plex, which falls off the plots in Figure 4, but its different behavior is more obvious in comparison of the reverse rate constants ($K_4^{-1}k_{-3}$) in Table IV. The reaction of $EDDA^{2-}$ with $Ni(CN)_4^{2-}$ is more than 100 times faster than $MIDA^{2-}$. This suggests that $EDDA^{2-}$ may react in a manner similar to the polyamines in that two nitrogens may be bonded in the rate-determining step but electrostatic repulsion causes the loss of a cyanide ion as with the other aminocarboxylates.

The K_1 values (the stability constant of the $NiLCN^{1-n}$ complex) increase in a regular fashion as the electrostatic repulsion decreases between CN^- and NiL^{2-n}. From this trend in K_1 values the stability constant for $Ni(trien)(CN)^+$ would be expected to be much larger than its value of $1.6 \times 10^4\ M^{-1}$. It is apparent that there are factors in addition to the availability of a coordination site and electrostatics which govern the relative stability of the monocyanide complexes. The same point has been made concerning the mixed biscyano complexes (K_1K_2 values in Table IV) which are remarkably stable for IDA and MIDA.

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Base Adducts of Nickel Dithiophosphate

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The reaction of a variety of nitrogen bases with $Ni[S_2P(OC_2H_5)_2]_2$ is reported. Bases such as 2-picoline and diethylamine form monoadducts with association constants smaller than 10 l./mol, while pyridine, 3-picoline, and 4-picoline form diadducts in two successive steps. The values of K_1 are, respectively, 29, 21.8, and 31.6 l./mol in benzene, and K_2 is much larger (78, 68.7, and 215.7 l./mol, respectively). $Ni(dtp)_2$ adds 2 mol of pyridine in nitrobenzene with an enthalpy change of −16.8 kcal/mol. The five-coordinate adducts of 2-picoline and 2,6-lutidine are diamagnetic (by nmr) but the diethylamine and di-*n*-butylamine monoadducts are paramagnetic, though the electronic spectra of the two series of molecules are quite similar. The complicated temperature dependence of the contact shifts in the 2:1 adducts is also reported.

The great difference in reactivity toward nitrogen bases of three diamagnetic planar nickel complexes, each with an NiS_4 coordination sphere, has been of interest to us. Bis(diethyldithiocarbamato)nickel(II) does not readily[1-3] form an adduct with pyridine, while bis(ethylxanthato)nickel(II) readily adds two molecules of pyridine.[2,4] Behavior intermediate between those two extremes is exhibited by bis(diethyldithiophosphato)nickel(II), $Ni(dtp)_2$, which adds two molecules of pyridine in a stepwise fashion.[2] Several reports concerning the 1:1 adducts of secondary amines with $Ni(dtp)_2$ have appeared, with particular attention being placed on an assignment of the spectra.[1,5,6]

We felt that it would be worthwhile to investigate more carefully the nature of both the 1:1 and the 2:1 adducts of $Ni(dtp)_2$ with a variety of bases in solution. First we sought to determine the factors which affect the stoichiometry of the adducts formed. Second, we sought information on the nature of the five-coordinate complexes, particularly their structure and their magnetic properties in solution. Finally, we have tried to characterize better the six-coordinate (2:1) adducts.

Experimental Section

Solutions and Materials.—Bis(O,O′-diethyldithiophosphato)-nickel(II), $Ni[S_2P(OC_2H_5)_2]_2$, was prepared according to the method outlined in the literature.[7] Because of the instability of this compound and because of the presence of charge-transfer bands in the near-ultraviolet spectrum, the compound was recrystallized periodically and stored in the dark. By following this procedure no decomposition was observed. All nitrogen bases were twice distilled from Zn dust before use.

Optical spectra were recorded in spectroscopic grade benzene while nmr spectra were recorded in deuteriochloroform using TMS as the internal reference. Solution susceptibility measurements were run in a 15% (v/v) solution of TMS in $CHCl_3$.

Crystallization of the 1:1 adduct from solution was attempted in the diethylamine, dibutylamine, 2-picoline, and 2,6-lutidine systems. Decomposition occurred in all cases when the solutions containing the amines were evaporated except for 2,6-lutidine, which yielded a crystalline material. At present this substance is incompletely characterized, since elemental analysis of two different samples has yielded indeterminate results.

Apparatus.—Optical spectra were recorded on a Cary Model 14 spectrophotometer equipped with fluid thermostated sample cell holders. All spectra were recorded at 25 ± 0.1°.

A Varian A-60A spectrometer equipped with the Model V6057 variable-temperature accessory was used to record proton contact shifts and their temperature variation.

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[1] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

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Phosphorus-31 spectra were recorded on a Bruker HFX-90 spectrometer operating at a fixed frequency of 36.4 MHz using 85% H_3PO_4 as an internal lock. This instrument, operating at 90 MHz, was used to check the field dependence of the proton contact shifts and as a more sensitive probe for the α protons in 3- and 4-picoline.

Procedures.—The heat of reaction of $Ni(dtp)_2$ with pyridine in nitrobenzene was determined calorimetrically using the procedure described in the literature.[8]

Equilibrium constants were determined by spectrophotometric titration and the equilibrium constants were calculated using one of two computer techniques.

(a) The procedure for the calculation of the stepwise addition of base has been described previously.[2] The spectrum of the six-coordinate species, necessary for the calculation, was recorded in 20% (v/v) base. As one might anticipate from the method employed, the calculation is very sensitive to the wavelength where the isosbestic point occurs and where the absorbance of the five-coordinate species is monitored.

(b) In the case of those systems where only 1:1 complexes were formed solution of the standard equation[8]

$$K_1 = \frac{(A - A_0)/(\epsilon_5 - \epsilon_4)}{\left[C_4^0 - \left(\dfrac{A - A_0}{\epsilon_5 - \epsilon_4}\right)\right]\left[C_B^0 - \left(\dfrac{A - A_0}{\epsilon_5 - \epsilon_4}\right)\right]} \qquad (1)$$

was accomplished by a least-squares percentage difference program in which ϵ_5 was varied. The use of a percentage least-squares fit was chosen over a fractional least-squares fit since the errors in the data are not uniform.

Because of the instability of $Ni(dtp)_2$, a stock solution of the complex was not used; rather the required amount of material was weighed directly into the volumetric flask. A known amount of base was dissolved in benzene and brought to 25° and solvent benzene was brought to temperature at the same time. The thermostated optical cells were placed in the instrument and balanced against benzene. A small amount of benzene was added to the volumetric flask to dissolve the complex, the required amount of base was added, and the solution was finally made up to volume with benzene. This solution was immediately placed in the sample cell and the absorbance readings were taken for 20 sec at the appropriate wavelength.

Nmr spectra were studied as a function of concentration by the following procedure. Since the base protons were monitored, it was necessary to vary the concentration of the metal complex holding the base concentration constant at approximately 0.1 *M*. Identification of the base protons was accomplished by observing the approach toward the diamagnetic values and by comparison of the relative intensities.

The temperature variation of the contact shifts was determined on solutions of known concentration. The lowest temperature to be used was determined by raising the temperature from the freezing point of $CDCl_3$ until no material appeared to freeze out in the nmr tube. A new solution of the same concentration was then inserted into the probe at the best lowest temperature. Calibration of the temperatures was accomplished using methanol or ethylene glycol. At every temperature these shifts were checked before and after recording the spectra. All resonances were referenced to TMS as an internal standard. The chelate–TMS separation was checked to verify internal consistency.

The concentration dependence of the magnetic susceptibility was accomplished using a titrimetric variation of Evans' method.[9] A stock solution of the particular base was prepared and successive amounts of base were added to a solution of constant metal complex concentration. The shift between reference TMS in the inner concentric tube and the sample TMS in the annular section of the tube was recorded. The mole ratio at which a shift occurred from the constant separation in the reference and solution–TMS signals was taken to indicate the formation of some paramagnetic species in solution.

Results

I. 1:1 Adduct Formation.—Equilibrium constants for the 1:1 complexes with various amines are presented in Table I along with the fitted extinction coefficients.

TABLE I

EQUILIBRIUM CONSTANTS FOR 1:1 ADDUCT FORMATION AT 25°

Base	ϵ_5[a]	K_1, l./mol
2,6-Lutidine	172.4	2.83 ± 0.13
2-Methylpiperidine	277.0	8.29 ± 0.10
Di-*n*-butylamine	319.4	7.15 ± 0.09
Diethylamine	309.4	6.07 ± 0.45
2-Picoline		<5

[a] At 460 mμ.

The spectrophotometric titration of $Ni(dtp)_2$ with 2-methylpiperidine is presented in Figure 1 and the changes observed between 19,200 and 22,700 cm^{-1} should be considered characteristic of these systems. In the case of 2-picoline, an equilibrium constant could not be calculated but the magnitude can be estimated to be less than 5. The isosbestic point is lost at considerably smaller mole ratios than in the other systems, but we have no evidence that suggests that the subsequent spectral change results from the formation of a 2:1 adduct.

The magnetic susceptibility of the substituted pyridine systems indicates that they are diamagnetic over a wide concentration range, particularly as the base: metal concentration ranges from 0:1 to greater than 2:1.

Furthermore, we have followed the proton resonance spectrum of 2,6-lutidine with metal:base mole ratios of $Ni(dtp)_2$ greater than 12:1. No shift or broadening of the proton resonances was observed in this experiment. The coupling of the ^{31}P nucleus to the methylene protons also was not affected.

II. 2:1 Adduct Formation.—Equilibrium data are presented in Table II for the stepwise addition of two molecules of base to the coordination sphere of $Ni(dtp)_2$. The values for 3-picoline and 4-picoline may be considered inaccurate to the extent that the "pure six-coordinate" spectrum remains uncertain. Thus, changes were observed to occur in the spectra even at extremely high base concentrations, *e.g.*, there was a change on going from 0.1 to 2.0 *M* and even to 4.0 *M*

TABLE II

EQUILIBRIUM CONSTANTS FOR 2:1 ADDUCT FORMATION AT 25°

Base	ϵ_1[b]	ϵ_2[c]	K_1, l./mol	K_2, l./mol
Pyridine[a]	365.5	24.5	29	78
3-Picoline	528.0	14.0	21.8	68.7
4-Picoline	500.0	22.0	31.6	215.7

[a] Reported previously.[2] [b] Fitted extinction coefficient of five-coordinate species at the wavelength where the four- and six-coordinate molecules have the same extinction coefficient. [c] Fitted extinction coefficient of five-coordinate species at 530 mμ; *i.e.*, the wavelength where absorption by the five-coordinate species is large relative to that of the six-coordinate species.

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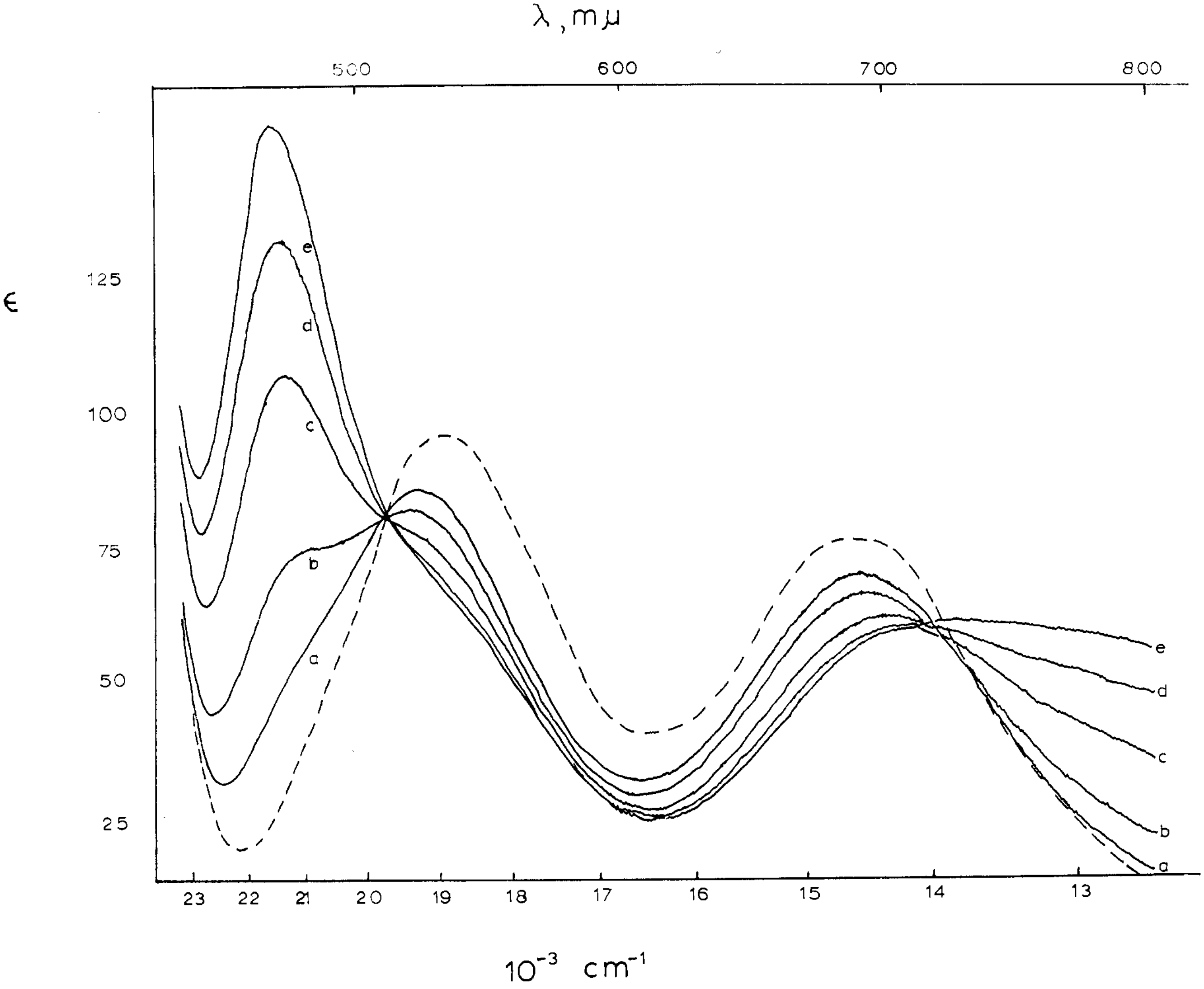

Figure 1.—Spectrophotometric titration of 7 × 10^{-3} M $Ni(dtp)_2$ (– – –) with 2-methylpiperidine at molar concentrations of (a) 1.7 × 10^{-2}, (b) 3.4 × 10^{-2}, (c) 6.8 × 10^{-2}, (d) 1 × 10^{-1}, and (e) 1.4 × 10^{-1}.

in base. Of course, since these solutions are no longer ideal, effects other than simple adduct formation may be influencing the spectra. This behavior was not observed for the pyridine system. The spectrophotometric titration of $Ni(dtp)_2$ with 4-picoline is depicted in Figure 2 and must be considered typical of the spectra obtained for these stepwise additions.

The heat of reaction for the addition of two molecules of pyridine has been determined by the temperature variation of the equilibrium constants.[2] Our value of −16.8 kcal/mol for the overall heat of reaction determined calorimetrically is in agreement with the enthalpy change of −18.6 kcal/mol determined (in benzene) by the less accurate method used earlier.

The contact shifts of the various protons of pyridine, 3-picoline, and 4-picoline as a function of the mole ratio were observed. The diamagnetic ligand resonances were taken from Holm, *et al.*[10] In all cases it was impossible to observe the α protons even on the more sensitive 90-MHz Bruker instrument at mole ratios greater than 0.01:1 (metal:base); equivalently, they could be observed only when the base protons were closest to their diamagnetic resonances. The temperature variation of the contact shifts was also measured. Only the most intense and furthest removed protons could be monitored over the entire temperature range.[11]

The diamagnetic chelate resonances at 60 MHz in $CDCl_3$ from TMS are for CH_2, −258 Hz and for CH_3, −85 Hz. The diamagnetic ^{31}P resonance occurs at −80 ppm from 80% H_3PO_4, while the phosphorus methylene proton coupling constant in the diamagnetic chelate is 2.6 Hz.

All attempts to observe a contact shift or dipolar coupling of the unpaired electron density on the ^{31}P nucleus proved fruitless both in the solution and solid state. As expected for octahedral Ni^{2+} no epr signal was observed in solution.

Discussion

The apparent formation of 1:1 complexes when secondary amines or substituted pyridines are added to

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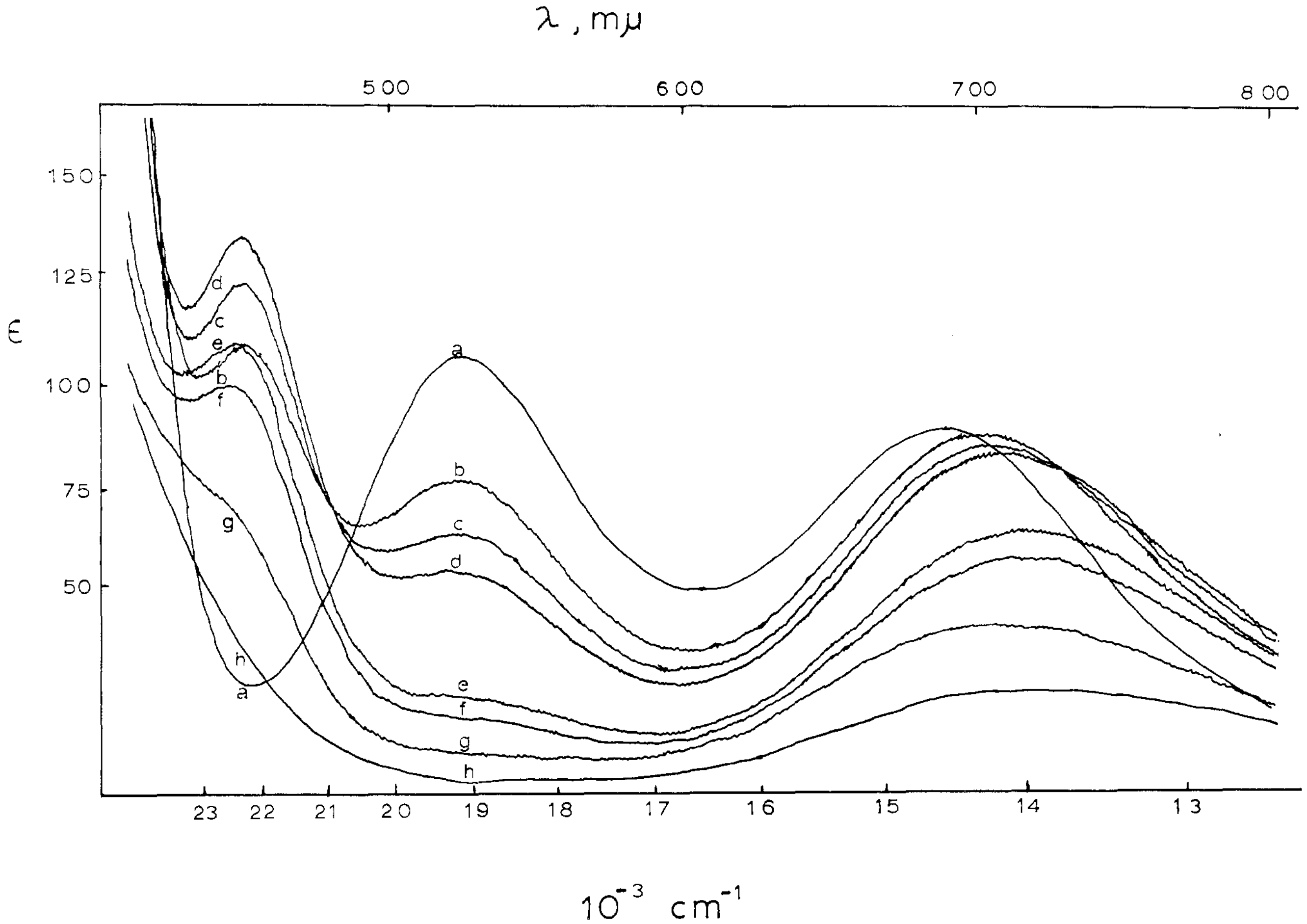

Figure 2.—Spectrophotometric titration of (a) 4.7×10^{-3} *M* $Ni(dtp)_2$ with 4-picoline at molar concentrations of (b) 1.6×10^{-2}, (c) 2.5×10^{-2}, (d) 3.3×10^{-2}, (e) 8.2×10^{-2}, (f) 1×10^{-1}, and (g) 2×10^{-1}. Curve h is the spectrum of $Ni(dtp)_2$ in 20% 4-picoline.

$Ni(dtp)_2$ is reflected in the ligand field spectra by two very intense bands at 21,000 and 13,000 cm^{-1}.[2,5,6] In addition to these prominent bands Sgamellotti and coworkers[6] reported four other considerably less intense bands at 18,000, 10,000–8000, and 6000 cm^{-1} for adducts of secondary amines.

In the 1:1 systems that we have examined these same general features are observed in the high-energy region. In addition it appears that a sterically hindered base is generally required for adduct formation to be completed after the addition of one molecule of base. A 1:1 equilibrium was assumed for these systems because of the single isosbestic point observed up to very high mole ratios. All of these systems exhibit small equilibrium constants, less than 10 for the addition of one molecule of base. It is interesting to note, however, that when we tried to isolate the five-coordinate molecule from its characteristic *brown* solution, all attempts resulted in either *green* crystals or else decomposition of the solutions. In the case of $Ni(dtp)_2$ (2,6-lut) (lut = lutidine), large crystals of a material we have not yet been able to characterize were deposited from the brown solution. The green color of these crystals may be compared with the recently reported[12] green five-coordinate species 2,9-dimethyl-1,10-phenanthrolinebis(O,O′-dimethyldithiophosphato)nickel(II). Three of the four sulfur atoms are coordinated, as are both nitrogens from the phenanthroline fragment, forming a distorted square-pyramidal structure. This compound is reported to be paramagnetic.

A ligand field calculation[6] has been reported for the 1:1 adducts with secondary amines, a triplet ground state having been chosen. This paramagnetism was inferred from Gouy susceptibility measurements on concentrated solutions of $Ni(dpt)_2$ with an excess of the secondary amine, either diethyl- or di-*n*-butylamine. Our data suggest that the ground state of the 1:1 adducts depends largely upon the choice of the amine. In particular, the 2-picoline and 2,6-lutidine adducts both appear to have a singlet ground state in solution. This has been verified by two methods. The solution susceptibility using Evans' method reveals no change in the magnetic susceptibility at mole ratios corresponding to significant formation of 1:1 adducts as measured in the 21,000-cm^{-1} region of the solution spectra. The second method has shown directly that there is no electron spin–nuclear spin interaction resulting in a resonance field shift for the protons on the amines. When varying the metal concentration in the (2,6-lut)-$Ni(dtp)_2$ system and holding the base concentration

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[12] P. S. Shetty, R. E. Ballard, and Q. Fernando, *Chem. Commun.*, 717 (1969).

constant, there is no hyperfine splitting of the protons and no relaxation of the phosphorus–proton spin–spin coupling on the chelate at mole ratios corresponding to significant formation of the 1:1 adduct. Although one varies the base concentration holding the metal ion concentration constant in the spectrophotometric study, the position of the equilibrium will be the same if the base concentration is held constant and the metal concentration is varied, assuming one equilibrium between two species. The extreme sensitivity of the nmr experiment to the presence of paramagnetic species in solution must rule out significant formation of 1:1 adducts with a triplet ground state. Unfortunately, however, the very nature of the nmr experiment limits the mole ratios which can be examined; the principal problem is one of solubility.

It is likewise well known[13,14] that the presence of a paramagnetic ion will significantly reduce the mean lifetime of a nucleus in any given spin orientation. The fact that this is not observed in the form of any decoupling of spins on either the chelate or the base is further evidence for the absence of paramagnetism in these solutions of $Ni(dtp)_2$ and the substituted pyridines.

However, the saturated heterocyclic amine 2-methylpiperidine and the secondary amines diethylamine and di-*n*-butylamine, with spectral characteristics in the visible region virtually identical with those of the above two systems, appear to be paramagnetic at reasonably low mole ratios (1:1 metal:base). In the case of diethylamine and di-*n*-butylamine the surprising feature of the hyperfine splitting is that we find an upfield shift for the protons. This is particularly unusual in view of the accepted mechanism for the occurrence of this upfield shift.

Generally it is observed that when spin density is transferred directly into a ligand σ-orbital system, only positive spin density will arise at the proton and therefore all shifts should be downfield.[15,16] If a π pathway is available in the molecule, there is the possibility for both positive and/or negative spin density in the system. Consequently either upfield or downfield shifts may be expected. Fricke and Suhr[17] have observed only downfield shifts where primary amines are coordinated to $Ni(acac)_2$, but shifts to higher fields were noted for the $Co(acac)_2$ systems. This difference results from a contact interaction in $Ni(acac)_2$ but, because of the anisotropic g value, dipolar coupling occurs in $Co(acac)_2$. This upfield shift in our system may be an indication of some anisotropy in the five-coordinate species under investigation.

There are slight changes between the two general categories in the visible spectra, especially a broadening of spectral lines between 14,300 and 12,250 cm^{-1} in the putative triplet molecules. The band at approximately 21,740 cm^{-1} is quite insensitive to the changes in the ground state of the five-coordinate molecule. Because of the inaccuracies of measurements in solution and the likelihood that whatever structure exists in solution is distorted no attempt has been made to assign the optical spectra.

The regular behavior for the 2-methylpiperidine adduct is to be contrasted with the irregular[5] behavior observed for the piperidine adduct. This system and its five-membered ring analog, pyrrolidine, were examined very carefully as a function of added base. Although there was no apparent decomposition with time, *i.e.*, formation of insoluble residue while working in $CHCl_3$ rather than dichloroethane,[5] there may be a progressive reaction or change to some other material absorbing in the same high-energy region. An isosbestic point is present up to a mole ratio of 20:1 (base:metal) and then disappears with an indication of some decomposition. The formation of dithiocarbamates from xanthates upon the addition of piperidine has recently been noted[18] and some such reaction may also be occurring here. Surprisingly the 2-methyl group appears to inhibit significantly this type of behavior in $Ni(dtp)_2$ solutions.

The equilibrium constants for the stepwise addition of pyridine to $Ni(dtp)_2$ have been previously determined.[2] Employing the same procedure for 3-picoline and 4-picoline, we obtained the values listed in Table II. Problems were encountered recording the pure six-coordinate spectra. As the concentration was changed, the spectra continued to change. There was the expected decrease in the extinction coefficient from the four-coordinate absorption band at 19,200 cm^{-1} with an increase in base concentration. Surprisingly, however, at very high base concentrations the extinction coefficient appeared to increase at 19,200 cm^{-1} rather than progressively decrease in the case of the 3- and 4-picolines. Because of these peculiarities perhaps the values for the stepwise equilibrium constants are less accurate than they are for pyridine. There is little doubt, though, that $K_2 > K_1$ in these systems, as was also noted for pyridine. Therefore, the formation of the 1:1 adducts of 3-picoline, 4-picoline, or pyridine is never complete.

The 2:1 adduct of pyridine is known[19] to be *trans* octahedral in the solid state and it is paramagnetic; our nmr results indicate that the other six-coordinate adducts are also paramagnetic. The short electron relaxation time associated with Ni^{2+} then allowed us to examine the proton spectra (contact shifts) of the adduct molecules. The contact shift behavior of variously substituted pyridines has been thoroughly investigated in the recent literature.[10,15,20] In these studies shifts have been observed to both high and low fields, indicating spin density must be introduced indirectly into the π orbitals as well as directly *via* the bonding system. Our results are in accord with this

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previous work and therefore are not presented in detail.[11]

Horrocks[21] has presented an equation relating the contact shift to the free energy change when there is a diamagnetic $\rightleftharpoons$ paramagnetic equilibrium in solution. Assuming that the monoadduct of $Ni(dtp)_2$ is diamagnetic in the picoline systems, we have tried to fit the temperature dependence of the chemical shift when the experimental free energy change for the reaction is used. While the fit is adequate at low temperatures (260–290°K), we find a divergence at higher temperatures (290–340°) between the experimental points and the calculated contact shift.[11] While several hypotheses are available to explain this behavior, we suggest that the high-temperature behavior might be accounted for by some kind of fluxional behavior. The fluxional nature of five-coordinate geometries is well known.[22] Perhaps one geometrical structure is diamagnetic but as the temperature is increased, another structure with a triplet ground state becomes preferred.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Kinetics and Mechanism of the Ligand Substitution Reactions of the Ethylenediamine-N,N′-diacetate and Nitrilotriacetate Complexes of Nickel(II) with 4-(2-Pyridylazo)resorcinol

BY SHIGENOBU FUNAHASHI AND MOTOHARU TANAKA

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Kinetics and mechanism of the ligand substitution reactions of the ethylenediamine-N,N′-diacetatonickel(II) (Ni^{II}–EDDA: NiEDDA) and the nitrilotriacetatonickelate(II) (Ni^{II}–NTA: $NiNTA^-$) complexes with 4-(2-pyridylazo)resorcinol (PAR: H_2R) have been studied spectrophotometrically at $\mu = 0.10$ and at 25.0°. In the Ni^{II}–EDDA system two distinct reaction steps are observed. The Ni^{II}–EDDA complex reacts rapidly with PAR to form an intermediate Ni^{II}–EDDA–PAR complex ($RNiEDDA^{2-}$ and $RNiHEDDA^-$), which undergoes subsequent unwrapping of EDDA. The first observable step of the reaction follows the rate law $d([RNiEDDA^{2-}] + [RNiHEDDA^-])/dt = k_1[NiEDDA][HR^-]$. The rate law for the second step is written as $d[NiR_2^{2-}]/dt = k_2[RNiEDDA^{2-}] + k_{2,H}[RNiHEDDA^-]$. Values of k_1, k_2, and $k_{2,H}$ are $(1.0 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$, $(2.7 \pm 0.2) \times 10^{-4}\ sec^{-1}$, and $(5.1 \pm 0.4) \times 10^{-3}\ sec^{-1}$, respectively. In the Ni^{II}–NTA system the rate equation of the formation of an intermediate $RNiNTA^{3-}$ is $d[RNiNTA^{3-}]/dt = k_1[NiNTA^-][HR^-]$ where the value of k_1 is $(4.2 \pm 0.3) \times 10^2\ M^{-1}\ sec^{-1}$. Some discussions are made on the effect of coordinated ligands on the lability of remaining water. The stability constant of the intermediate $RNiEDDA^{2-}$ is determined at 25.0° and $\mu = 0.1$ ($NaClO_4$): $K^R{}_{RNiEDDA} = [RNiEDDA^{2-}]/[NiEDDA][R^{2-}] = 10^{8.2\pm0.2}$.

Introduction

For the ligand substitution reactions of metal chelates with multidentate ligands, it has been proposed that the substitution proceeds through an intermediate in which a central metal ion is bonded with both leaving and entering ligands and that the cleavage of the bond between the metal and leaving ligand is the rate-determining step.[1-4] In order to detect spectrophotometrically an intermediate with two different multidentate ligands and to provide a direct experimental evidence for the proposed mechanism, we have taken up ethylenediamine-N,N′-diacetic acid (EDDA: tetradentate) and nitrilotriacetic acid (NTA: tetradentate) as leaving ligands and 4-(2-pyridylazo)resorcinol (PAR: tridentate) as an entering ligand. The present paper describes the result on the ligand substitution reactions

$$Ni^{II}\text{–EDDA} + PAR \rightleftharpoons Ni^{II}\text{–PAR} + EDDA \quad (1)$$

$$Ni^{II}\text{–NTA} + PAR \rightleftharpoons Ni^{II}\text{–PAR} + NTA \quad (2)$$

The divalent anions of PAR and EDDA and trivalent anion of NTA are represented as R^{2-}, $EDDA^{2-}$, and NTA^{3-}, respectively.

Experimental Section

Reagents. EDDA.—Reagent grade EDDA, obtained from Dojin-do Chemical Co., Kumamoto, Japan, was purified by recrystallization from aqueous methanol. Care was taken to use fresh solutions of EDDA because cyclization of the free ligand occurs.[5]

NTA.—Reagent grade NTA, obtained from Dojin-do Chemical Co., was recrystallized twice from distilled water.

Sodium Perchlorate.—Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. Heavy-metal impurities in sodium perchlorate were precipitated as hydroxides at pH 9 and extracted as PAN complexes (PAN:

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