metal are interpreted mainly as differences in the degree of solvation of metal and ligand ions in the two solvents. In comparing the enthalpy data of one ligand with those of another, differences in chelate geometries must be considered in accounting for the results. Further, the results in aqueous solution have to be discussed with caution, since it is likely that the heats of crystallization for complexes of different geometry are different. Since the magnitude of these crystallization heats are not known at this time, com-

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