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Kinetics of Ligand Exchange in Bis(4-picoline) Adducts of Bis(β-diketonato)nickel(II) Complexes Using Nuclear Magnetic Resonance[1a]

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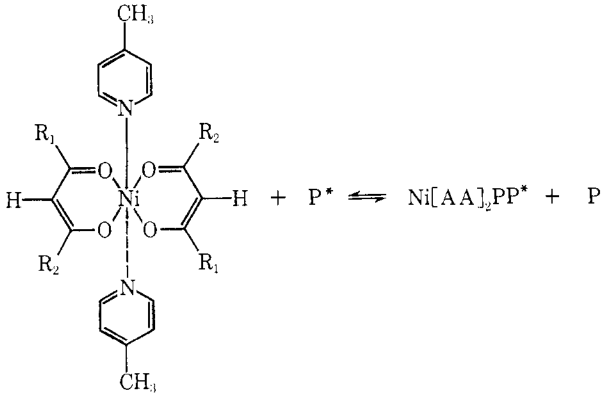
The exchange rates of excess 4-picoline with various bis(4-picoline)bis(β-diketonato)nickel(II) complexes in deuteriochloroform solutions were measured using nmr techniques based on isotropic shifts and line broadening. The exchange is first order in the nickel complex and independent of 4-picoline concentration. Electron-withdrawing groups attached to the β-diketone ring slow the rate of exchange. The exchange rates correlate with the sum of the Taft σ^* parameters for the β-diketone substituents. The exchange rate for the 2,4-pentanedionatocobalt(II) complex is an order of magnitude faster than that of the analogous nickel(II) compound.

Introduction

β-Diketone chelates of nickel(II), Ni(AA)$_2$, are known to interact with an excess of amines such as 4-picoline, P, to form the hexacoordinate 2:1 ligand to chelate adducts, Ni(AA)$_2$P$_2$, I.[2] In solutions containing an excess of picoline, exchange of the coordinated and bulk solvent picoline occurs, and the rate of such exchange can be studied using proton nmr techniques.[3] Previously such techniques have been used to measure the exchange rates of octahedral nickel(II) species, mostly of the type NiL$_6^{2+}$,[4] however, a study of the individual factors affecting the exchange rates in such complexes cannot readily be made, since changing L simultaneously alters the nature of the complex and the nature of the exchanging ligand, as well as the characteristics of the solvent. In the present system, the environment around the nickel atom has been systematically changed by varying the substituents on the β-diketone ring. The results of these changes on the rates of exchange are herein reported.



I

Experimental Section

Preparation of the 2:1 Adducts.—These were prepared by either or both of two general methods. (A) The bis(β-diketonato)nickel(II) complex was isolated, generally as the hydrate, and recrystallized with azeotropic distillation of water from a mixed solvent containing 4-picoline. (B) To 10 mmol of nickel acetate in 20 ml of water and 5 ml of 4-picoline was added 20 mmol of β-diketone. The crude product isolated was recrystallized from a picoline-containing solvent. Except where noted below, the β-diketone was purchased and used directly.

I (**R$_1$ = R$_2$ = *t*-C$_4$H$_9$**).—The anhydrous chelate was recrystallized from ligroin–4-picoline and the violet-blue crystals which precipitated, mp 190–193°, were dried at 56° for 30 min *in vacuo*. *Anal.* Calcd for C$_{34}$H$_{52}$N$_2$O$_4$Ni: C, 66.78; H, 8.57. Found: C, 66.82; H, 8.91.

I (**R$_1$ = R$_2$ = CH$_3$**).—Recrystallization of the anhydrous Ni(AA)$_2$ from benzene–4-picoline and drying the precipitate at 56° *in vacuo* for 30 min gave blue crystals, mp 208–210°. *Anal.* Calcd for C$_{22}$H$_{28}$N$_2$O$_4$Ni: C, 59.62; H, 6.37; Found: C, 59.84; H, 6.33.

I (**R$_1$ = CH$_3$, R$_2$ = CH$_2$OCH$_3$**).—The adduct formed by procedure B was dissolved in 4-picoline and water was added. The violet-blue crystals which deposited were air dried and then dried *in vacuo* at 56° for 30 min. The blue powder isolated melted at 134–136°. The infrared spectrum contained an ether absorption[5] at 1130 cm^{-1}. At 40° the nmr spectrum showed the OCH$_3$ proton resonance at -275 cps compared with -203 cps in the uncomplexed β-diketone. *Anal.* Calcd for C$_{24}$H$_{32}$N$_2$O$_6$Ni: C, 57.28; H, 6.41; N, 5.56; Ni, 11.66. Found: C, 57.51; H, 6.53; N, 5.60; Ni, 11.97.

I (**R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$**).—Using procedure A, the chelate was azeotropically distilled with benzene and 4-picoline. Petroleum ether, bp 30–60°, was added and the green crystals thus obtained were dried at 56° *in vacuo* for 6 hr. They melted at 192° and showed a strong infrared peak, characteristic of the phenyl[5] ring at 711 cm^{-1}. *Anal.* Calcd for C$_{32}$H$_{32}$N$_2$O$_4$Ni: C, 67.75; H, 5.69; N, 4.94. Found: C, 67.52; H, 5.73; N, 4.89.

I (**R$_1$ = CH$_3$, R$_2$ = CH$_2$F**).—The ligand was prepared by the

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(2) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

(3) W. D. Horrocks, Jr., R. W. Kluiber, and R. A. Low, Proceedings of the IXth International Conference on Coordination Chemistry, St. Moritz, Switzerland, Sept 1966, p 489; W. D. Horrocks, Jr., R. W. Kluiber, and R. A. Low, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. O-182; R. W. Kluiber and R. Kukla, Abstracts of Papers, Metrochem 69 Regional Meeting of the American Chemical Society, May 1969, p 21.

(4) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **46**, 4164 (1967); Z. Luz and S. Meiboom, *ibid.*, **40**, 2686 (1964); N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, **6**, 1127 (1967); N. A. Matwiyoff, *ibid.*, **5**, 788 (1966); A. L. Van Geet, *ibid.*, **7**, 2026 (1968); D. K. Ravage, T. R. Stengle, and C. H. Langford, *ibid.*, **6**, 1252 (1967); W. L. Rice and B. B. Wayland, *ibid.*, **7**, 1040 (1968); R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *Z. Elektrochem.*, **69**, 110 (1960).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

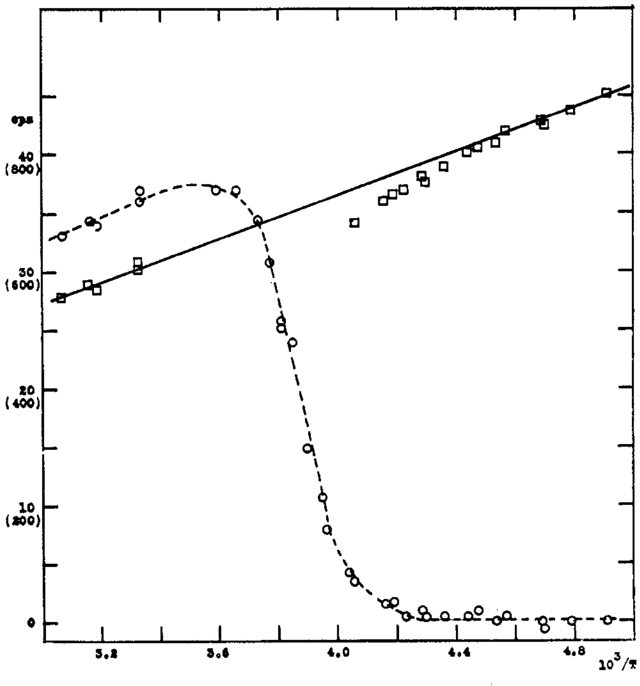

Figure 1.—Isotropic shifts (cps) of 4-picoline CH_3 proton resonance in the system $Ni(AA)_2P_2$ ($R_1 = R_2 = CH_3$) as a function of reciprocal absolute temperature. Data are those observed for the system $Ni(AA)_2$ (0.0592 *M*) and 4-picoline (1.991 *M*): O, bulk solvent 4-picoline shifts; □, shifts for the resonance in the pure paramagnetic complex (calculated in the fast-exchange region).

procedure of Cotton and Fackler[6] and was found to contain a maximum of 10% of the 3-fluoro isomer by nmr analysis. The adduct was prepared by procedure A, azeotropically removing the water using boiling benzene followed by addition of 4-picoline and rapid cooling. The blue crystals melted at 157–158° dec (turning brown) after drying *in vacuo* at 56° for 6 hr. A strong infrared peak at 1052 cm^{-1}, characteristic of the C–F bond,[5] was observed. *Anal.* Calcd for $C_{22}H_{26}F_2N_2O_4Ni$: C, 55.14; H, 5.47; N, 5.85; Ni, 12.25. Found: C, 55.05; H, 5.47; N, 5.82; Ni, 12.2.

I ($R_1 = R_2 = C_6H_5$).—The chelate obtained by procedure A was recrystallized from 4-picoline and water and dried at 56° for 3 hr *in vacuo*. The yellow product melted at 235° and showed a characteristic phenyl peak[5] at 719 cm^{-1}. *Anal.* Calcd for $C_{42}H_{36}N_2O_4Ni$: C, 72.96; H, 5.24; N, 4.05; Ni, 8.49. Found: C, 73.21; H, 5.25; N, 4.15; Ni, 8.4.

I ($R_1 = CH_3$, $R_2 = CF_3$).—The β-diketone–nickel complex hydrate was converted by dissolving it in boiling benzene containing 4-picoline. Ligroin (bp 60–80°) was added and the blue crystals thus obtained after drying at 56° *in vacuo* for 2 hr melted at 245°. The CF_3 group[5] absorbed strongly at 1133 and 1176 cm^{-1}. *Anal.* Calcd for $C_{22}H_{22}F_6N_2O_4Ni$: C, 47.94; H, 4.02. Found: C, 47.69; H, 3.87.

I ($R_1 = R_2 = CF_3$).—The adduct prepared by procedure B was recrystallized from ligroin and 4-picoline and dried at 56° for 1 hr. It had a blue-green to blue transition at about 100° and melted at 182°. *Anal.* Calcd for $C_{22}H_{16}F_{12}N_2O_4Ni$: C, 40.09; H, 2.45. Found: C, 40.50; H, 2.35.

Spectra.—Infrared spectra were obtained using a Beckman IR 10 spectrophotometer. Samples were prepared as mineral oil mulls mounted between KBr plates. The electronic spectra were obtained using a Cary 14 recording spectrophotometer. Samples were prepared as solutions in chloroform containing 2.0 *M* 4-picoline and also as mineral oil mulls mounted on filter paper. Nmr spectra were obtained at 60 Mcps using either a Varian A-60 or A-60A instrument. Tetramethylsilane, TMS, was used as the internal standard and the side-band technique was used for frequency calibration. Temperature calibration was made using the separation of the methanol or ethylene glycol peaks.

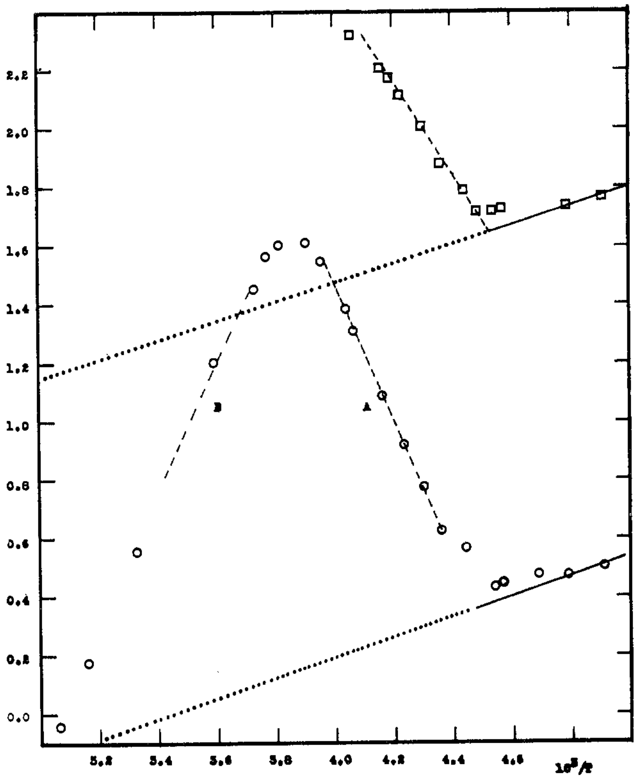

Figure 2.—Log of full line widths (cps) at half-height of 4-CH_3 proton resonances for the system described in Figure 1 as a function of reciprocal absolute temperature: O, data for the 4-picoline in the bulk solvent corrected for the line width of the 4-CH_3 resonance in the absence of any paramagnetic species; □, line width data for the resonance in the paramagnetic complex.

Melting Points.—The melting behavior of the above compounds is dependent on the rate of heating and the total time required to melt the sample. To standardize the melting points reported in this work, capillaries containing the sample were introduced into an oil bath being heated at approximately 5°/min at about 7–10° below the melting point.

Kinetics.—Samples were prepared using the preformed picoline complexes, by adding 4-picoline, distilled and stored over molecular sieves, and diluting with deuteriochloroform. Anhydrous β-diketone–nickel(II) complexes were also used to prepare samples ($R_1 = R_2 = t\text{-}C_4H_9$; $R_1 = R_2 = CH_3$; $R_1 = CH_3$, $R_2 = C_6H_5$), and the results obtained using either route were identical. The use of deuteriochloroform obtained from different suppliers as obtained, as well as specially dried and distilled deuteriochloroform, had no effect on the results. Samples which required heating above 60° were sealed in a thick-walled nmr tube at −195° *in vacuo*. Concentration of the paramagnetic complex was varied from 0.025 to 0.10 *M* and the picoline concentration was varied from 1 to 2 *M*. The mole fraction of complexed picoline was kept in the range 0.03–0.10. Data from three to six samples were used to evaluate the rate parameters. Temperature control was maintained at ±1° except at temperatures below −65° where somewhat greater variation was observed.

Method of Analysis and Results

Solutions of bis(β-diketonato)nickel(II) complexes with an excess of 4-picoline show only a single set of nmr resonances at ambient or higher temperatures,

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[6] F. A. Cotton and J. P. Fackler, Jr., *J. Chem. Soc.*, 1435 (1960).

characteristic of rapid exchange of picoline between the bulk solution and the paramagnetic complex. At low temperatures, *ca.* −60°, the exchange of 4-picoline becomes relatively slow and two sets of picoline proton resonances are observed. A relatively narrow set, unshifted from the diamagnetic position, is attributed to the uncomplexed picoline in the bulk solvent. A set of broadened and greatly shifted resonances, exhibiting a Curie ($1/T$) temperature dependence, is attributed to the picoline in the paramagnetic complex, $Ni(AA)_2P_2$, I. (Comparable experiments with added β-diketone indicate that the chelate ring exchange is slow over the temperature range −60 to 100°.) Typical isotropic shift data for the bulk and complexed 4-picoline resonances are given in Figure 1 and corresponding line width data are given in Figure 2. At intermediate temperatures, the observed frequency shifts for the picoline in the bulk solvent (Figure 1) and the resonance half-widths at half-height (Figure 2) can be interpreted in terms of the mean lifetime of the picoline in the paramagnetic complex, τ_m, using eq 1 and 2. These equations were developed

$$\Delta\omega_f = \frac{P_m \Delta\omega_m}{[(\tau_m/T_{2m}) + 1]^2 + (\tau_m \Delta\omega_m)^2} \tag{1}$$

$$(T_{2p})^{-1} = \frac{P_m}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right] \tag{2}$$

by Swift and Connick[7] for systems studied under conditions of slow passage and containing a large excess of the proton in the bulk solution. $\Delta\omega_f$ and $\Delta\omega_m$ are the observed isotropic shifts (in radians per second relative to the resonance position of the proton in the absence of complex) in the bulk solvent and in the paramagnetic complex, respectively. The latter cannot be observed at higher temperatures but can be obtained by linear extrapolation of the low-temperature data or use of the relationship $\Delta\omega_f = \Delta\omega_m P_m$ under conditions of rapid exchange (Figure 1). T_{2m} is the transverse relaxation time of the proton in the pure paramagnetic complex in the absence of exchange and its reciprocal is the half-width at half-height of the complexed proton resonance in radians per second. At higher temperatures T_{2m}^{-1} can be approximated by a linear $1/T$ extrapolation of the low-temperature data (Figure 2). The line thus obtained indicates an activation energy of 1.5 kcal for the relaxation process, in moderate agreement with the activation energies found for other systems.[4] Fortunately in eq 1, errors in T_{2m} have very little effect on the evaluation of τ_m. P_m is the mole fraction of total picoline bonded to the paramagnetic complex. By using the extrapolated values of T_{2m} and the interpolated values of $\Delta\omega_m$, τ_m was obtained by direct solution of eq 1. A computer program was set up to handle this routine solution of a quadratic equation.

T_{2p}^{-1} is obtained from the observed half-width at half-height of the picoline resonance in the bulk solvent by subtracting the resonance half-width in the absence of exchange. This correction involves (a) the half-width in the absence of paramagnetic species, a quantity readily determined experimentally and being in the present case less than 1 cps over the entire temperature range, and (b) a correction to the bulk proton line width owing to the relaxation caused by the magnetic dipole of the paramagnetic species. This latter correction was made in the present work using a $1/T$ linear extrapolation to higher temperatures of the log of the observed line width under conditions of slow exchange. This correction ignores the possibility of preferred solvation by 4-picoline at low temperatures. Unfortunately, the extrapolation involves a great amount of uncertainty and is critical to the determination of τ_m, particularly at low temperatures. Therefore, in this research emphasis in the evaluation of τ_m was placed on the use of eq 1.

Table I

Kinetic Parameters for 4-Picoline Exchange in $Ni(AA)_2P_2$

R_1	R_2	$k_1(25°)$, sec^{-1}	$\Sigma\sigma^*$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol deg
t-C_4H_9	t-C_4H_9	1.1×10^6	−0.60	12.8	8.0
CH_3	CH_3	1.0×10^5	0.00	11.4	2.8
CH_3	CH_2OCH_3	4.5×10^4	0.52	12	5
CH_3	C_6H_5	3.8×10^4	0.60	11.6	3.0
CH_3	CH_2F	3×10^4	1.10	...	...
C_6H_5	C_6H_5	2.3×10^4	1.20	12.9	4.9
CH_3	CF_3	1.4×10^3	2.75	14.6	4.6
CF_3	CF_3	$\sim 10^2$ [a]	5.5[a]	...	...
CH_3	CH_3[b]	10^6 [a,b]	...	9[b]	1[b]

[a] Approximated. [b] Data for the corresponding Co(II) complex.

Under conditions where $\Delta\omega_m^2 \gg T_{2m}^{-2}, \tau_m^{-2}$, eq 2 simplifies to $T_{2p}^{-1} = P_m/\tau_m$ and applies to region A in Figure 2.[7] Alternatively under conditions where $\tau_m^{-2} \gg (\Delta\omega_m)^2 \gg (T_{2m}\tau_m)^{-1}$ the equation $T_{2p}^{-1} = P_m \tau_m \Delta\omega_m^2$ is valid and applies to region B in Figure 2. In addition the exchange contribution to the broadening of the pure paramagnetic resonance line can be interpreted in terms of the lifetime of the picoline in the paramagnetic complex using eq 3, where T_{2mp}^{-1}

$$T_{2mp}^{-1} = T_{2m}^{-1} + \tau_m^{-1} \tag{3}$$

is the observed half-width at half-height for the resonance of the proton in the paramagnetic complex.[8]

The mean lifetimes of the picoline in the paramagnetic complexes can be converted to first-order rate constants using the relationship $k_1 = \tau_m^{-1}$. The temperature dependences of the first-order rate constants were interpreted using the transition-state theory, with the transmission coefficient assumed to be unity (eq 4). Typical results of this correlation are shown in

$$k_1 = \frac{kT}{h}\exp[-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT] \tag{4}$$

Figure 3 and the activation parameters obtained are given in Table I. While these parameters may be subject to considerable absolute uncertainty, their

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(7) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(8) L. H. Piette and W. A. Anderson, *ibid.*, **30**, 899 (1959).

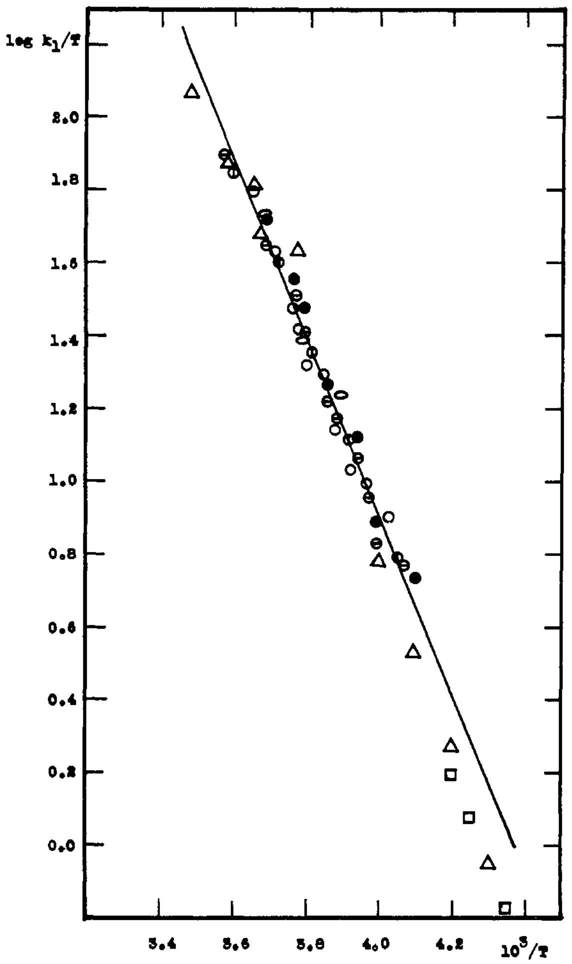

Figure 3.—Typical first-order rate data, log (k_1/T), for the system $Ni(AA)_2P_2$ ($R_1 = R_2 = CH_3$) as a function of reciprocal absolute temperature. The data obtained by various methods and at various concentrations are compared: ○, frequency shift data, 4-CH_3 resonance, 0.0508 *M* $Ni(AA)_2P_2$, 2.0326 *M* 4-picoline; ●, frequency shift data, 4-CH_3 resonance, 0.0302 *M* $Ni(AA)_2P_2$, 1.051 *M* 4-picoline; ⊖, frequency shift data, 4-CH_3 resonance, 0.0305 *M* $Ni(AA)_2P_2$, 0.6047 *M* 4-picoline; ⦶, frequency shift data, 4-CH_3 resonance, 0.0592 *M* $Ni(AA)_2$, 1.991 *M* 4-picoline; ⬭, frequency shift data, 3-H resonance, 0.0595 *M* $Ni(AA)_2$, 1.01 *M* 4-picoline; △, data from line width of 4-CH_3 resonance of 4-picoline in bulk solvent; □, data from line width of 4-CH_3 resonance in the paramagnetic complex.

relative values, having been evaluated by similar methods, are meaningful.

The rate constants were most conveniently determined using the picoline 4-CH_3 resonance because of its greater intensity, its narrower line width, the absence of interfering resonances both near the paramagnetic and diamagnetic peaks, and the absence of strong coupling with other protons. Identical rates however were obtained using frequency shift data for the 3-H proton resonance. The diamagnetic positions of these resonances relative to TMS are −140 (4-CH_3) and −428 cps (3-H) and are relatively insensitive to concentration and temperature changes. The rate of exchange of the trifluoro derivative (I, $R_1 = CH_3$, $R_2 = CF_3$) was complicated by the presence of a second component observed as a small upfield shoulder on the main complexed 4-CH_3 peak. Fortunately, the exchange rate for both species appears to be approximately the same and eq 1 provides a satisfactory means for the reduction of the observed data. On the other hand, the hexafluoro derivative (I, $R_1 = R_2 = CF_3$) shows two definite resonances for the 4-CH_3 protons in the complex and k_1 was not obtained. It was, however, estimated to be an order of magnitude slower than the rate for the trifluoro derivative, since rapid exchange was not observed even at temperatures in excess of 100°. [An attempt to study a series of bis(picoline)bis(salicylaldehyde)nickel(II) complexes as a two-component system also failed owing to the presence of major amounts of two paramagnetic species.] The monofluoro derivative (I, $R_1 = CH_3$, $R_2 = CH_2F$) was unique in that it, unlike any of the other complexes, underwent an irreversible reaction upon heating or long standing with picoline, presumably involving the fluoromethyl group. However, reproducible data could be obtained from this complex between 0 and 15° and the extrapolated rate constants from these data are given in Table I.

Electronic spectral data for these complexes in chloroform solutions and as mulls are presented in Table II. Although the real symmetry of these complexes is less than D_{2h}, the distortion of the complex from octahedral symmetry seems to have little effect on the gross spectra and the observed absorptions can be interpreted in terms of an octahedral model. The observed transitions are thus assigned as $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow {}^3T_1$. In addition to these spin-allowed transitions, the solution spectra all show a very weak absorption at approximately 12,900 cm^{-1}, generally assigned to the transition $^3A_2 \rightarrow {}^1E$. These results are similar to those previously reported for other pyridine–β-diketone–nickel(II) complexes.[9,10] Deviations between the mull and solution spectra increase as the groups R_1 and R_2 become more electron withdrawing. Some caution must be used in interpreting the mull spectra as in several cases (for example, $R_1 = CH_2OCH_3$, $R_2 = CH_3$) an irreversible color change was noted in the sample upon standing in the spectrometer beam.

Table II

Ligand Field Spectra of Complexes (cm^{-1})

R_1	R_2	State	$A_2 \rightarrow T_2$ (ϵ, M^{-1} cm^{-1})	$A_2 \rightarrow T_1$ (ϵ, M^{-1} cm^{-1})
t-C_4H_9	*t*-C_4H_9	Soln	10,100 (8.9)	17,000 (9.7)
CH_3	CH_3	Soln	10,200 (5.7)	17,000 (8.5)
		Mull	10,200	17,100
CH_3	CH_2OCH_3	Soln	10,200 (6.1)	17,000 (8.9)
CH_3	C_6H_5	Soln	10,100 (7.7)	17,100 (13.1)
		Mull	10,400	17,400
CH_3	CH_2F	Mull	10,000	17,200
C_6H_5	C_6H_5	Soln	10,100 (10.0)	17,100 (20.0)
		Mull	10,400	17,700
CH_3	CF_3	Soln	10,100 (7.1)	16,900 (10.0)
		Mull	10,500	17,500
CF_3	CF_3	Soln	10,100 (7.0)	16,800 (12.0)

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(9) D. P. Graddon, R. Schulz, E. C. Watton, and D. G. Weedon, *Nature*, **198**, 1299 (1963).

(10) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

In the infrared spectral region, the two very strong absorptions in the region 1520 and 1600 cm^{-1}, characteristic of the multiple bonding in the β-diketone ring system, are always observed.[11] In addition, the 4-picoline peaks are generally shifted to higher frequencies in the complexes compared to the uncomplexed liquid ligand.[12] For example, the strong out-of-plane deformation mode found at 800 cm^{-1} in 4-picoline is found shifted 5–20 cm^{-1} to higher frequencies in the complexes. Similar shifts are noted for the hydrohalides of 4-picoline[12] and such shifts have been correlated with a general bond shortening on the complexed pyridine ring.[13,14]

Discussion

Structure of the Complexes.—While the present system allows isolation of factors affecting the kinetics of substitution in hexacoordinate nickel(II) complexes, it also introduces several potentially complicating factors regarding the stoichiometry and stereochemistry of the paramagnetic species in solution. It is known that the interaction of a ligand, P, with $Ni(AA)_2$ can result in the formation of species having stoichiometry $Ni(AA)_2P_2$, $[Ni(AA)_2P]_n$, or $[Ni(AA)_2]_2P$ depending on the relative concentrations of the reactants and the structure of P and $Ni(AA)_2$.[2] In addition, an octahedral system of structure MA_4B_2 can exist as *cis* or *trans* isomers. An added geometrical isomerization possible in the present system where an unsymmetrical β-diketone is used, that of *cis–trans* arrangement of the R_1 groups on adjacent β-diketones, will not be considered further in this discussion for its effects on the exchange rate are expected to be small. Except for the trifluoro and hexafluoro derivatives (*vide infra*), no evidence was found for the presence in solution of more than one paramagnetic species for any of the compounds in Table I. The collective evidence summarized below supports the postulate that the species actually being studied are the *trans* isomers having structure I.

At low temperature (*ca.* $-65°$), where exchange is slow, the solution stoichiometry was demonstrated by dissolving pure $Ni(AA)_2P_2$ complex in deuteriochloroform and observing virtually no nmr resonances for uncomplexed 4-picoline. Under the conditions of the experiment, this indicates less than $\sim$5% dissociation of $Ni(AA)_2P_2$ at this temperature. At such temperatures, in the presence of a 10–20-fold excess of picoline, under conditions identical with those used in obtaining kinetic data, the ratio of the areas of the complexed to uncomplexed 4-CH_3 proton nmr resonances gives a P:Ni ratio of $(2 \pm 0.3)/1$ in the paramagnetic complex. At ambient temperatures in the absence of added picoline, lower than expected isotropic shifts are observed for the 4-CH_3 resonance indicating that appreciable dissociation occurs. However, in solutions containing an excess of 4-picoline, the isotropic shifts observed under conditions of fast exchange—after correction for the excess of picoline—lie on a $1/T$ linear extrapolation of the coordinated resonances (Figure 1). The stoichiometry of the complex involved in this rate study must, therefore, be that represented by structure I and is in qualitative agreement with published equilibrium data.[15]

Less certain is the exact stereochemistry of the species in solution. In the crystalline phase, the pyridinenickel–acetylacetonate complex, $Ni[AA]_2P_2$, has been shown to have the *trans* configuration.[14] An earlier comparison of the vibrational and electronic spectra of this complex as a solid and in solution reached the tentative conclusion that in solution it also exists mainly in the *trans* configuration.[10] Similarly, nmr studies based on the interpretation of dipolar shifts for $Co(AA)_2P_2$ complexes indicated that these complexes, which in the solid phase are isostructural with the corresponding nickel(II) complexes, can also be characterized in solution as having the *trans* configuration.[16,17] In the present work, only a single resonance for the complexed 4-CH_3 protons was observed, indicating the presence of only a single isomer (or, alternately, a small difference in position of the *cis* and *trans* resonances or rapid *cis–trans* isomerization). Two noteworthy exceptions are the trifluoro ($R_1 = CH_3$, $R_2 = CF_3$) and the hexafluoro ($R_1 = R_2 = CF_3$) chelates. The nmr spectrum of the trifluoro complex shows a small (approximately 10% of total intensity of complexed 4-CH_3) shoulder, upfield by about 50 cps from the main resonance at $-61°$. The hexafluoro derivative shows two separate paramagnetic 4-CH_3 resonances at $-61°$, one with the anticipated isotropic shift of 870 cps and the other approximately twice as intense with a shift of 975 cps. As the position and intensity of these peaks are insensitive to P:Ni ratios from 2:1 to 20:1, the upfield peak is attributed to the presence of the *cis* isomer. If the presence of isomers is significant in systems other than the polyfluoro complexes, they appear to have little or no effect on the spin-density distribution in the picoline ring as the observed isotropic shift ratios in all cases were $10.0:(2.7 \pm 0.1):(0.96 \pm 0.06)$ [for the 2 proton:3 proton:4-CH_3 proton; these are also the ratios observed by Happe and Ward[16]]. Furthermore, the absolute magnitude of the 4-CH_3 isotropic shifts, an observable resonance which involves the pyridine-ring π system, is also insensitive within $\pm$2% to the nature of the chelate ring, although the chelate rings with phenyl groups appear generally to show a slightly greater shift than those with *t*-butyl groups. Attempts to obtain evidence for the presence of *cis* isomers using electronic spectra were not convincing. The *cis* isomer, not being centrosymmetric, would be expected to give rise

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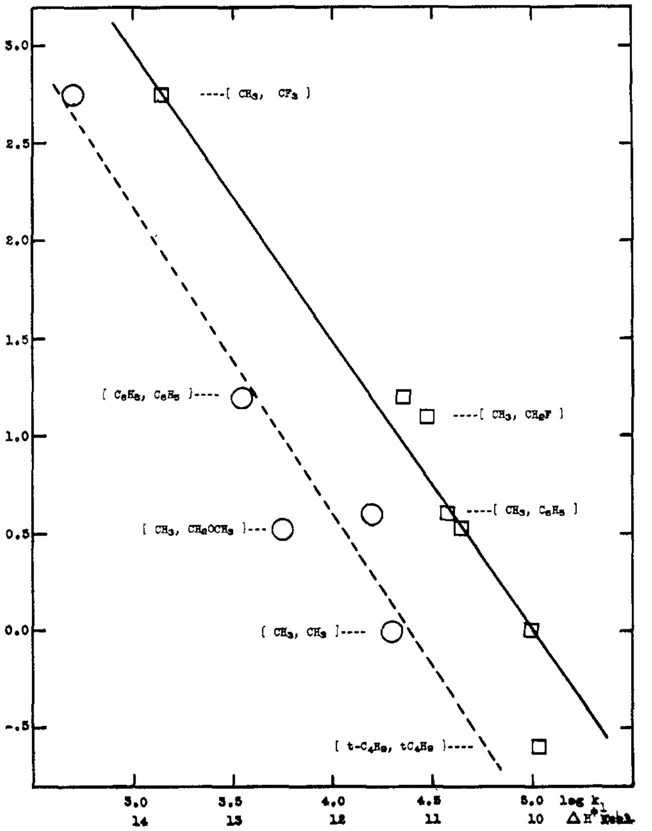

Figure 4.—Variations of rate of 4-picoline exchange at 25°, log k_1, □, and the activation energy, ○, for the system Ni-$(AA)_2P_2$ as a function of the sum of the Taft parameters σ^* for the groups R_1 and R_2.

to d-d transitions of greater intensity and the presence of both *cis* and *trans* isomers in solution may well be manifested in either separate absorbances or at least an increased line width if the transition energy differences is too small for resolution. Neither of these effects is clearly demonstrated by the spectral data.

Kinetics.—The observed rate of picoline exchange in these complexes (see the reaction in the Introduction) is first order in complex and independent of picoline concentration in all cases and follows the rate law rate $= 2k_1[\mathrm{Ni(AA)_2P_2}]$. Such first-order kinetics support a dissociative mechanism in which only the nickel–picoline bond-breaking process is of major importance in the transition state.[18] However since the evaluation of the kinetics using the Swift and Connick treatment demands data obtained in the presence of a large excess of uncomplexed 4-picoline, the reaction could also be associative with pseudo-first-order kinetics being observed over a large 4-picoline concentration range owing to preferential solvation of the complex by picoline.[19]

If metal–picoline bond breaking dominates the rate-controlling process, the rates of ligand exchange should correlate with equilibrium constants for the dissociation of the 2:1 adduct, $\mathrm{Ni(AA)_2P_2}$. While these are not known for many nickel β-diketonate adducts, the equilibria involving dissociation of the corresponding mono adducts of copper(II) β-diketonates have received considerable study.[13,20] The dissociation constants for the reaction $\mathrm{Cu(AA)_2P} = \mathrm{Cu(AA)_2} + \mathrm{P}$ decrease in the following order (R_1, R_2): (t-C_4H_9, t-C_4H_9) > (CH_3, CH_3) > (C_6H_5, CH_3) > (CF_3, CH_3) > (CF_3, CF_3). This is approximately the order of decreasing rate of exchange. The observed ligand-exchange retardation by electron-withdrawing chelate ring substituents may be described more quantitatively by the Hammett equation: $\log (k/k_0) = \rho\sigma$, where σ is the sum of the Taft σ^* parameters for the groups R_1 and R_2.[21,22] The sums of these parameters, which are a measure of the inductive and field effects of these groups, correlate rather well with the kinetic data, Figure 4. The phenyl group which is in conjugation with the chelate-ring π system[23] also follows the correlation but it has been shown that the σ^* parameter of this group also contains a significant resonance contribution.[24] The small ρ value (−0.6) is not unexpected since the removal of picoline does not result in the formation or destruction of a large charge in the activation process and the groups R_1 and R_2 are relatively remote from the reaction site. In addition to the above free energy correlations, $\Delta H^{\ddagger}$ also correlates roughly with the rate of exchange. While this parameter results from a difference in enthalpies of the ground and transition states, the simplest explanation suggests that this difference is due to stronger ligand to metal bonding in the adducts having the most electron-withdrawing groups. This and the positive, although small, entropies for the activation process again support a dissociative mechanism. However both of these parameters are subject to considerable uncertainties, and a more detailed analysis cannot be made. The retarding effects of electron-withdrawing substituents on the rate of ligand exchange observed in the present work are also in agreement with results of previously reported kinetic studies on the reactions of aquonickel(II) chelates with various ligands using temperature-jump techniques.[25]

A notable exception to these correlations is complex I ($R_1 = R_2 = t$-C_4H_9). Factors such as the electron-releasing nature and the steric bulk of the t-butyl groups would be expected to destabilize the ground state and lead to faster than expected exchange rates. The observed exchange rate is, however, slower than predicted. In this case the destabilization of the

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ground state may be at least partially compensated by the destabilization of the activated complex due to steric inhibition of solvation. The leaving picoline group coupled with the bulky *t*-butyl groups can effectively shield the approach of solvent to the reaction site. Such an interpretation is in agreement with the more positive activation parameters observed for this exchange.

Finally, the kinetics of the corresponding cobalt(II) analog of I [$R_1 = R_2 = CH_3$] was studied. The rate of exchange of this complex is approximately an order of magnitude larger than that for the corresponding nickel complex, and this rate difference is associated with a large difference in activation energy. Such differences for Ni(II) and Co(II) complexes have been observed in other systems.[4] They are predicted by the crystal field model for a square-pyramidal or trigonal-bipyramidal intermediate and also expected from the greater Co–N bond lengths in the *trans* 2:1 complex.[14]

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A Kinetic Study of the Reduction of Copper(II) by Tin(II) Chloride

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The reduction of Cu(II) by Sn(II) in aqueous hydrochloric acid yields kinetics and stoichiometry consistent with the reaction

$$\mathrm{Cu(II)} + \mathrm{Sn(II)} \rightleftharpoons \mathrm{Cu(I)} + \mathrm{X}$$
$$\mathrm{Cu(II)} + \mathrm{X} \longrightarrow \mathrm{Cu(I)} + \mathrm{Sn(IV)}$$

where X represents a species containing trivalent tin. The overall reaction rate is particularly sensitive to the chloride concentration, the steady state approximation failing in systems prepared with sulfuric acid instead of hydrochloric acid. A numerical curve fitting computer program was used to gain order of magnitude estimates of the separate rate constants for the nonsteady-state reactions at 25°.

Introduction

The presence of trace amounts of Cu(I) in aqueous acidic Sn(II) chloride solutions has been shown to enhance the reactivity of the solution toward dissolved nitric oxide[1] and Fe(III).[2] The identity of the reactive species does not appear to have been determined, although Powell and Nunes suggested the existence of a Cu(II) complex containing the $SnCl_3^-$ ion as a ligand. Experiments indicate that the reactive species in the nitric oxide reduction is not one of the stable oxidation states of copper or tin.[1,3]

If the reactive species in the Sn(II)–Cu(I) system is an active intermediate existing at low concentrations during a reduction, then a kinetic study of the reduction of Cu(II) by Sn(II) in hydrochloric acid solution might shed some light on the question of the nature of this intermediate. To the author's knowledge, this work represents the first such study.

Experimental Section

Apparatus.—The absorbance of reacting solutions was followed on a Beckman DB uv–visible spectrophotometer equipped with a thermostated sample compartment and a Beckman Model B spectrophotometer without thermostating. The reaction cell was constructed from a 3.6-cm length of Pyrex tubing equipped with two side arms to allow its use as a flow cell. The ends were ground parallel, and optical-quality cell windows were affixed with either polyester casting resin or Canada Balsam. A Beckman 1.0-cm optical path length flow cell was used for some runs at high Cu(II) concentration.

A stopped-flow technique was used employing a mixing system constructed from two three-way stopcocks, two 5-ml ground-glass syringes, and a "Y" cell designed for efficient mixing. Two 25-ml burets were used as reservoirs. A schematic of the system appears in Figure 1.

Both syringes could be emptied through the mixing cell simultaneously in less than 1 sec. The volume of the mixing cell was approximately 1 ml while the tube from the mixing cell to the reaction cell contained another 1.5 ml. Consequently, the maximum time between mixing and observing was approximately 0.25–0.5 sec. The time required for the Beckman DB meter to indicate 90% of a full-scale deflection was approximately 1 sec. The first half-life of all runs was 10 sec or longer with succeeding half-lives growing progressively longer for each second-order reaction. It was felt that the response time of the system was short enough compared to the reaction rates to allow meaningful measurements to be made.

Reagents.—Fisher Certified ACS reagents were used without purification except stannous chloride dihydrate, which was boiled in hydrochloric acid solution in the presence of tin pellets and recrystallized under nitrogen. All solutions were prepared with boiled distilled water and stored under nitrogen. Sulfuric and hydrochloric acid solutions were standardized by accepted procedures.[4]

Copper(I) chloride was prepared by boiling a hydrochloric acid solution of copper(II) chloride in the presence of copper pellets.

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